

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**DEVELOPMENT OF METHANOL PRODUCTION CATALYSTS
FROM SYNTHESIS GAS OBTAINED FROM COAL
GASIFICATION**

ŞİRİNGÜL AY
**A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF CHEMICAL ENGINEERING**

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GEBZE
2021

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

KÖMÜRÜN GAZLAŞTIRILMASI
SONUCU ELDE EDİLEN SENTEZ
GAZINDAN METANOL ÜRETİM
KATALİZÖRLERİNİN GELİŞTİRİLMESİ

ŞİRINGÜL AY
DOKTORA TEZİ
KİMYA MÜHENDİSLİĞİ ANABİLİM DALI

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GEBZE
2021

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SUMMARY

The thesis is composed of three main parts. In the first part, CuO/ZnO/Al₂O₃/MgO-Cr and -Mn catalysts were synthesized. The catalysts calcined at 250, 300, 350 and 450 °C were characterized by XRD, BET H₂-TPR and H₂-TGA. Increasing the calcination temperature crystallite size increased and BET surface area decreased. The optimum H₂ consumption value of 52% was obtained with CuO/ZnO/Al₂O₃/MgO-Mn catalyst calcined at 350 °C. In the second part, Cu-based catalysts synthesized by addition of Mg and Cr. Catalysts calcined at 450°C were examined by XRD, SEM, BET, H₂-TPR, H₂-TGA and TPAD-TGA. Addition of Mg and Cr caused formation of smaller CuO crystallite size, and increased surface area of catalysts by improving dispersion of CuO. Cr also prolonged the shelf life. The catalyst containing 6.4 mol % Cr gave 14.2 g methanol production which was the highest among other synthesized catalysts. In the last part, Cu/ZnO/Al₂O₃ catalysts which had different amount of Cr and/or Mg were synthesized. After calcination at 350 °C, catalysts were analyzed by BET, XRD, H₂-TGA and H₂-TPR. Catalytic activity, selectivity and deactivation rates of synthesized catalysts were tested at 270 °C and 30 MPa for 144 h. Mg or Cr addition to the catalyst formulation reduced the methanol productivity whereas the co-addition of Cr and Mg increased the methanol productivity. At 144 h reaction time, catalysts with Mg:Cr molar ratios of 2:1 and 1:1 had the highest methanol selectivities and methanol weight time yields of 97.7 and 98.3%, and 0.53 and 0.52 g_{total methanol production}·g_{catalyst}⁻¹·h⁻¹, respectively. The catalysts without Cr promoter deactivated rapidly. Deactivation rates of Mg and Cr co-promoted catalysts followed a sinusoidal trend and exhibited self-regenerative characteristics.

Key Words: Catalyst Deactivation, Catalyst Synthesis, Co-precipitation Method, Cr/Mn Promoter, Methanol Production, Mg Promoter.

ÖZET

Bu tez çalışması üç farklı bölümden oluşmaktadır. İlk bölümde, CuO/ZnO/Al₂O₃/MgO-Cr ve -Mn içeren katalizörler sentezlendi. 250, 300, 350 ve 450 °C sıcaklıkta kalsine edilen katalizörler XRD, BET, H₂-TPR ve H₂-TGA ile incelendi. Kalsinasyon sıcaklığı arttıkça kristal boyutunda artış ve BET yüzey alanında azalma gözlemlendi. En uygun H₂ tüketim değeri olan %52, 350 °C sıcaklıkta kalsine edilen CuO/ZnO/Al₂O₃/MgO-Mn katalizöründe tespit edildi. İkinci bölümde, Mg ve Cr katkılı Cu-esaslı katalizörler sentezlendi. 450°C sıcaklıkta kalsine edilen katalizörler XRD, BET, H₂-TPR, H₂-TGA ve TPAD-TGA ile incelendi. Mg ve Cr katkıları daha küçük CuO kristallerinin oluşmasına sebep oldu ve CuO yayılımını geliştirerek katalizör yüzey alanını artırdı. Ayrıca, Cr katalizörlerin kullanım ömrünü uzattı. %6,4 mol Cr içeren katalizör %83,5 metanol seçiciliği ve 14,2 g metanol üretimi göstererek diğer katalizörler içerisinde en yüksek performansı sergiledi. Son bölümde, farklı oranlarda Cr ve/veya Mg içeren Cu/ZnO/Al₂O₃ katalizörler sentezlendi. 350 °C sıcaklıkta kalsine edilen katalizörler BET, XRD, H₂-TGA ve H₂-TPR ile analiz edildi. Sentezlenen katalizörlerin katalitik aktivitesi, seçiciliği ve aktivitesini kaybetme hızları 270 °C ve 30 MPa’da 144 saat boyunca test edildi. Mg veya Cr’nin katalizör kompozisyonuna eklenmesi metanol üretimini azaltırken Mg ve Cr’nin eş zamanlı olarak eklenmesi metanol üretimini artırdı. 144 saatlik reaksiyon süresinde Mg:Cr mol oranı 2:1 ve 1:1 olan katalizörler sırasıyla en yüksek değer olan %97,7 ve %98,3 metanol seçiciliği ve 0,53 ile 0,52 $g_{\text{toplam metanol}} \cdot g_{\text{katalizör}}^{-1} \cdot s^{-1}$ zamana bağlı metanol üretim verimi gösterdi. Cr içermeyen katalizörler hızlı bir şekilde aktivitesini kaybetti. Mg ve Cr içeren katalizörlerin aktivitesini kaybetme hızları sinüs eğrisine benzer bir eğilim sergiledi ve kendi kendine tekrar aktif olabilme özelliği gösterdi.

Anahtar Kelimeler: Katalizör Deaktivasyonu, Katalizör Sentezi, Eş-çöktürme Metodu, Cr/Mn Promotörleri, Metanol Üretimi, Mg Promotörü.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations and Acronyms</u>	<u>Explanations</u>
A°	: Armstrong
β	: Full width at half maximum of the diffraction peak
cm^3	: Cubic centimeter
D	: Mean crystallite size
θ	: Bragg diffraction angle
h	: Hour
K	: Debye-Scherrer constant (0.89)
K	: Kelvin
kV	: Kilovolt
M	: Molar
mA	: Milliampere
mg	: Milligram
min	: Minute
mL	: Milliliter
nm	: Nanometre
ppm	: Parts per million
rpm	: Round per minute
Al	: Aluminum
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	: Aluminum Nitrate Nonahydrate
Al_2O_3	: Aluminium Oxide
Ba	: Barium
BaO	: Barium Oxide
BET	: Brunauer Emmett Teller
CaO	: Calcium Oxide
Ce	: Cerium

CH_3OH	:	Metanol
CO	:	Carbon Monoxide
Co	:	Cobalt
CO_2	:	Carbon Dioxide
Cr	:	Chromium
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	:	Chromium Nitrate Nonahydrate
Cr_2O_3	:	Chromium (III) Oxide
Cu	:	Copper
$\text{Cu}_2\text{CO}_3(\text{OH})_2$	:	Malachite
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	:	Copper (II) Nitrate Trihydrate
CuO	:	Copper oxide / tenorite
$(\text{Cu,Zn})_2\text{CO}_3(\text{OH})_2$	:	Rosasite
CZA	:	$\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst
CZAM	:	$\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3/\text{MgO}$ catalyst
DTG	:	Differential Thermogravimetry
Fe	:	Iron
FWHM	:	Full Width at Half Maximum
H_2	:	Hydrogen
ICP-MS	:	Inductively Coupled Plasma – Mass Spectrometer
Mg	:	Magnesium
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	:	Magnesium Nitrate Hexahydrate
MgO	:	Magnesium Oxide
Mn	:	Manganese
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	:	Manganese (II) Nitrate Tetrahydrate
MWTY		Methanol Weight Time Yield
N_2	:	Nitrogen
Na	:	Sodium
Na_2CO_3	:	Sodium Carbonate Anhydrous
NH_3	:	Ammonia
Ni	:	Nickel

OH	:	Hydroxyl
SEM	:	Scanning Electron Microscopy
SrO	:	Strontium Oxide
TGA	:	Thermal Gravimetric Analyzer
TPAD	:	Temperature Programmed Ammonia Desorption
TPR	:	Temperature Programmed Reduction
W	:	Tungsten
XRD	:	X-Ray Diffraction
Zn	:	Zinc
ZnO	:	Zinc Oxide / Zincite
$(\text{Zn,Cu})_5(\text{CO}_3)_2(\text{OH})_6$	:	Aurichalcite
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	:	Zinc Nitrate Hexahydrate
Zr	:	Zirconium
ZrO ₂	:	Zirconium Dioxide

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1. INTRODUCTION

Energy and environmental issues have become two major concerns with rapid changes and development in modern industry. In recent years, high level of energy and simple storage properties of fossil fuels have made them the most commonly used source of energy [1]. In the face of climate change associated with global warming, the greatest challenge is to supply global energy demand while reducing greenhouse gas emissions and reliance on fossil fuels.

Methanol (CH_3OH) with wide range of industrial applications is an alternative fuel, which can be used in internal combustion engines with lower toxic gas emissions [2]. Besides, methanol is used as a feedstock for the production of formaldehyde, acetic acid and several important chemicals [3]–[5]. It is also used for storage and transportation of hydrogen (H_2). Methanol is generated from synthesis gas (syngas) composed of carbon monoxide (CO), carbon dioxide (CO_2) and H_2 via copper (Cu)-based catalysts. Zinc oxide/chromium oxide ($\text{ZnO}/\text{Cr}_2\text{O}_3$)-based catalysts have been used for generating methanol from syngas via methanol synthesis at high temperatures (350–450 °C) and high pressures (250–350 bar) since 1920's [6]. This process was improved in 1960's by including utilization of copper/zinc oxide/aluminum oxide ($\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$)-based catalysts that are able to operate at lower temperatures (230–280 °C) and pressures (50–120 bar) [6]. Yet, there are still important drawbacks in the use of Cu -based catalysts such as intolerance to poisoning, lower thermal stability-mechanical strength and shorter lifetime [7].

It is well-known that a small variation in the catalyst composition and addition of promoter/support material can induce significant changes on surface structure and yield different reaction performances. The major factors that determine catalytic activity, selectivity, resistance against poisoning, lifetime and methanol yield of the catalyst are catalyst composition, preparation method, precursor type, drying, calcination and reduction conditions [8]. Cu is an active metal for methanol synthesis, and particle size of Cu has an important effect on methanol production. Cu/Zn mol ratio, pH, reaction temperature, calcination temperature and the addition rate of reagent solution influence Cu particle size [9], [10]. Methanol synthesis catalysts are produced by using dry-chemical or wet-chemical methods, but co-precipitation method, which is one of the wet-chemical methods, is the most commonly used process for the

industrial production of methanol synthesis catalysts. Likhittaphon et al. [11] worked on the synthesize methods of Cu-based catalysts and they reported that the catalysts synthesized by ultrasonic-assisted precipitation have larger surface area and better dispersion than the catalysts which were prepared by conventional methods. Dasireddy et al. [12] investigated the effect of pH on the activity of copper/magnesium oxide/aluminum oxide (Cu/MgO/Al₂O₃) catalysts and found that the catalyst prepared at pH 8 showed higher methanol productivity at temperatures below 250 °C due to improved H₂ adsorption by enhanced Cu and BET surface areas. The surface acidity of the catalyst is another important point, and high surface acidity causes formation of higher hydrocarbons and/or dimethyl ether [13]. Adsorption of CO₂ by the catalysts is related to the surface alkalinity because of the acidic characteristic of CO₂ [14]. Addition of ZnO, which is a basic oxide, neutralizes the surface acidity of catalysts and provides higher methanol selectivity [15]. Alkaline-earth metal oxides (BaO, CaO, MgO and SrO) cause the formation of strong basic sites on the catalysts, and therefore, increase methanol selectivity [14]. Ay et al. [16] investigated the effect of calcination temperature on H₂ consumption and surface area characteristics of Cu-based catalysts and determined that the best calcination temperature was 350 °C.

Methanol selectivity and catalyst activity are affected by the type of support and promoter [17], [18]. Hus et al. [19] synthesized Cu-based binary catalysts via co-precipitation by using chromium (Cr), iron (Fe), magnesium (Mg) and zinc (Zn) additives, and found that Cu/Cr catalyst gave the lowest surface area and Cu/Zn catalyst had the best performance among binary Cu-based catalysts. Although Cu/Zn methanol synthesis catalysts have low resistance to sulfur impurities in syngas and low thermal stability, they are used conventionally because they need mild operating pressure and temperature [13]. Zn/Cr₂O₃ catalysts have higher thermal stability and resistance against sulfur poisoning than Cu-based catalysts, but their operation conditions require high temperatures and pressures [20]. Ternary catalysts or catalysts possessing multiple promoters have been developed to overcome the problems associated with the usage of binary catalysts. Kilo et al. [21] synthesized binary Cu/Zr (copper/zirconium), ternary Cu/Zr/Cr and Cu/Zr/Mn (copper/zirconium/manganese) methanol synthesis catalysts and found that Cu/Zr/Cr catalyst gave the highest methanol generation due to the formation of the highest Cu/Zr surface concentrations. Sadeghinia et al. [22] determined that the addition of trivalent elements such as aluminum (Al³⁺) or chromium (Cr³⁺) into the ternary catalysts improved the catalytic

activity by increasing the dissolution rate of Cu in ZnO and decreasing Cu particle size [22]. Al_2O_3 is generally used for the Cu-based catalysts, and has a promotional effect on Cu/ZnO catalyst [23]. Similar to Al, Cr also increases catalyst activity, thermal stability and regenerability of Cu/ZnO/ Cr_2O_3 catalysts [24]. Chen et al. [25] investigated the effects of doping trivalent metal ions into Cu/ZnO/ Al_2O_3 catalyst for methanol synthesis and found that Cr_2O_3 could enhance both enrichment and stabilization of Cu^+ on the surface during reduction and reaction processes by increasing the concentration of Cu^+ on the surface of the catalyst. Hu et al. [26] synthesized Cu/ Al_2O_3 /ZnO-Zn ternary catalysts and their binary analogues and determined that 10% Al_2O_3 in the catalyst composition inhibited the reduction of Cu^{2+} to inactive Cu^0 , and stabilized Cu^+ by retarding the reduction of Cu^{2+} and maintaining it in the form of active Cu^+ . Dasireddy et al. [14] synthesized Cu/Al catalysts with different promoters and reported that Mg-promoted catalyst gave higher Cu metallic surface area and Cu^+/Cu^0 ratio and thus exhibited higher conversion. Hayward et al. [27] reported that Cu/Mg binary catalyst with a molar ratio of 70:30 had lower methanol activity although it provided higher Cu surface area. Addition of 3.5% Mg into Cu/ZnO/ Al_2O_3 catalysts was found to be more effective for the CO_2 hydrogenation mainly due to the enhancement of the catalyst surface area [28]. Although methanol is commercially produced via the catalytic reaction of CO and H_2 , CO_2 also exists in the reaction mixture in small concentrations (2-6%) to prevent deactivation of Cu-based methanol synthesis catalysts [29].

1.1. Hypothesis

Methanol generation activity and resistance against sintering can be improved by adjusting the Cr and Mg ratio in the Cu based Cu/ZnO/Al₂O₃ methanol synthesis catalysts.

1.2. Objectives

The thesis is composed of three main parts, and the objectives of this study are :

- i) to determine the effects of multiple promoters (Mg, Mn and Cr) on the reduction characteristics, surface area, CuO particle size and H₂ consumption of Cu/ZnO/Al₂O₃ catalyst.
- ii) to determine the Mg and Cr additives on the surface area, reduction characteristics and methanol generation activity of Cu/ZnO/Al₂O₃ catalyst.
- iii) to increase the methanol generation activity and improve resistance of Cu/ZnO/Al₂O₃ catalyst against sintering by adjusting the Cr and Mg ratio in the catalyst composition.

2. COMPARISON OF HYDROGEN CONSUMPTION BEHAVIOR OF CHROMIUM AND MANGANESE PROMOTED COPPER-BASED CATALYSTS

Methanol is a very important bulk chemical with a wide range of applications. In addition to the usage in the production of several important chemicals such as formaldehyde, acetic acid and chloromethane, it is also used for the production of various products, including plastics, paints, cosmetics and fuels [30], [31]. The world's methanol demand is about 100 million tons per year, and it is the most-shipped chemical all around the world [30], [32]

Copper/Zinc oxide/Aluminum oxide ($\text{Cu/ZnO/Al}_2\text{O}_3$) catalysts are critically important commercial catalysts and used in the production of methanol from the catalytic reaction of syngas (CO , CO_2 and H_2) [1], [18], [33]. Although methanol generation activity of Cu-based catalysts is known, Zinc-Chromium (Zn-Cr) catalysts have been used in the industry [32]. Over the years, Copper/Zinc/Chromium (Cu/Zn/Cr) and Copper/Zinc/Aluminum (Cu/Zn/Al) catalysts have been developed and used in the industry [32]. These catalysts have poor tolerance to poisoning, low thermal stability, low mechanical strength and short lifetime [7].

It is well-known that a small variation in the catalyst composition and addition of promoter/support material can induce significant changes on surface structure and yield different reaction performances. Copper oxide (CuO) particle size, surface area and metallic Cu surface area of the catalyst are key parameters that affect the catalytic processes which strongly depend on the catalyst composition. In the last decade, several methods have been developed to prepare Cu-based methanol synthesis catalysts with broader Cu surface areas, fine particle size and optimized compositions, but the most preferred and used method is the co-precipitation method [34].

There are a few studies in the literature related to the effect of calcination and reduction conditions on the methanol production activity of Cu-based catalysts. Fujita et al. [35] investigated the effects of calcination and reduction conditions on the activity of Cu/ZnO methanol synthesis catalysts and found that decomposition of the precursor proceeded over a longer period of time when the heating rate of calcination was about $1\text{ }^\circ\text{C.min}^{-1}$, resulting in formation of smaller CuO crystals. Kowalik et al.

[36] studied the effect of calcination temperature on the activity of Cu/ZnO/Al₂O₃ methanol synthesis catalysts where catalytic activity decreased by increasing the calcination temperature. In addition to the calcination temperature, aging time has a significant effect on the structure of the precursor and activity of the catalyst. Fang et al. [37] found that (Cu,Zn)₂CO₃(OH)₂ and (Zn,Cu)₅(CO₃)₂(OH)₆ formation took place by increasing the aging time where CuO-ZnO solid solution was obtained after the calcination of (Cu,Zn)₂CO₃(OH)₂ and (Zn,Cu)₅(CO₃)₂(OH)₆ was observed to improve the interaction between Cu and ZnO; thus, increasing the catalytic activity of Cu-based catalysts.

Addition of trivalent metal ions as promoter or support has an important effect on the activity. Chen et al. [25] investigated the effects of doping trivalent metal ions into a Cu-based (Cu/ZnO/Al₂O₃) catalyst for methanol synthesis and found that chromium (III) oxide (Cr₂O₃) could increase the concentration of Cu⁺ on the surface of the catalyst; thus, enhancing both enrichment and stabilization of Cu⁺ on the surface during reduction and reaction processes. Lachowska et al. [38] synthesized Copper/Zinc/Zirconium (Cu/Zn/Zr) catalysts using manganese (Mn) as a promoter. They reported that the maximum activity was accomplished by the addition of small amount of Mn into the Copper oxide/Zinc oxide/Zirconium dioxide (CuO/ZnO/ZrO₂) catalyst [38]. Fei et al. [39] prepared Cu-based catalysts impregnated on zeolite and examined the relation between activity and reduction characteristics of the synthesized catalysts where co-addition of Mn and Zn not only supported uniform dispersion of CuO, but also increased the reducibility of CuO and conversion of CO via synergetic effects of metallic components. Meshkini et al. [40] synthesized Cu/ZnO/Al₂O₃ catalysts using co-precipitation method by adding small amounts of Ba (Barium), Ce (Cerium), Cr, Mg (Magnesium), Mn, W (Tungsten) and Zr oxides, and found that the dispersion of Cu, Cu crystallite size, surface composition, catalytic activity and stability of the catalysts were affected by these additives. Kee Koh et al. [41] investigated the effect of Cr, Co, Fe, Mn and Ni promoters on the activity of Cu-based catalyst and determined that the addition of Mn formed the strongest interaction between CuO and other oxides by reducing the Cu crystallite size that yielded the highest methanol production activity. There is a close relationship between H₂ reducibility of CuO and catalytic activity of Cu-based catalysts. Beiramar et al. [42] modified Cu/Zn/Al catalyst by using different metallic promoters where the addition

of small amounts of Cr and Mn gave higher H₂ reducibilities and methanol production activities than other promoters.

The aim of this part is to: (i) prepare CuO/ZnO/Al₂O₃/MgO-Cr and -Mn using nitrate route via co-precipitation method, (ii) characterize precursors by XRD and analyze the decomposition behavior of the precursors under air by Thermal Gravimetric Analyzer (Air-TGA), (iii) characterize the catalysts which calcined at four different temperatures (250, 300, 350 and 450 °C) by XRD and BET, (iv) analyze reduction characteristics of the catalysts via TPR and TGA under H₂ (H₂-TGA), (v) reduce CuO particle size and enhance active surface area of the catalysts, (vi) determine active CuO sites by measuring H₂ consumption, and (vii) analyze the effect of multiple promoters (Mg, Mn and Cr) on the activity of Cu/ZnO/Al₂O₃ catalysts.

2.1. Materials and Methods

2.1.1. Materials

Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) (>99%, w/w) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (>98%, w/w) were purchased from Acros Organics (Geel, Belgium). Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) (>98%, w/w) and sodium carbonate anhydrous (Na₂CO₃) (>99.5%, w/w) were obtained from Carlo Erba (Paris, France). Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) (>99%, w/w) and manganese (II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O) (>98.5%, w/w) were purchased from Merck (Darmstadt, Germany) and chromium nitrate nonahydrate (Cr(NO₃)₃·9H₂O) (>98%, w/w) was obtained from Carl Roth (Karlsruhe, Germany). All reagents were at analytical grade and used as received. All solutions used in the experiments were prepared with deionized water.

2.1.2. Catalyst Preparation

Conventional co-precipitation method was used for the synthesis of the catalysts [43]. One molar (M) aqueous solutions of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O and either Cr(NO₃)₃·9H₂O or Mn(NO₃)₂·4H₂O

called as metal solution and 1.6 M aqueous solution of Na_2CO_3 called as base solution were prepared. The composition of the metal solution was adjusted according to the molar ratios of the metal components (Table 2.1).

Table 2.1: Catalyst compositions (Mol %).

Precursor Name	Cu	Zn	Al	Mg	Cr	Mn
K38-Cr	50.0	21.2	14.8	2.9	11.1	–
K38-Mn	50.0	21.2	14.8	2.9	–	11.1

One hundred mL's of metal solution and base solution were simultaneously transferred into 200 mL of deionized water using a peristaltic pump (Cole-Parmer, Masterflex L/S Easy Load, IL, USA) at a flow rate of $10 \text{ mL} \cdot \text{min}^{-1}$. The suspensions were aged in mother liquor at 65°C by continuously stirring at a rate of 150 rpm for 24 h. The change of color from blue to green shows the formation of crystalline malachite phase (Figure 2.1) [44].

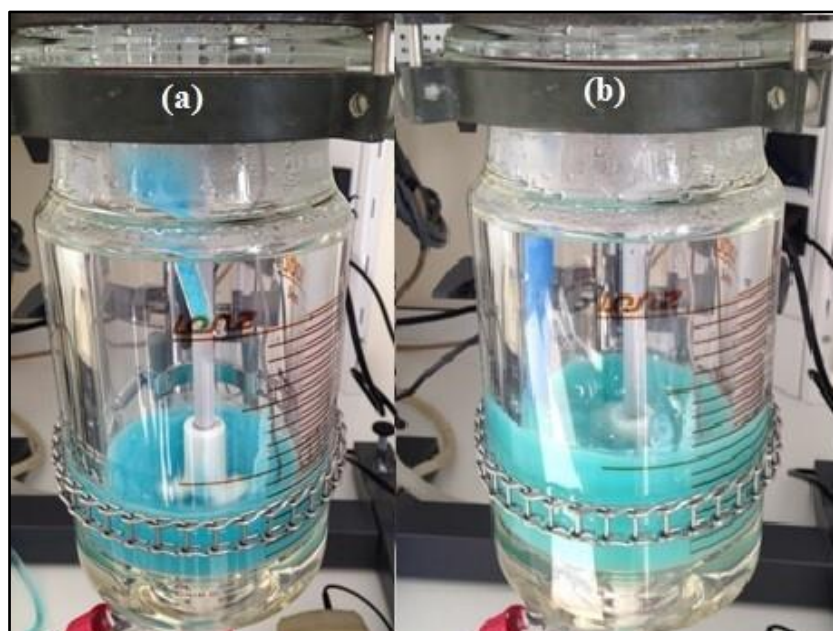


Figure 2.1: The appearance of the reaction mixture (a) before and (b) after aging.

After aging, the precipitates were filtered and washed with deionized water at 65°C to adjust the pH of the washing liquor near to 7.0. The sodium (Na) contents of the

precipitates were analyzed by an inductively coupled plasma – mass spectrometer (ICP-MS) (Thermo Fischer Scientific, iCAP RQ, MA, USA) to make sure that Na concentration is below 20 ppm in the precipitates. Then, the precipitates were dried under air at 105 °C overnight. These two precursors were heated up to 250, 300, 350 and 450 °C with a heating rate of 1 °C·min⁻¹, and they were calcined at these temperatures for 10 h. The calcined catalysts were labeled as K38-Cr-T and K38-Mn-T where T is the corresponding calcination temperatures at 250, 300, 350 and 450 °C.

2.1.3. Catalyst Characterization

The structure and crystallinity of precursors and calcined catalysts were analyzed by the XRD. XRD diffractograms were taken with an XRD diffractometer (Rigaku Corp., Miniflex 600, Tokyo, Japan) by using Cu-K α radiation at $\lambda=1.54$ Å, 40 kV and 15 mA. TGA analysis (Air-TGA and H₂-TGA) were performed by using a thermogravimetric analyzer (Shimadzu Corp., DTG-60H TG/DTA, Tokyo, Japan). Thermal decomposition of precursors was studied by Air-TGA. For this purpose, ~10 mg of precursor was placed in the sample holder. The decomposition of the sample was monitored by recording the weight loss during the heating period between 25 and 700 °C at a heating rate of 10 °C·min⁻¹ under air at a flow rate of 300 mL·min⁻¹. The weight loss during the reduction process of calcined catalysts was measured by H₂-TGA. In H₂-TGA, ~10 mg of calcined catalyst was heated from 25 to 700 °C at a heating rate of 10 °C·min⁻¹ under H₂-N₂ mixture (20% H₂ and 80% N₂) at a flow rate of 50 mL·min⁻¹.

Surface areas of the calcined catalysts were determined by N₂ adsorption isotherm at 77 K by using a surface area analyzer (Quantachrome Instrument Corp., Quadrasorb-S1, FL, USA). Prior to the measurements, the samples were degassed under vacuum at 150 °C overnight.

The reduction characteristics of the calcined catalysts were analyzed with TPR by using a fixed bed reactor equipped with an on-line mass spectrometer (HIDEN Analytical, HAL201 RC, Warrington, UK). One gram of catalyst was placed into the stainless-steel tubular reactor. The sample was pretreated with N₂ at 25 °C for 10 min. Then, the sample was reduced under a 10% H₂/N₂ stream flowing at 0.2 L·min⁻¹ and heated from 25 to 750 °C at a heating rate of 5 °C·min⁻¹.

2.2. Results and Discussion

2.2.1. Crystal Structure Analysis of Precursors

The main XRD reflections of the phases found in K38-Cr and K38-Mn precursors are determined as for rosalite ($(\text{Cu,Zn})_2\text{CO}_3(\text{OH})_2$) at $2\theta=14.637^\circ$, 17.467° , 24.075° and 29.591° , for malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) at $2\theta=14.715^\circ$, 17.496° , 24.029° and 29.470° , and for aurichalcite ($(\text{Zn,Cu})_5(\text{CO}_3)_2(\text{OH})_6$) at $2\theta=13.028^\circ$, 24.032° , 27.857° and 32.655° . The same 2θ values were also reported in the literature [45], [46]. The XRD patterns of the precursors are shown in Figure 2.2. Ageing of the precipitates in mother liquor results in the formation of crystalline malachite, rosalite and aurichalcite phases, and the crystallization of amorphous solids [47]. The presence of rosalite and aurichalcite phases in the XRD diffractogram showed that Cu was well dissolved in ZnO. The formation of a Cu-ZnO solid solution was also confirmed by other studies [32], [37]. Higher peak intensities in XRD diffractogram of the K38-Mn revealed that better dissolution of Cu in ZnO was achieved compared to the dissolution of the K38-Cr.

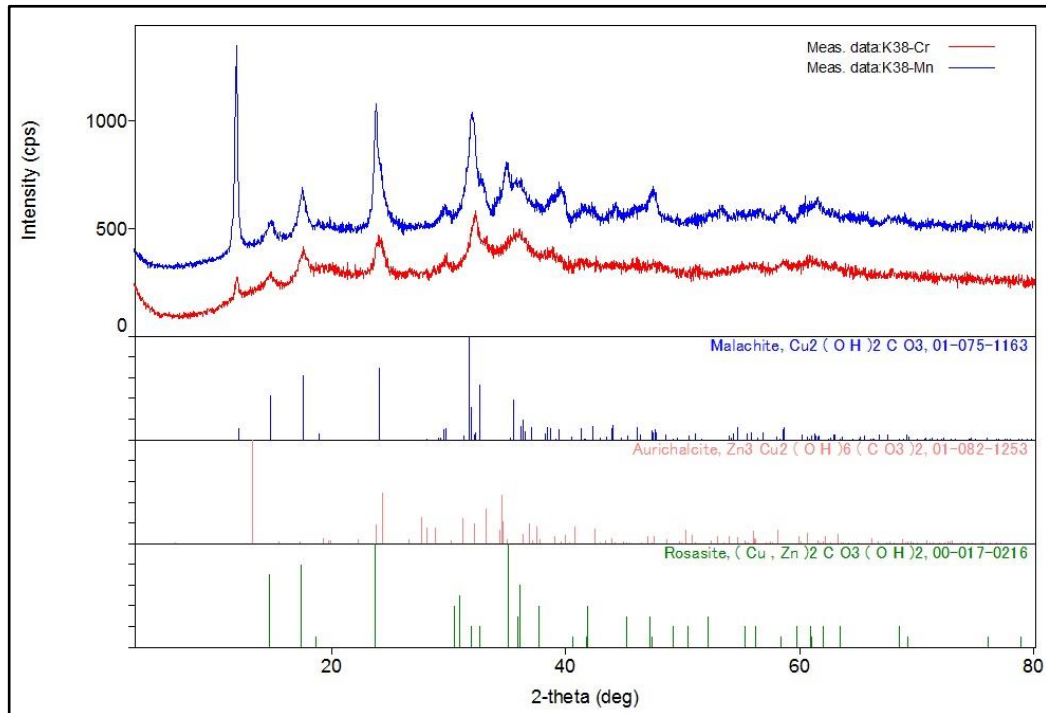


Figure 2.2: XRD diffractograms of precursors.

2.2.2. Decomposition Characteristics of Precursors

The decomposition steps in Air-TGA were not clearly detectable (Figure 2.3a). Therefore, TGA data were transformed to the DTG (Differential Thermogravimetry) data through derivation (Figure 2.3b). The weight losses till 100 °C can be attributed to the evaporation of physically adsorbed water. The same findings were also observed by Li et al. [48] where they studied the effect of Zn addition to Cu-ZnO/Al₂O₃ catalysts. The pronounced weight loss within the temperature range of 120 and 300 °C can be associated with the loss of hydroxyl (OH) groups [49]. The weight loss between 350 and 450 °C shows the release of CO₂. The peak at 495 °C for the K38-Mn precursor can be attributed to the transformation of Mn in amorphous phase to crystalline phase [50]. The peak at around 600 °C for the K38-Mn precursor can be assigned to the decomposition of carbonate groups within the precursor structure [49].

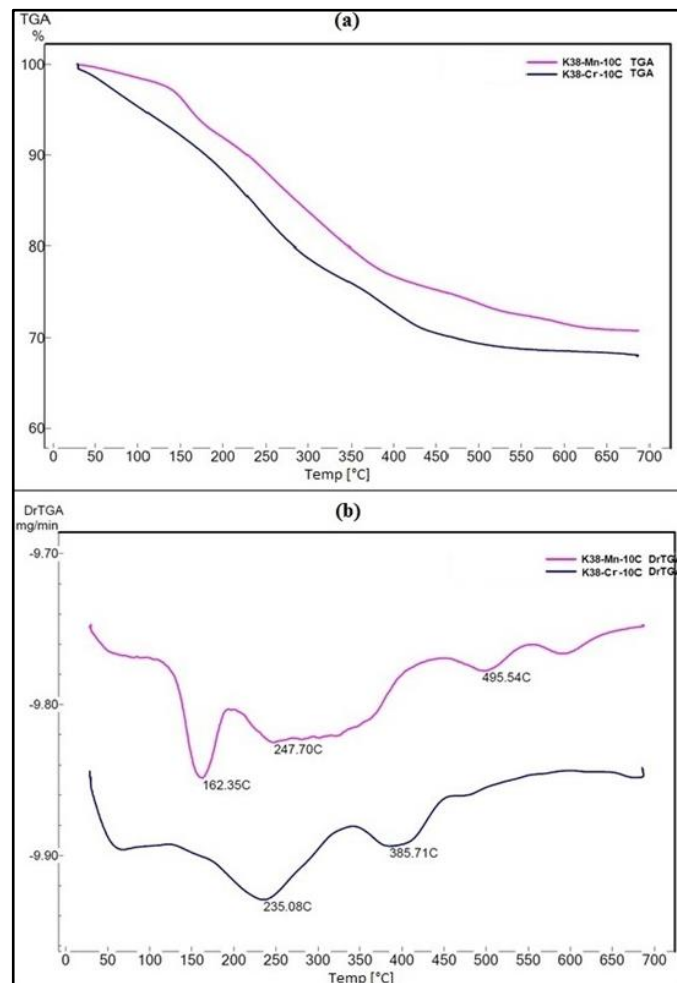


Figure 2.3: (a) Air-TGA and (b) Air-DTG curves of precursors.

When the Air-TGA profiles for the K38-Mn and K38-Cr precursors were compared, the final weight losses for both precursors were almost the same (~35%). This can be explained based on the presence of similar hydroxycarbonate precursors with different cationic species as confirmed by the XRD diffractograms of the two precursors (Figure 2.2).

2.2.3. Crystal Structure, Particle Size and Surface Area Analysis of Calcined Catalysts

In the comparative XRD diffractograms of the calcined catalysts, the CuO signals and crystallite size increased by increasing the calcination temperature. XRD patterns of the K38-Cr-T and K38-Mn-T catalysts calcined at four different temperatures are shown in Figure 2.4 and Figure 2.5, respectively. The catalysts containing Cr gave sharper peaks than the ones containing Mn. In the literature, it was reported that the optimum calcination temperature is between 330 and 350 °C for these precursors [27], [35], [51]. The formation of CuO phase in the catalysts calcined at 250 and 300 °C is not sufficient, and there were carbonate and hydroxide phases. CuO phase formation was first observed and the smallest CuO particles were obtained for the catalyst calcined at 350 °C. CuO particle size increased and BET surface areas decreased by further increasing the calcination temperature. The calcination at 450 °C was performed to validate sintering effect of high temperature. Above 350 °C, the CuO phase gave sharper signal indicating the formation of larger crystallites.

After the XRD analysis, particle size of the CuO phase was calculated by using Debye-Scherrer formulae given in Equation (2.1) [52]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2.1)$$

where D is the mean crystallite size (nm), K is the Debye-Scherrer constant (0.89), λ is the X-ray wavelength (1.54 °Å), β is the full width at half maximum (FWHM) of the diffraction peak (radian) and θ is Bragg diffraction angle (degree).

The BET surface area values decreased by increasing crystallite size within each catalyst (Table 2.2). The Cr containing catalysts have higher CuO crystallite size and

surface area when compared with the Mn containing catalysts calcined at 350 and 450 °C. This could be attributed to Cr containing substances existed in the K38-Cr catalysts.

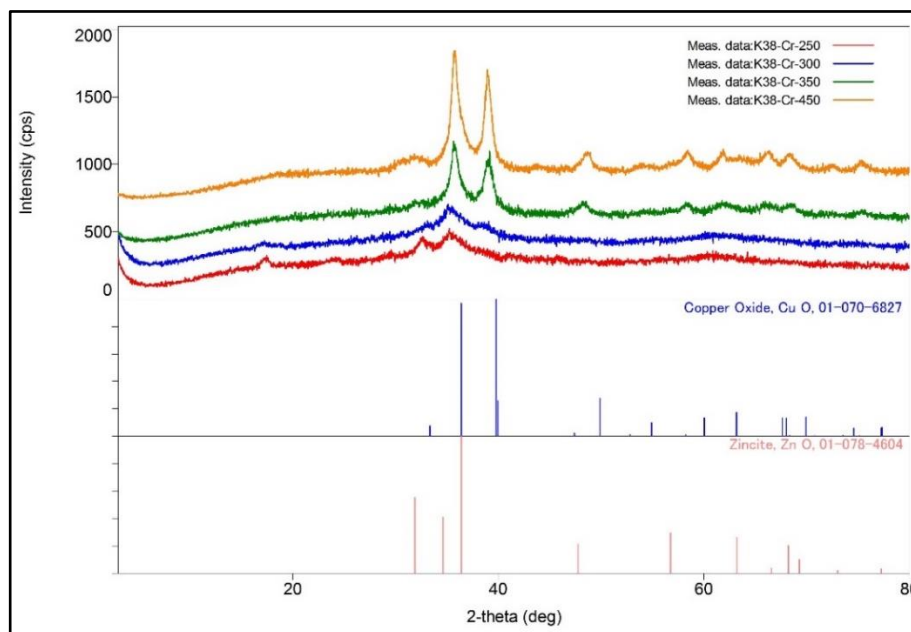


Figure 2.4: Comparative XRD diffractograms of the Cr promoted catalysts calcined at 250, 300, 350 and 450 °C.

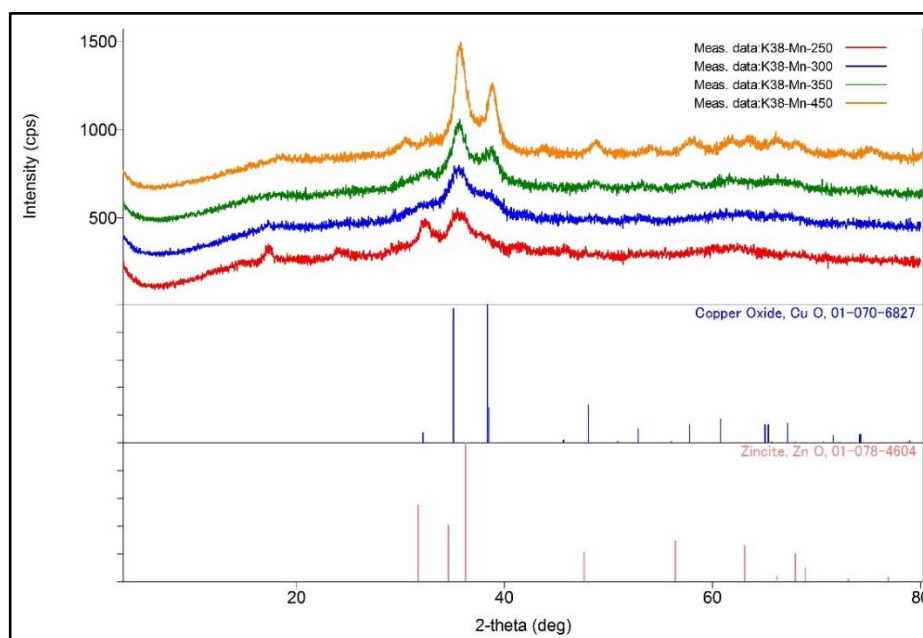


Figure 2.5: Comparative XRD diffractograms of the Mn promoted catalysts calcined at 250, 300, 350 and 450 °C.

Cen et al. [7] prepared Cu-based catalysts via co-precipitation method without any promoter and observed that BET surface area of the catalyst after calcination at 350 °C was 61.60 m²·g⁻¹. In the present work, BET surface areas of Cu-based catalysts containing Cr and Mn promoters prepared with co-precipitation method and calcined at 350 °C yielded 91.89 and 86.74 m²·g⁻¹, respectively. Meshkini et al. [40] synthesized Cu-based catalysts with Mn promoter by co-precipitation method, calcined them at 350 °C and measured BET surface areas. They obtained BET surface area of 82.77 m²·g⁻¹ for Mn promoted Cu-based catalysts whereas BET surface area of 86.74 m²·g⁻¹ was obtained in our study for Mn promoted Cu-based catalyst calcined at 350 °C. These results revealed that the catalyst synthesized in our work had higher BET surface area than the BET surface areas reported by Cen et al. [7] and Meshkini et al. [40]. This means that the higher the BET surface area the more the catalytic activity of the catalyst is expected [40]. Another parameter which caused an increase in surface area and pore volume by inhibiting the structural growth was Mg additive [43] .

Table 2.2: CuO crystallite size and BET surface areas of calcined catalysts.

Catalyst Name	BET Surface Area (m²·g⁻¹)	d_{CuO}^a (nm)
K38-Cr-450	65.619	9.8734
K38-Cr-350	91.890	7.256
K38-Cr-300	140.019	—
K38-Cr-250	140.639	—
K38-Mn-450	62.688	6.266
K38-Mn-350	86.741	3.328
K38-Mn-300	96.035	—
K38-Mn-250	93.646	—

^a Crystallite size of CuO was determined by Debye-Scherrer equation ($2\theta=35.50^\circ$)

Previous studies investigated the effects of Mg and Mn promoters on the activity of catalysts [43], [53]. In these studies, it was found that the addition of weakly alkaline additives or oxides of metals with variable valences could affect the CO₂ adsorption capacity of catalysts. Magnesium oxide changes the acid–base properties of the catalysts and manganese oxide influences their redox properties [53]. Therefore, these promoters are good choices for catalyst additives [53].

2.2.4. Reduction Properties of Calcined Catalysts

H₂-TGA results showed that CuO in the samples reacted with H₂ and transformed into active Cu form (Cu⁺). The H₂-TGA and H₂-DTG profiles of Cr and Mn promoted catalysts are shown in Figure 2.6 and Figure 2.7, respectively. There are single peaks on the H₂-DTG diagram for Cr and Mn. Cen et al. [7] analyzed the reduction behavior of Cu-based catalyst by H₂-TGA, and they stated that the first peak existing on the H₂-DTG curve belonged to the reduction of Cu²⁺ to Cu⁺. This could be attributed to the reduction of CuO to Cu⁺. The maximum weight loss was observed for the catalysts calcined at 250 °C. The XRD patterns suggested that this weight loss could be attributed to the decomposition of the carbonate phases found in the catalysts calcined below 350 °C. The weight loss of the catalysts calcined at 350 °C or above indicated the active Cu⁺ content. The highest weight loss for the Cr and Mn promoted catalysts was observed for the catalysts calcined at 350 °C. This indicated that these catalysts had the highest Cu content [36].

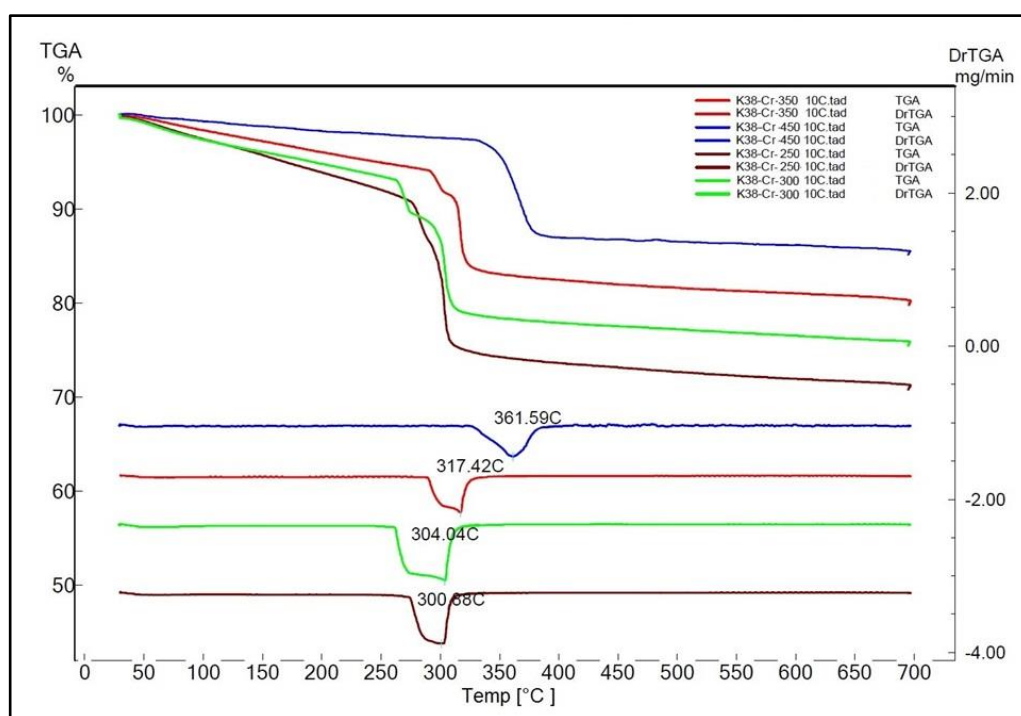


Figure 2.6: Comparison of the H₂-TGA and H₂-DTG curves of the Cr promoted catalysts calcined at 250, 300, 350 and 450 °C.

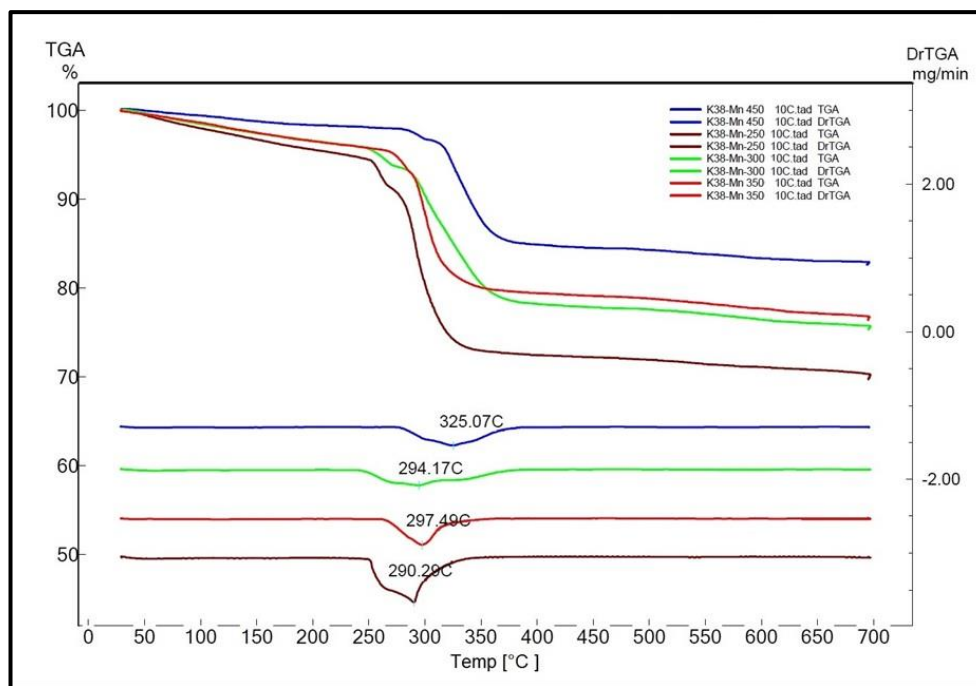


Figure 2.7: Comparison of the H₂-TGA and H₂-DTG curves of the Mn promoted catalysts calcined at 250, 300, 350 and 450 °C.

The reduction characteristics of the calcined catalysts was also analyzed by TPR (Figure 2.8). The reduction process proceeded in single stage. The total reduction of CuO forms for Mn containing catalysts was obtained in the temperature range up to 300 °C while the total reduction of CuO forms for Cr containing catalysts was 340 °C. The maximum H₂ consumption value (46%) among Cr containing catalysts was obtained for K38-Cr-300 at the peak temperature of ~270 °C (Figure 2.8a). The H₂ consumption values for K38-Cr-250, K38-Cr-350 and K38-Cr-450 were between ~40 and 44% for the peak temperatures of 275-285 °C. Although the CuO formation was not observed for the catalysts calcined at 250 and 300 °C, the H₂ consumption values of all Cr containing catalysts were similar to each other. This could be attributed to the reaction of Cr containing structures with H₂. H₂ consumption values of Mn containing catalysts calcined at 250 and 300 °C were about 20% because the CuO phases were not observed for these catalysts calcined at these temperatures as confirmed by the XRD results (Figure 2.8b). The highest H₂ consumption values for K38-Mn-350 and K38-Mn-450 catalysts were 52 and 57%, respectively. The H₂% consumption results are in good agreement with the H₂-TGA and XRD results (Figure 2.4 and Figure 2.7). The H₂-DTG and TPR peak temperature values of the Mn containing catalysts were lower than the Cr containing catalysts. Wang et al. [54] reported that the reduction

peaks present on TPR at lower temperatures were relevant with methanol production activity. Ud Din et al. [55] carried out H₂-TPR experiments using Cu/Zr based catalysts and observed a two-step reduction ($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}$). After the methanol activity experiments, they reported that decreasing the peak temperature of the first reduction stage and increasing the area of this peak could significantly increase methanol production capacity of the catalysts [55]. Le-Phuc et al. [56] found that methanol production activity increased by decreasing the TPR peak temperatures and by expanding associated peak areas. Thus, H₂-DTG and H₂-TPR results showed that lower H₂-DTG peak temperatures and higher peak areas were related to higher methanol production activity. The H₂-DTG peak temperature values of the Mn containing catalysts were lower than the Cr containing catalysts, and this pointed out higher activity (Figure 2.6) (Figure 2.7) (Figure 2.8). In addition to TPR results, XRD, BET surface area, H₂-TGA and H₂-DTG results indicated that the optimum calcination temperature for both catalysts is 350 °C.

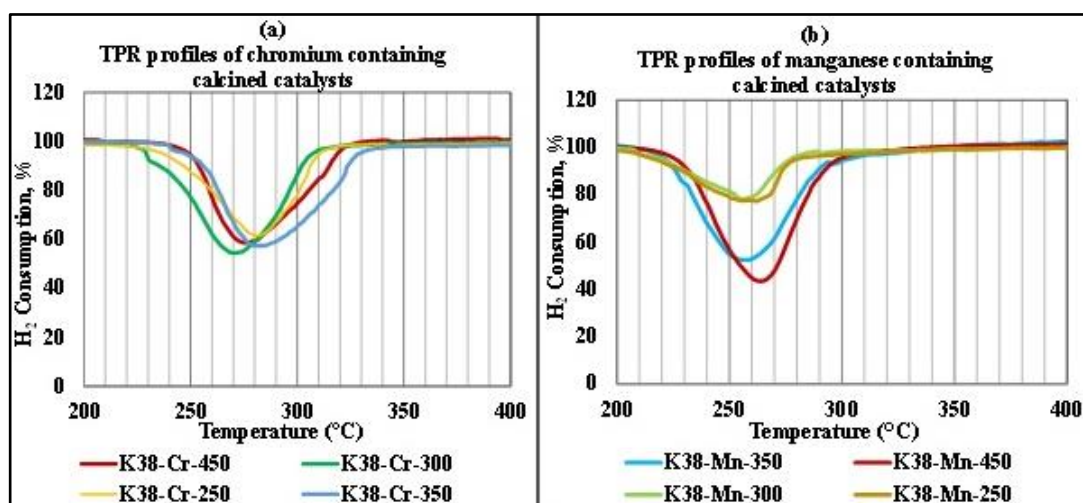


Figure 2.8: Comparative TPR profiles of (a) Cr and (b) Mn containing catalysts calcined at 250, 300, 350 and 450 °C.

3. EFFECTS OF MAGNESIUM AND CHROMIUM ADDITION ON STABILITY, ACTIVITY AND STRUCTURE OF COPPER-BASED METHANOL SYNTHESIS CATALYSTS

Methanol with wide range of industrial applications is an alternative fuel, which can be used in internal combustion engines with lower toxic gas emissions such as carbon monoxide (CO) and nitrous oxides (NO_x) [2]. Besides, methanol is used as a feedstock for the production of formaldehyde, acetic acid and several important chemicals [3]–[5]. It is also used for storage and transportation of hydrogen (H₂). Conventionally, methanol is produced from syngas that contains CO, carbon dioxide (CO₂) and H₂ by using copper-based catalysts. The catalytic methanol synthesis from syngas was first developed in 1920's based on a process that operates at high pressure (250-350 bar) and high temperature (350-450 °C) with zinc oxide/chromium oxide (ZnO/Cr₂O₃)-based catalysts [6]. In 1960's, the process was improved by using copper/zinc oxide/aluminum oxide (Cu/ZnO/Al₂O₃)-based catalyst that could be operated at a relatively low pressure (50-120 bar) and low temperature (230-280 °C) [6]. Yet, as of today, there are still many shortcomings for Cu-based catalysts such as poor tolerance to poisoning, low thermal stability, low mechanical strength and short lifetime [7].

Catalyst preparation, synthesis and process optimization are crucial parameters that affect methanol synthesis [8]. The major factors that determine catalytic activity, selectivity, resistance against poisoning, lifetime and methanol yield of the catalyst are catalyst composition, preparation method, precursor type, drying, calcination and reduction conditions [8]. Cu is an active metal for methanol synthesis, and particle size of Cu has an important effect on methanol production. Cu/Zn mol ratio, pH, reaction temperature, calcination temperature and the addition rate of reagent solution influence Cu particle size [9], [10]. Methanol synthesis catalysts are produced by using dry-chemical or wet-chemical methods but co-precipitation method, which is one of the wet-chemical methods, is the most commonly used process for the industrial production of methanol synthesis catalysts. Likhittaphon et al. [11] worked on the synthesize methods of Cu-based catalysts and they reported that the catalysts synthesized by ultrasonic-assisted precipitation have larger surface area and better

dispersion than the catalysts which were prepared by conventional methods. Dasireddy et al. [12] investigated the effect of pH on the activity of copper/magnesium oxide/aluminum oxide (Cu/MgO/Al₂O₃) catalysts and found that the catalyst prepared at pH 8 showed higher methanol productivity at temperatures below 250 °C due to improved H₂ adsorption by enhanced Cu and BET surface areas. The surface acidity of the catalyst is another important point, and high surface acidity causes formation of higher hydrocarbons and/or dimethyl ether [13]. Adsorption of CO₂ by the catalysts is related to the surface alkalinity because of the acidic characteristic of CO₂ [14]. Addition of ZnO, which is a basic oxide, neutralizes the surface acidity of catalysts and provides higher methanol selectivity [15]. Alkaline-earth metal oxides (BaO, CaO, MgO and SrO) cause the formation of strong basic sites on the catalysts, and therefore, increase methanol selectivity [14].

The type of support and promoter affect catalyst's selectivity for methanol and its activity [17], [18]. Hus et al. [19] synthesized copper/chromium (Cu/Cr), copper/iron (Cu/Fe), copper/magnesium (Cu/Mg) and copper/zinc (Cu/Zn) binary catalysts via co-precipitation, and Cu/Cr catalyst gave the lowest surface area and showed that Cu/Zn catalyst had the best performance among binary Cu-based catalysts. Cu/Zn methanol synthesis catalysts are used conventionally at mild operating pressures and temperatures, but they have low resistance to sulfur impurities in syngas and low thermal stability [13]. Zn/Cr₂O₃ catalysts have higher thermal stability and resistance against sulfur poisoning than Cu-based catalysts, but their operation conditions require high temperatures and pressures [20]. To overcome the problems associated with the utilization of binary catalysts, ternary catalysts or catalysts that include multiple promoters have been developed. Kilo et al. [21] synthesized binary Cu/Zr, ternary Cu/Zr/Cr and Cu/Zr/Mn methanol synthesis catalysts and found that Cu/Zr/Cr catalyst gave the highest methanol production rate by providing the highest Cu/Zr surface concentrations. Sadeghinia et al. [22] synthesized ternary catalysts by the addition of trivalent elements such as aluminum (Al³⁺) or chromium (Cr³⁺) as the third metal and determined that these additives increased the dissolution rate of Cu in ZnO, decreased Cu particle size, and thereby improved the catalytic activity. It was reported Cr increased activity, thermal stability and regenerability of Cu/ZnO/Cr₂O₃ catalysts similar to Al [24]. Al₂O₃ is generally used for the Cu-based catalysts, and has a promotional effect on Cu/ZnO catalyst [23].

Chen et al. [25] investigated the effects of doping trivalent metal ions into a Cu-based (Cu/ZnO/Al₂O₃) catalyst for methanol synthesis and found that chromium (III) oxide (Cr₂O₃) could increase the concentration of Cu⁺ on the surface of the catalyst; thus, enhancing both enrichment and stabilization of Cu⁺ on the surface during reduction and reaction processes. Cu/Al₂O₃/ZnO-Zn ternary catalysts and their binary analogues containing 10% Al₂O₃ in the catalyst composition inhibited the reduction of Cu²⁺ to inactive Cu⁰, and stabilized Cu⁺ by slowing down the reduction of Cu²⁺ and holding it in active Cu⁺ form [26]. Addition of 3.5% Mg into Cu/ZnO/Al₂O₃ catalysts was found to be more active for the hydrogenation of CO₂ mostly due to the improvement of the catalyst surface area [28]. Dasireddy et al. [14] synthesized Cu/Al catalysts with MgO, CaO (calcium oxide), SrO (strontium oxide) and BaO (barium oxide) and reported that Mg promoted catalyst gave higher conversion due to higher Cu metallic surface area and Cu⁺/Cu⁰ ratio. Hayward et al. [27] reported that Cu/Mg catalyst with a molar ratio of 70:30 had lower methanol activity although it provided higher Cu surface area.

In many studies in the literature, the ageing time of the suspensions was limited to a few hours [5], [22], [23], [27], [40], [46], [57]–[60]. The first novelty of our research was that the suspensions were aged at a certain pH value for a longer period of time up to 24 hours to obtain high malachite phase formation which is the indication of increased Cu-ZnO contact and enhanced Cu surface areas [44], [61]. In many works, only a single promoter was used in the composition of methanol synthesis catalysts [7], [24], [27], [28], [57], [62]. Only in a few studies, the effects of multiple promoters were studied, and the promotional effect of Cr and Mg on Cu/ZnO/Al₂O₃ catalysts has been investigated individually [40]. Cr and Mg additives have not been simultaneously used for enhancing catalytic and structural properties of commercially prepared Cu/ZnO/Al₂O₃ catalysts. The second novelty of our research was that simultaneous effects of Cr and Mg additions on the catalytic activity of methanol synthesis catalysts were investigated. Therefore, the objectives of this part are to: (i) prepare Cu/ZnO/Al₂O₃ catalysts with and without Mg and Cr promoters using nitrate route via co-precipitation, (ii) characterize the catalysts using H₂-temperature programmed reduction (H₂-TPR), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), thermal gravimetric analyzer (TGA) and scanning electron microscopy (SEM), (iii) enhance active surface area of the prepared catalysts by reducing CuO particle size, (iv) investigate effect of multiple promoters on the activity of Cu/ZnO/Al₂O₃ catalysts,

(v) improve the catalytic activity, methanol selectivity, durability and stability of Cu/ZnO/Al₂O₃ catalysts by the addition of multiple promoters including Mg and Cr, and (vi) enhance operational lifetime of the prepared catalysts.

3.1. Materials and Methods

3.1.1. Materials

Copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) (>99%, w/w) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (>98%, w/w) were purchased from Acros Organics (Geel, Belgium). Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) (>98%, w/w) and sodium carbonate anhydrous (Na₂CO₃) (>99.5%, w/w) were obtained from Carlo Erba (Paris, France). Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) (>99%, w/w) was purchased from Merck (Darmstadt, Germany) and chromium nitrate nonahydrate (Cr(NO₃)₃·9H₂O) (>98%, w/w) was obtained from Carl Roth (Karlsruhe, Germany). All reagents were analytical grade and used as received. All solutions used in the experiments were prepared with deionized water.

3.1.2. Catalyst Preparation

Conventional co-precipitation method explained by Zander was used for the synthesis of the catalysts [63]. One molar (M) aqueous solutions of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O called as metal solution and 1.6 M aqueous solution of Na₂CO₃ called as base solution were prepared. The composition of the metal solution was adjusted according to the molar ratios of the metal components (Table 3.1). Copper/zinc/aluminum (CZA) and copper/zinc/aluminum/magnesium (CZAM) precursors were synthesized. CZAM-10Cr was synthesized by adding 10% (mol/mol) of the total Cu in the CZAM as Cr, and CZAM-50Cr was synthesized by adding 50% (mol/mol) of the total Cu in the CZAM as Cr. The calculations were made for the oxide forms of Cu and Cr.

Table 3.1: Catalyst compositions (Mol %).

Catalyst Code	Cu	Zn	Al	Mg	Cr
CZA	65.0	26.0	9.0	-	-
CZAM	64.0	25.0	8.0	3.0	-
CZAM-10Cr	57.6	25.0	8.0	3.0	6.4
CZAM-50Cr	32.0	25.0	8.0	3.0	32.0

One hundred mL of metal solution and 100 mL base solution were simultaneously pumped by using a peristaltic pump (Cole-Parmer, Masterflex L/S Easy Load, IL, USA) at a rate of 10 mL·min⁻¹ into 200 mL's of deionized water. During the reaction, precipitation medium was kept at 65 °C and it was stirred at a rate of 150 rpm. After completing the charging process, the suspensions were aged in the mother liquor at 65 °C with continuous stirring at 150 rpm for 24 h and the resulting suspension was kept at pH 8.1 ± 0.3 by using a micro automated pH controller (BlueLab, New Zealand). The precipitate received upon aging was filtered, washed with hot deionized water at 65 °C until adjusting the pH of the washing liquor near to about 7. The sodium (Na) contents of the precipitates were analyzed by an inductively coupled plasma–mass spectrometer (ICP-MS) (Thermo Fischer Scientific, iCAP RQ, MA, USA) to make sure that Na concentration is below 20 ppm in the precipitates. Then, the precipitates were dried under air at 105 °C overnight. The dried precursors were heated up to 450 °C with a heating rate of 1 °C·min⁻¹, and they were calcined at these temperatures for 10 h. The calcined catalysts were grinded and passed through a sieve with a US sieve size of 140 equivalent to Tyler mesh sizes of 150 (105 µm). Schematic overview of the experimental synthesis route is shown in Figure 3.1.

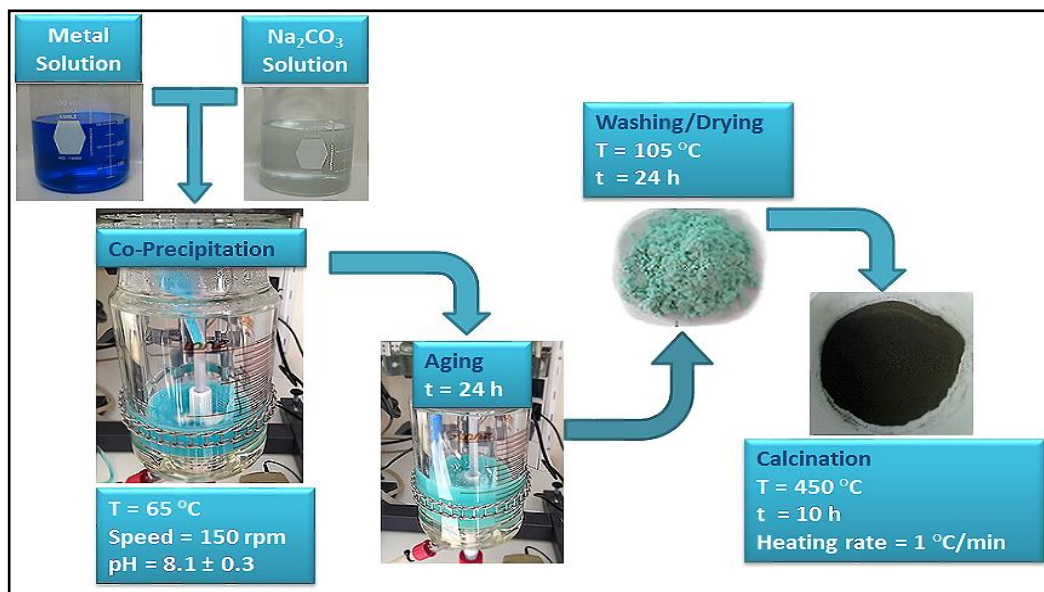


Figure 3.1: Schematic overview of the multistep experimental synthesis route.

3.1.3. Catalyst Characterization

Structure and crystallinity of i) catalyst precursors, ii) calcined catalysts, iii) reduced catalysts and iv) catalysts stored at 23 °C and 50% RH conditions for two years in a climacteric chamber (Sanyo, model MLR-351, Tokyo, Japan) were characterized by an XRD diffractometer (Rigaku Corp., Miniflex 600, Tokyo, Japan) operated under Cu-K α radiation at $\lambda=1.54$ Angstrom, 40 kV and 15 mA. The Cu and CuO crystallite sizes of the catalysts were calculated from the broad diffraction line of XRD pattern according to modified Scherrer formula given in Equation (3.1) [64]:

$$\ln(\beta) = \ln\left(\frac{1}{\cos\theta}\right) + \ln\left(\frac{K\lambda}{D}\right) \quad (3.1)$$

where D is the mean crystallite size (nm), K is the Scherrer constant (0.89), λ is the X-ray wavelength (1.54 °Å), β is the full width at half maximum of the diffraction peak (radian) and θ is Bragg diffraction angle (degree).

TGA analyses (H₂-TGA and Air-TGA) were performed by using a thermogravimetric analyzer (Shimadzu Corp., DTG-60H TG/DTA, Tokyo, Japan). Thermal decomposition of precursors was studied by Air-TGA. The sample holder was loaded with ~10 mg of precursor. The weight loss of the sample was monitored

during the heating period up to 700 °C with a heating rate of 10 °C·min⁻¹ under air flow (300 mL·min⁻¹). Weight loss during reduction process of calcined catalysts was analyzed using H₂-TGA. For this purpose, ~10 mg of calcined catalyst was heated from 25 to 700 °C at a heating rate of 10 °C·min⁻¹ under H₂-N₂ mixture (20% H₂ and 80% N₂) at a flow rate of 50 mL·min⁻¹.

Morphology and surface texture of the catalysts were examined by a scanning electron microscopy (SEM) (Tescan Orsay, Vega 3 Sbh, Kohoutovice, Czech Republic) operating at a voltage of 10 kV. The calcined catalysts were mounted on SEM stubs and sputter coated with a thin layer of carbon using a sputter coater (Quorum Technologies, Quorum CA7625, East Sussex, UK).

Surface areas of the calcined and reduced catalysts were determined by N₂ adsorption isotherm at 77 K by using a surface area analyzer (Quantachrome Instrument Corp., Quadrasorb-S1, FL, USA). Prior to the measurements, the samples were degassed under vacuum at 150 °C overnight.

Reduction characteristics of the catalysts were studied with the H₂-TPR experiments by using a continuous flow tubular fixed bed reactor equipped with an on-line mass spectrometer (HIDEN Analytical, HAL201 RC, Warrington, UK). One gram of catalyst was put into a stainless-steel tubular reactor. After the samples were pretreated with N₂ at 25 °C for 10 min, they were reduced under 10% H₂/90% N₂ stream at a flow rate of 0.2 L·min⁻¹ and heating up to 750 °C with a heating rate of 5 °C·min⁻¹.

Surface acidity of the catalysts was determined with TGA by using temperature programmed ammonia desorption (TPAD) method (TPAD-TGA) [65], [66]. The sample holder was loaded with ~10 mg of catalyst, and the catalyst was reduced at 300 °C under H₂-N₂ mixture (20% H₂ and 80% N₂) at a flow rate of 50 mL·min⁻¹. After the samples were cooled down to 100 °C under 50 mL·min⁻¹ N₂ flow, NH₃-N₂ mixture (5% NH₃ and 95% N₂) was fed to the system at a flow rate of 50 mL·min⁻¹ for 60 min. Excess NH₃ was removed from the system at 100 °C with N₂ at a flow rate of 50 mL·min⁻¹ until there was no change in weight loss. NH₃ adsorbed catalysts were then heated from 100 to 500 °C with a heating rate of 5 °C·min⁻¹ under N₂ at a flow rate of 50 mL·min⁻¹, and the change in weight was recorded.

3.1.4. Catalyst Evaluation

The catalytic performance tests of the calcined catalysts were carried out in a stainless steel (316L) fixed-bed reactor with 15 mm ID and 130 mm length (Figure 3.2). The system had a gas feeding unit, eight reactor ovens working in parallel with each other, independent liquid product collectors for each reactor, and an analysis unit monitoring reactor effluents.

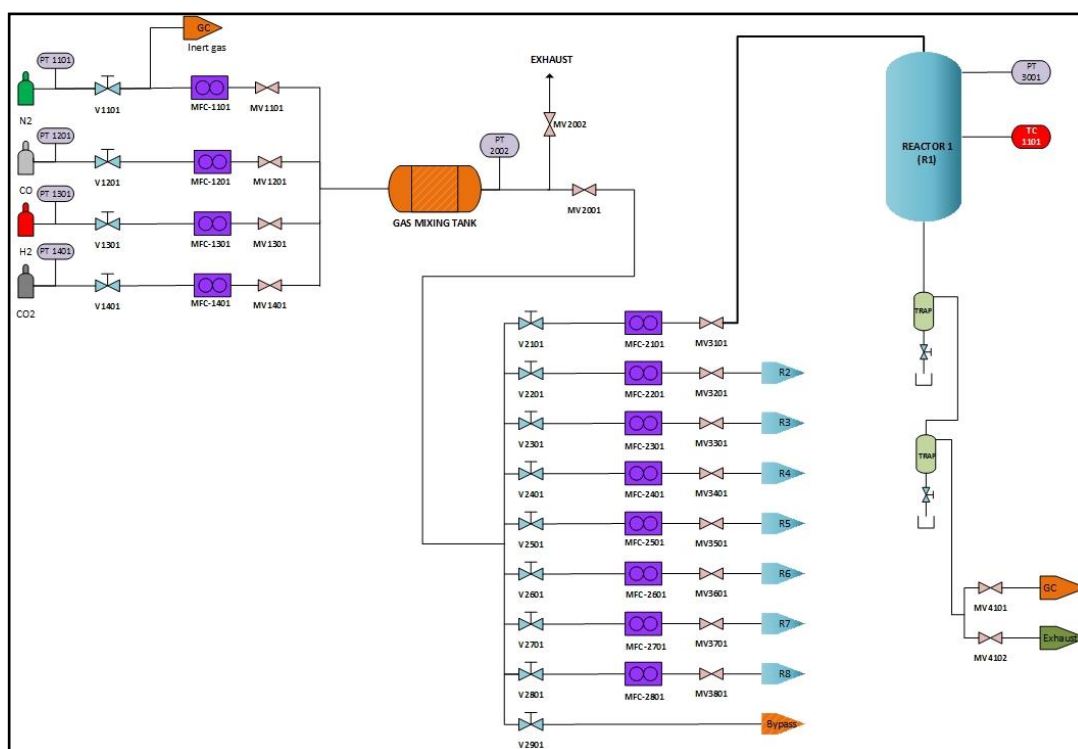


Figure 3.2: Flow diagram of the methanol synthesis reactor.

Prior to the performance tests, fresh catalysts (1000 mg of calcined catalyst mixed with 1000 mg quartz sand (100-200 mesh)) were subjected to a reduction process in order to convert CuO to active Cu^+ form. The reduction was carried out using a $125 \text{ cm}^3 \cdot \text{min}^{-1}$ $\text{N}_2\text{-H}_2$ mixture (9:1) flowing at 240°C for 15 h. After the reduction was completed, the reactor was purged with N_2 with a flow rate of $50 \text{ cm}^3 \cdot \text{min}^{-1}$ for 5 h until the reactor bed temperature was reduced to 170°C . Afterwards, high purity ($> 99\%$) reactant gases with a composition of 8% N_2 (as an internal standard for mass balance calculations), 5% CO_2 , 29% CO and 58% H_2 were fed to the reactor. The system was set to 230°C and 48 bar. The reaction temperature was

continuously measured by a K-type thermocouple placed in the center of the catalyst bed to assure isothermal conditions. Gas hourly space velocity values were adjusted to 5000 h⁻¹. The reactant and reactor effluents separated from the liquid products were monitored with on-line running gas chromatography (Agilent Technologies Inc., Agilent 6890 GC System, CA, USA) equipped with a thermal conductivity detector (TCD) and HP plotQ (30 m x 0.53 mm x 40 µm), HP plotQ (15 m x 0.53 mm x 40 µm) and HP Molsieve (30 m x 0.53 mm x 50 µm) capillary columns. Liquid products condensed in the cooling traps were collected and analyzed offline with a gas chromatography (Agilent Technologies Inc., Agilent 7890A GC System, CA, USA) equipped with a flame ionization detector (FID) and DB wax (30 m x 0.25 mm x 0.25 µm) capillary column for methanol selectivity. Methanol selectivity was calculated according to Equation (3.2) given below [11]:

$$\text{Methanol selectivity} = \frac{\text{Moles of methanol in liquid product}}{\text{Total moles of all liquid products}} \times 100 \quad (3.2)$$

3.2. Results and Discussion

3.2.1. Crystal Structure Analysis of Precursors

The main XRD reflections of the phases existed in the copper/zinc/aluminum (CZA) and copper/zinc/aluminum/magnesium (CZAM) containing precursors were determined for rosasite ((Cu,Zn)₂CO₃(OH)₂—DB card number: 00-017-0216) at 2θ=14.637°, 17.467°, 24.075° and 29.591° for malachite (Cu₂(OH)₂CO₃—DB card number: 01-072-8421) at 2θ=14.715°, 17.496°, 24.029° and 29.470° for aurichalcite ((Cu,Zn)₅(OH)₆(CO₃)₂—DB card number: 01-082-1253) at 2θ=13.028°, 24.032°, 27.857° and 32.655°, and for copper aluminum hydrotalcite ((Cu_{2.5}Al₂C_{1.7}O_{8.9}·5.2H₂O—DB card number: 00-046-0099) at 2θ=11.750°, 23.579°, 35.617° and 39.258°. The same 2θ values showing the presence of rosasite, malachite, aurichalcite and hydrotalcite was also reported in the literature [45], [46] which was parallel to our results. Copper hydronitrates and zinc hydrocarbonates showed XRD diffraction patterns similar to the mixed precipitates (Figure 3.3a).

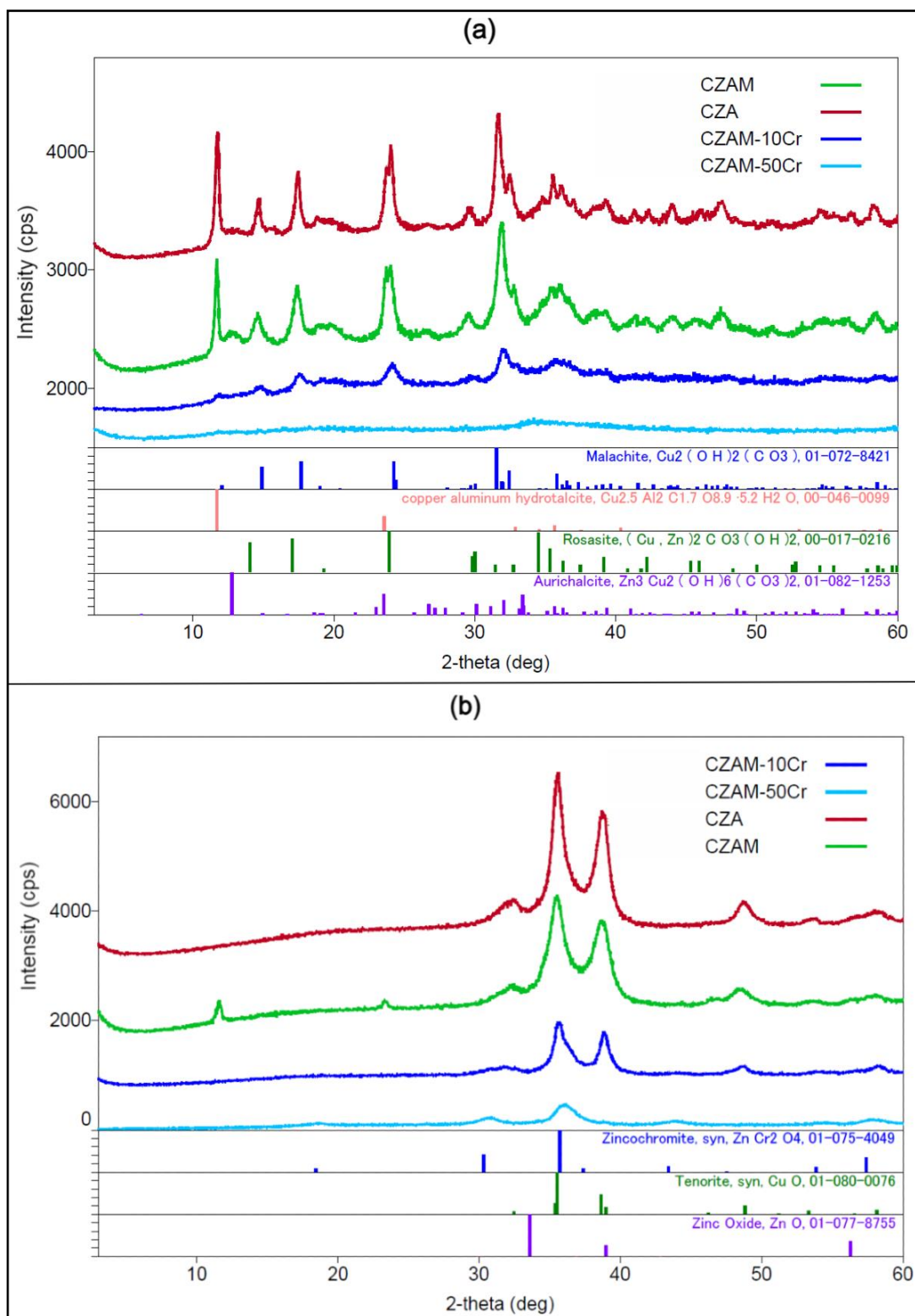


Figure 3.3: XRD diffractograms of (a) precursor samples and (b) calcined catalyst samples.

The intensity of the diffraction lines for precursors containing Cr decreased by increasing the Cr content (Figure 3.3a). This behavior was attributed to the increase in ZnCr_2O_4 content by increasing the amount of Cr in the precursor where ZnCr_2O_4 exhibited the amorphous phase before calcination [67]. This is the reason why no diffraction line was observed for CZAM-50Cr which has the maximum Cr content. Rosasite, malachite and poor hydrotalcite-like phase intensities were observed for CZAM-10Cr precursor contained only hydroxycarbonate phases including rosasite and malachite. Hydrotalcite-like phase was also detected in CZAM-10Cr, CZAM and CZA precursors [45]. The existence of hydrotalcite-like phase in the precursor is an indication of homogeneous dispersion of M(II) (such as Cu^{2+} , Zn^{2+} and Mg^{2+}) with M(III) (such as Al^{3+} , Cr^{3+} and Ga^{3+}) and improved interaction between Cu and oxide phases [8], [12]. Catalysts prepared by using hydrotalcite-like phase showed higher specific surface area, CO_2 conversion and methanol selectivity alongside with improved resistance against sintering [8]. Catalysts derived from malachite precursors yielded higher methanol synthesis activity due to increased Cu-ZnO contact and Cu surface area [44], [61]. Aurichalcite phase had an improved effect on increasing Cu dispersion and methanol synthesis activity [8]. Comparison of the XRD diffractograms of the precursors indicated that addition of Cr decreased malachite and rosasite formation and even led to the disappearance of these phases by further increasing the Cr content.

3.2.2. Decomposition Characteristics of Precursors

Peak temperatures and weight loss patterns were evaluated from Air-TGA and Air-DTG curves of the precursors (Figure 3.4a and b). Weight losses up to 100 °C could be attributed to the loss of physically adsorbed water. First weight loss observed for CZA and CZAM precursors between 100 and 160 °C is associated with the crystal water losses from $\text{Cu}_2\text{Zn}_4\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ [45], [48]. The second weight loss occurred in the temperature range between 150 and 400 °C is attributed to decompositions of hydroxycarbonate (rosasite, zinc malachite and aurichalcite), hydrotalcite carbonate and hydroxynitrate species to their oxide forms [48].

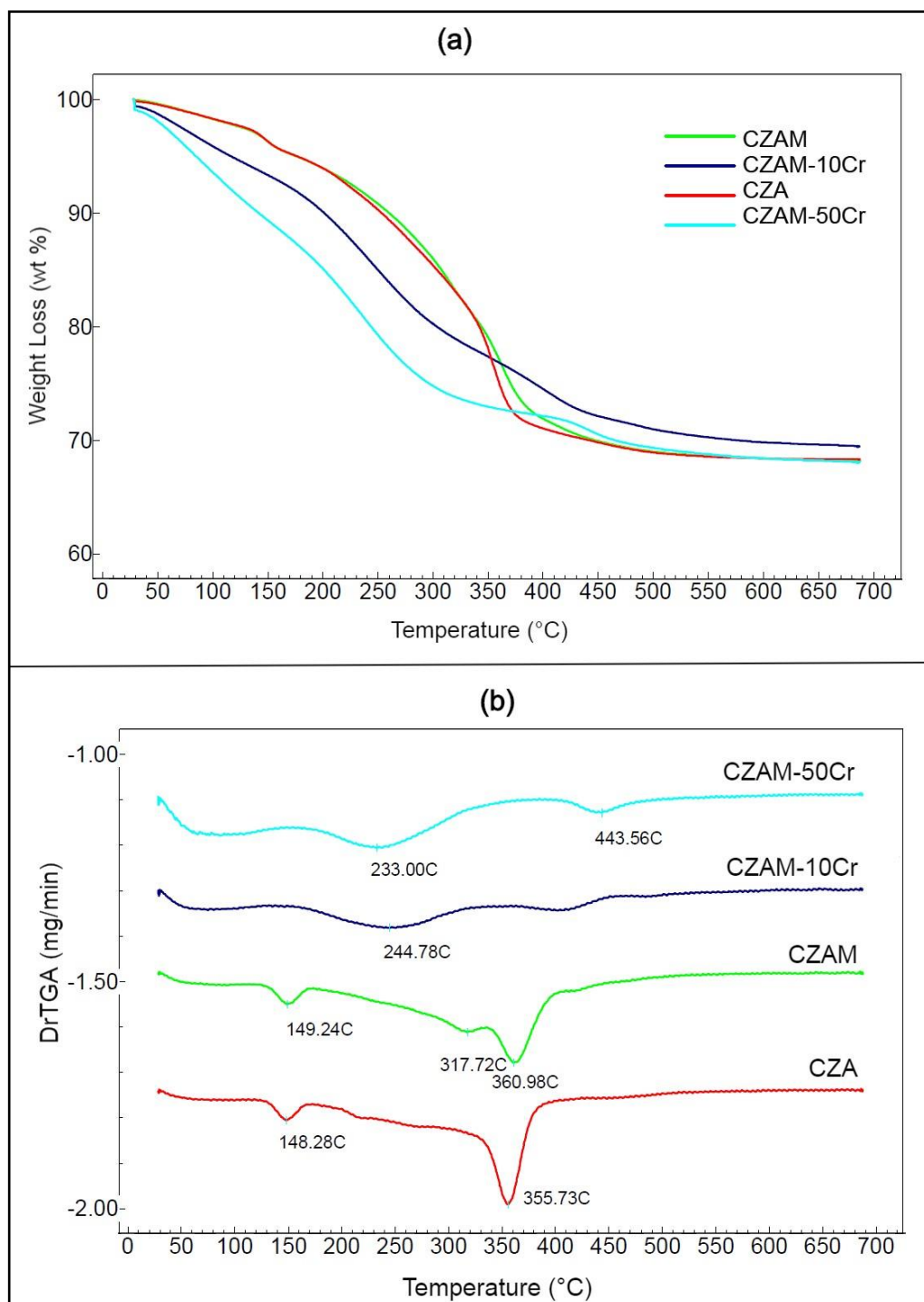


Figure 3.4: (a) Air-TGA and (b) Air-DTG curves of catalyst precursors.

Air-DTG curves of CZAM-10Cr and CZAM-50Cr precursors were different from the CZA and CZAM. There was no crystal water loss peak around 100 °C. This was due to the nonexistence of hydroxalcalite like phase, corresponding to crystal water in the Cr containing precursors. The first endothermic peak observed between 200 and 250 °C was attributed to the decomposition of hydroxide phases that existed in the

CZAM-10Cr and CZAM-50Cr precursors. The last endothermic peak between 400 and 450 °C was due to the initiation of crystallization reaction of ZnCr_2O_4 phase. According to Air-TGA profiles of the four precursors, the final weight losses were almost the similar, namely at around 35%. This behavior can be explained by the presence of similar hydrocarbonate or nitrate precursors, but in different cationic species.

3.2.3. Crystal Structure, Particle Size and Surface Area Analysis of Calcined Catalysts

Broad XRD diffraction peaks of the calcined catalyst for tenorite (CuO —DB card number: 9015887) and zincite (ZnO —DB card number: 01-075-1526) suggested that structures of hydroxyl carbonates were decomposed during calcination, and the resulting CuO and ZnO in the samples existed in a microcrystalline state (Figure 3.3b). In CZAM-10Cr, in addition to CuO and ZnO , there were signals at 2θ angles of 30.56° , 35.41° , 43.71° , 53.82° , 58.11° , 63.91° , 72.53° and 74.99° , which belong to zincochromite (ZnCr_2O_4 —DB card number: 1011278). The dried ZnCr_2O_4 gives smooth diffractogram until calcination, and then gave signals [67]. This could be attributed to the disappearance of amorphous phase and the detection of ZnCr_2O_4 in CZAM-50Cr after calcination. The CZAM-50Cr precursor had no Cu/Zn hydroxycarbonate phase due to high Cr load and low Cu content. After calcination, CuO and ZnCr_2O_4 phases were formed. None of the Cr containing catalysts exhibited diffraction lines belonging to chromium oxide (Cr_2O_3) due to the amorphous nature of Cr_2O_3 [59]. XRD diffractograms of CZA with CZAM revealed that the CuO phase in CZA gave sharper signals indicating the formation of larger crystalline structures.

The BET surface area and calculated CuO crystallite size values showed that larger crystallite size can cause smaller surface area (Table 3.2). Smaller CuO particle size is an indicator for good dispersion of CuO on the support surface. Therefore, smaller CuO particle size indicates higher surface area. Addition of Mg and Cr providing well dispersed metal oxide mixture caused the formation of smaller CuO crystallite size; therefore, increased surface area and pore volume. Co-precipitation of Cr is more effective for the catalytic reaction because it gives additional surface area. The smallest CuO crystallite size values were determined for CZAM-50Cr coded

catalyst that had the minimum Cu/Zn ratio. Decreasing the Cu/Zn ratio can decrease CuO particle size, and the existence of ZnO can affect the formation of smaller Cu crystallites [68].

Table 3.2: BET surface areas, pore volumes and CuO crystallite size of calcined catalysts.

Catalyst Name	BET Surface Area (m²·g⁻¹)	Pore Volume BJH (cm³·g⁻¹)	dCuO^a(nm)
CZA	33.826	0.320	6.541
CZAM	39.720	0.415	6.354
CZAM-10Cr	84.397	0.491	4.947
CZAM-50Cr	93.127	0.495	4.588

^a Crystallite size of CuO was determined by modified Scherrer equation

Surface area is not the only parameter for enhanced catalytic activity. Other parameters such as reduction characteristics, chemical structures of phase formations and surface acidity could be analyzed to understand the effects of promoters on catalytic activity. In the current study, all the aforementioned analyses were carried out.

3.2.4. Crystal Structure, Particle Size and Surface Area Analysis of Reduced Catalysts and Catalysts Stored at 23 °C and 50% RH

At two years of storage at 23 °C and 50% RH, XRD patterns of the calcined catalysts were taken. In CZA and CZAM catalysts, formation of Copper Zinc Aluminum Carbonate Hydroxide Hydrate (Cu₃Zn₃Al₂(OH)₁₆CO₃·4H₂O–DB card number: 00-037-0629) phase was observed (Figure 3.5a). The formation of this phase could be attributed to the interaction of the catalyst with moisture and CO₂ in the air. In CZAM-10Cr, signals belonging to this phase were very low, but in CZAM-50Cr, this phase was not detected. These results showed that Cr additive could extend the shelf life of catalysts by increasing their stability against ambient conditions and

improved resistance against sintering. It was reported that presence of water as a byproduct could accelerate Cu sintering [69]. In addition, Cr inhibits the sintering by preserving the catalyst against humidity, O₂ and CO₂ in the air [21].

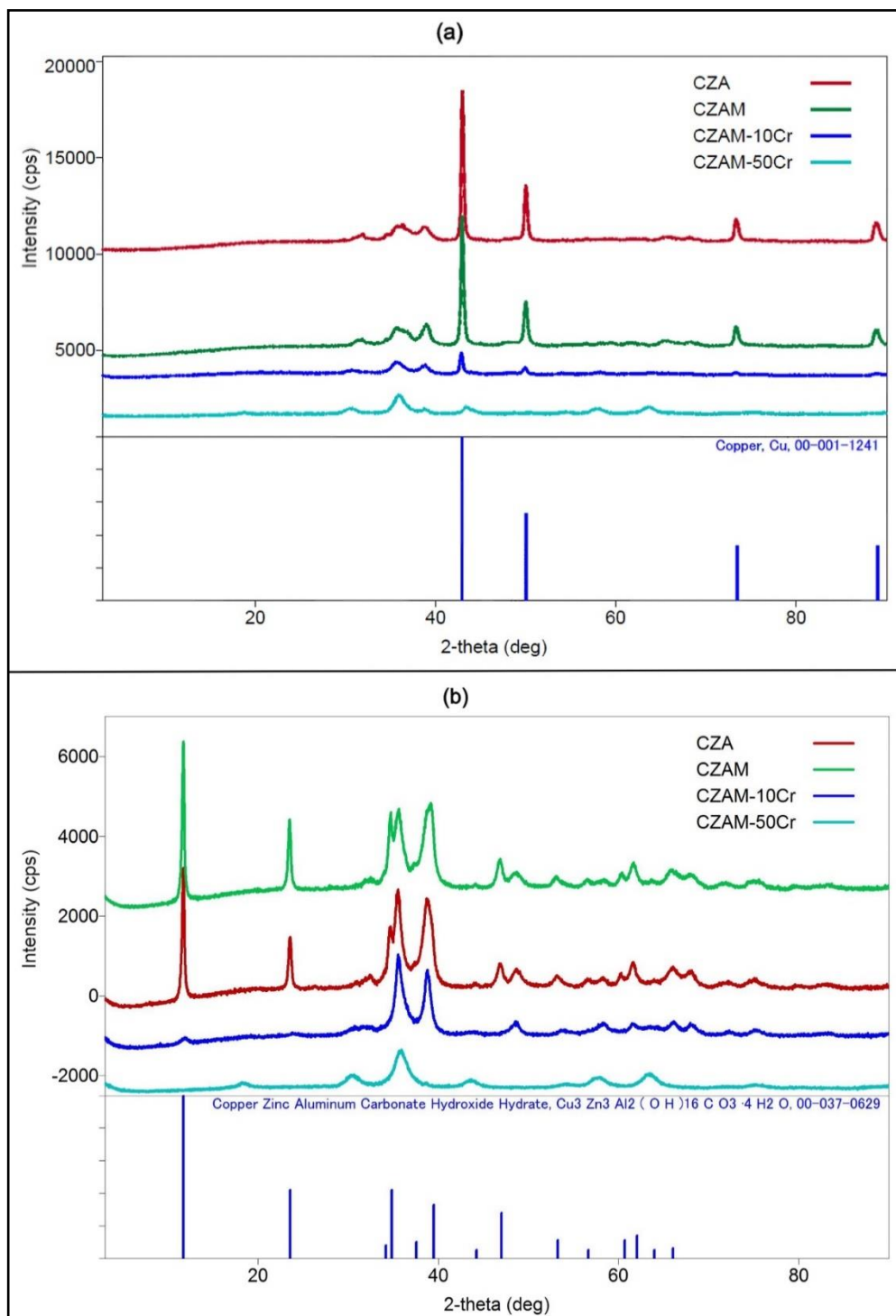


Figure 3.5: XRD patterns of the catalysts (a) after being kept at 23 °C and 50% RH for two years and (b) after H₂-TPR studies.

BET surface area and XRD diffractograms of the reduced catalysts were determined by H₂-TPR analysis (Figure 3.5b). Cu phase (Cu-DB card number: 9013017) was observed in all of the reduced catalysts. Cu signals in the CZA and CZAM catalysts were sharper than the signals existed in the Cr containing CZAM-10Cr and CZAM-50Cr catalysts. Cu crystallite size values of the reduced catalysts were calculated by using Equation (3.1) (Table 3.3). Compared to the BET surface area of the catalysts, lower BET surface areas were obtained for the reduced catalysts. This could be attributed to high temperature treatment of the catalyst (up to 750 °C) during H₂-TPR studies which caused sintering and brass formation in the catalyst structure. The reduction in the BET surface areas of Cr containing catalysts were lower than the CZA and CZAM catalysts. Thus, Cr can provide a significant increase in the thermal stability of the catalysts [24]. Findings for the Cu crystallite sizes supported the BET surface area results found for the reduced catalysts. The minimum Cu crystallite size was observed for the reduced CZAM-50Cr catalyst, which had the smallest particle size, and therefore had the largest BET surface area.

Table 3.3: BET surface areas and Cu crystallite size of reduced catalysts.

Catalyst Name	BET Surface Area (m²·g⁻¹)	d_{Cu}^b(nm)
CZA	18.313	29.314
CZAM	21.394	23.678
CZAM-10Cr	54.587	32.667
CZAM-50Cr	62.797	7.056

^b Crystallite size of Cu was determined by modified Scherrer equation

3.2.5. Reduction Properties and Surface Acidity of Calcined Catalysts

The catalyst reducibility was examined by H₂-TPR via analyzing the H₂ concentration in the outlet gas. Reduction temperatures of the catalysts were estimated using the minimum H₂ concentrations (Figure 3.6). Ud Din et al. [55] carried out H₂-TPR experiments using Cu/Zr based catalysts and observed a two-step reduction

($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}$). After the methanol activity experiments, they reported that decreasing the peak temperature of the first reduction stage and increasing the area of this peak could significantly increase methanol production capacity of the catalysts [55]. Le-Phuc et al. [56] found that methanol production activity increased by decreasing the H_2 -TPR peak temperatures and by expanding associated peak areas. The lowest peak temperature values were obtained for CZAM-10Cr and CZAM-50Cr, and the highest peak area was attained for CZAM-10Cr, which are in good agreement with the previous studies [55], [56]. CZAM-10Cr was expected to give the highest methanol production activity [55], [56].

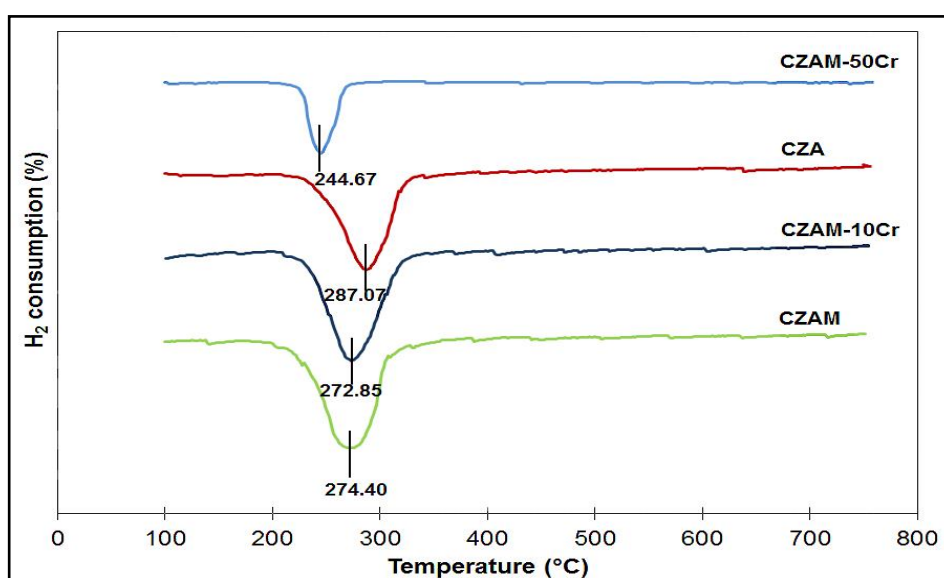


Figure 3.6: H_2 -TPR profiles of calcined catalysts.

High flow rate in the H_2 -TGA analyses eliminates external mass transfer resistance [70]. The H_2 -TPR method carried out at the typical flow conditions (low catalyst weight/ H_2 flow rate ratio) did not provide sufficient H_2O removal and H_2 concentration throughout the catalyst bed. The percentage weight losses of the catalysts showed changes taking place on the catalysts (water desorption) rather than the H_2 uptake (Figure 3.7a).

The Cu^+ that forms at the end of reduction reaction indicates active copper. Mass reduction at the end of H_2 -TGA analyses indicated the Cu^+ and/or Cu^0 content of the catalysts. The maximum weight loss occurred in CZA and CZAM (Figure 3.7a). CZA and CZAM catalysts had the similar H_2 -TGA curves. Two endothermic peaks were

determined in the H₂-DTG curves of CZA and CZAM (Figure 3.7b). The first low temperature shoulder peaks (144.8 °C and 149.3 °C) could be assigned to the reduction of CuO with smaller particle size and/or the reduction of CuO to Cu⁺. The high temperature peak could be attributed to the reduction of CuO with larger particle size and/or the reduction of Cu⁺ to metallic copper Cu⁰ [7], [48], [70]. Cen et al. [7] analyzed the reduction behavior of Cu-based catalysts by H₂-TGA, and stated that the first peak existing on the H₂-DTG curve belongs to the reduction of Cu²⁺ to Cu⁺. This could be attributed to the reduction of CuO to Cu⁺. In our research, we analyzed the reduction behavior of the catalysts with H₂-DTG and H₂-TPR methods. In H₂-DTG curves, Cr containing catalysts gave only one peak, which confirms the formation of Cu⁺ and inhibitory effect of Cr against sintering.

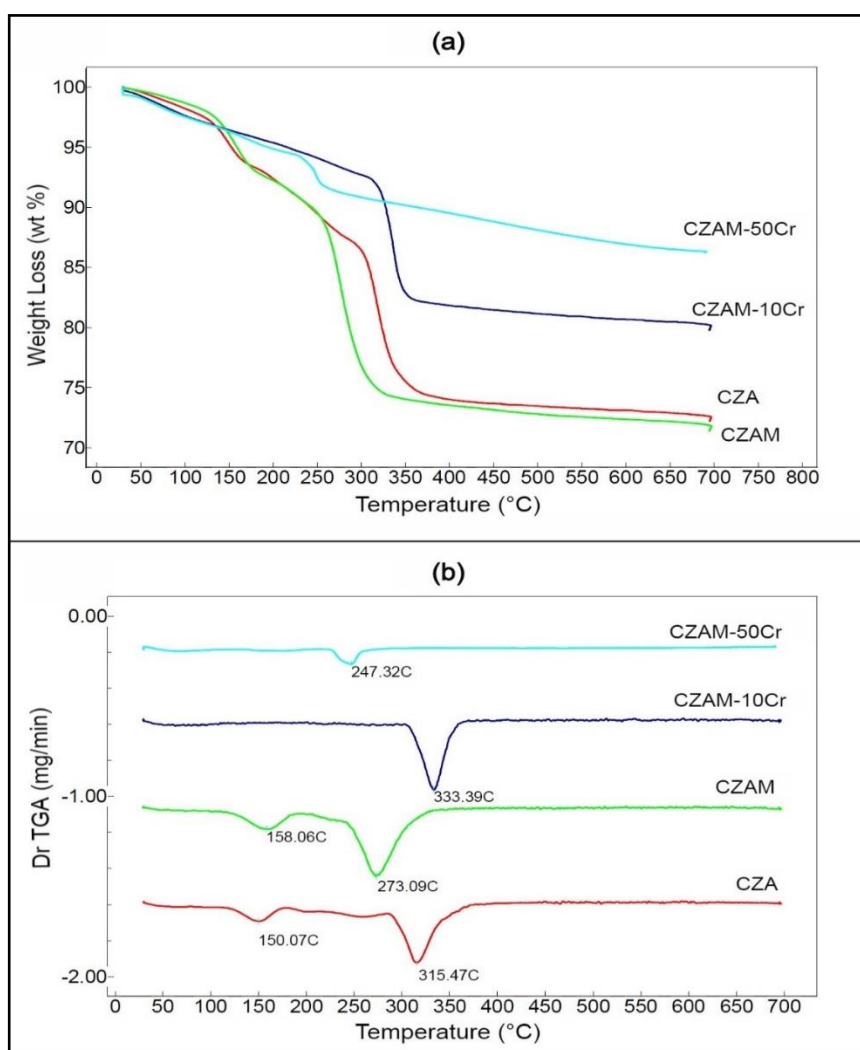


Figure 3.7: Comparison of (a) H₂-TGA and (b) H₂-DTG curves of the calcined catalysts at a heating rate of 10 °C·min⁻¹.

CZAM-10Cr had the maximum peak area (Table 3.4) (Figure 3.7b). CZAM-50Cr had the highest BET surface area, yielded the lowest reduction temperature and the smallest H₂-DTG peak area. The lowest catalytic activity was expected for the CZAM-50Cr because it has the minimum Cu content. The peak areas of CZA and CZAM were close to each other, but small amount of Mg in the CZAM reduced the peak temperature and slightly increased the BET surface area. CZAM and CZA catalysts gave two reduction peaks in H₂-DTG analysis which is the indicator of the formation of inactive Cu⁰.

Table 3.4: H₂-DTG peak areas and H₂-TPR peak temperatures of catalysts.

Catalyst Name	H₂-DTG Peak Area	H₂-TPR Peak Temperature (°C)
CZA	1.001	287.070
CZAM	1.005	274.400
CZAM-10Cr	1.861	272.850
CZAM-50Cr	0.354	244.670

In addition to reduction characteristics, surface acidity of the catalyst has also an effect on the catalytic activity. The surface acidity of the catalysts was determined from TPAD-TGA and TPAD-DTG curves of NH₃ adsorbed catalysts (Figure 3.8a and b). Maximum weight loss was observed for the CZA catalyst showing the highest NH₃ adsorption and acidity. The addition of Mg and Cr decreased weight loss and acidity of the catalysts.

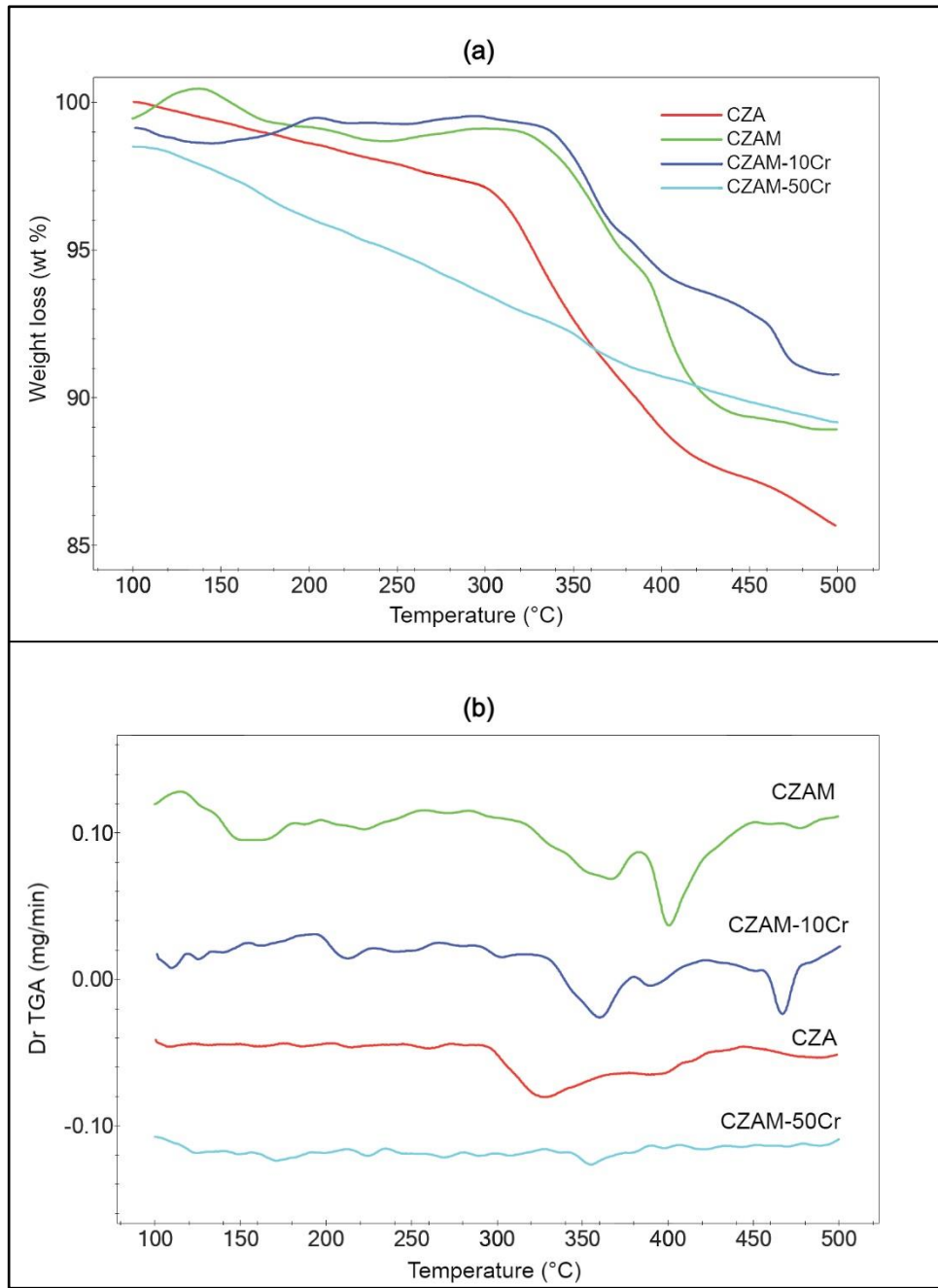


Figure 3.8: (a) TPAD-TGA and (b) TPAD-DTG curves of NH_3 adsorbed catalysts.

Weight loss peaks due to NH_3 desorption were observed in the temperature range of 100 – 250 °C and 250 – 500 °C, which are the indications of weak and strong acid sites, respectively [66]. The surface acidity of the catalysts was calculated by using Equation (3.3) [66].

$$\text{Surface acidity} = \frac{W(g) \times \left(\frac{1}{\text{MW of } \text{NH}_3} \right) \times \left(\frac{1000 \text{ mg}}{1 \text{ g}} \right)}{\text{Mass of catalyst after pretreatment (g)}} \quad (3.3)$$

where W is the mass loss due to the desorption of NH_3 in the corresponding temperature range, and MW is the molecular weight of NH_3 ($17 \text{ g}\cdot\text{mol}^{-1}$).

Surface acidity results showed that Mg addition to the catalyst composition decreased total acidity (Table 3.5). The co-addition of Mg and Cr caused a higher decrease in surface acidity of the catalysts. The lowest total acidity value was obtained for the CZAM-50Cr catalyst which had the highest Cr content. The methanol selectivity of the Cu-based catalysts is related to the existence of basic sites on the catalyst surface, and the methanol production activity and selectivity increased by decreasing the surface acidity [12]–[14]. The decrease in the surface acidity results in the formation of larger surface area and provides a good dispersion of metal components [12]. The BET surface area, CuO particle size and surface acidity results obtained in the current study are in good agreement with the previous studies [12]–[14].

Table 3.5: Weak, strong and total acidity of catalysts ($\text{mmol NH}_3\cdot\text{g}_{\text{catalyst}}^{-1}$).

Catalyst Name	Weak Acidity	Strong Acidity	Total Acidity
CZA	1.238	7.234	8.471
CZAM	1.025	5.972	6.996
CZAM-10Cr	0.364	5.021	5.385
CZAM-50Cr	2.124	3.382	5.506

Fiber like thin particles were spotted in SEM images of CZA (Figure 3.9a). Spherical agglomerated lumps were observed in the interior cavities of the CZAM (Figure 3.9b). In the catalysts with Cr promoter, a spongy like morphology containing agglomerated platelets with irregular edges were observed in CZAM-10Cr (Figure 3.9c) and CZAM-50Cr (Figure 3.9d). The fiber-like phase could be originated from zinc malachite while the platelet-like phase could be related to the formation of hydrotalcite compounds [60]. Hydrotalcite-like compounds are generally formulated as $[\text{M(II)}_{1-x}\text{M(III)}_x(\text{OH})_2]^{x+}[\text{A}^{n-}_{x/n}]^x\cdot m\text{H}_2\text{O}$ where M(II) and M(III) are bi- and trivalent metal cations, A is the exchangeable anion with charge -n, x is the molar ratio of M(III)/[M(III)+M(II)] and m is the moles of H_2O [71]. They kept their morphologies after calcination due to chemical memory effect [71].

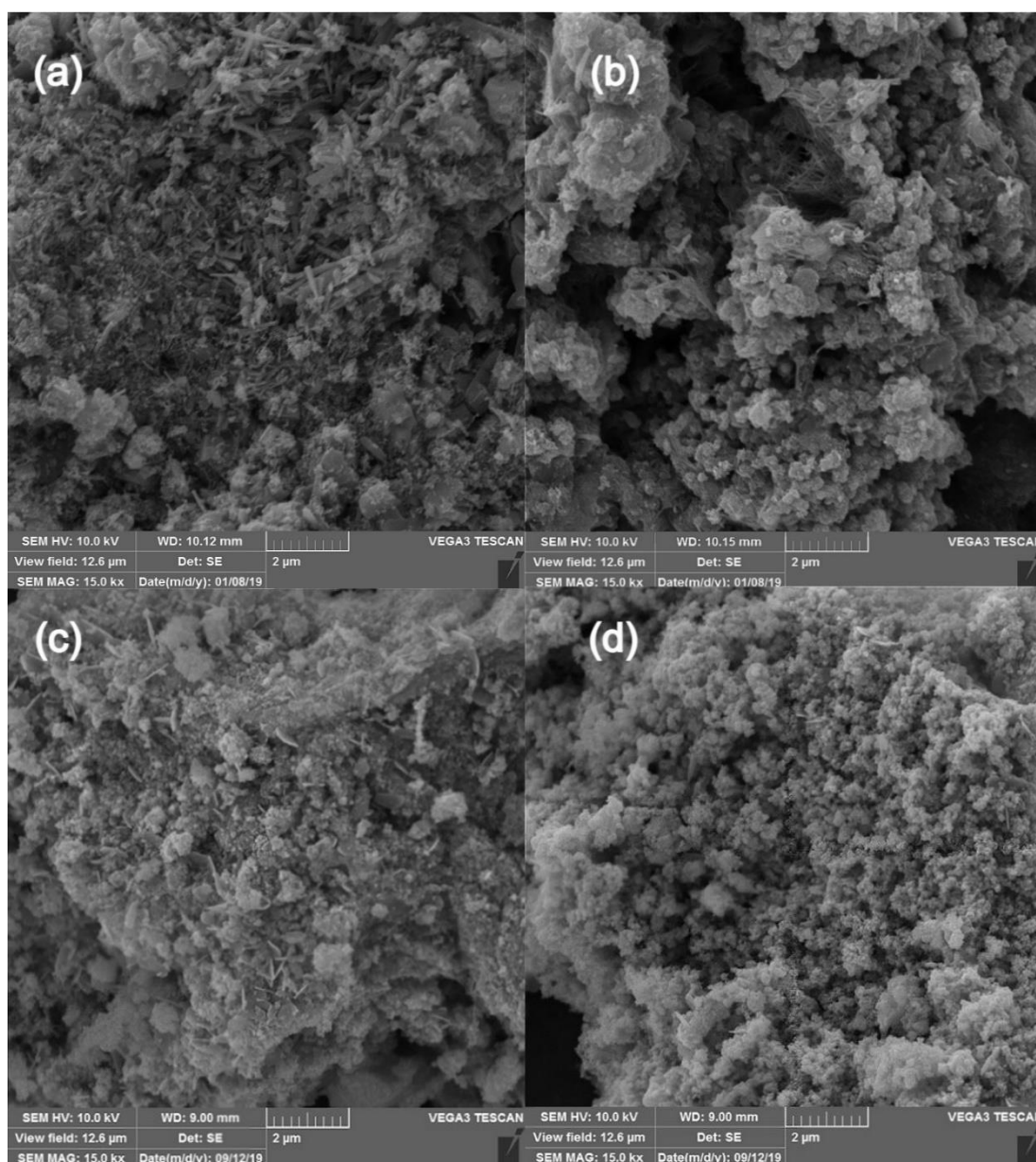


Figure 3.9: SEM images of (a) CZA, (b) CZAM, (c) CZAM-10Cr and (d) CZAM-50Cr.

3.2.6. Catalytic Activities of the Catalysts

Liquid products of CZAM, CZAM-10Cr, CZA and CZAM-50Cr obtained from the fix bed reactor system were collected in the cold trap and analyzed at 27.2, 50.3, 73.3 and 142.3 h. Methanol, ethanol and trace amounts of C₂-C₅ hydrocarbons were detected in condensed liquid product phase. The gaseous reactor effluent was analyzed

and paltry amount of methane and ethane were detected as byproducts. The maximum methanol weight time yield was achieved by CZAM-10Cr (Figure 3.10a). CZAM and CZA gave higher methanol production activity than CZAM-50Cr at the beginning of the reaction, yet these catalysts were deactivated much faster than CZAM-50Cr. The deactivation rates of the catalysts were determined by using the results of long-term activity test. The CO to methanol conversion rates were calculated at 27.2, 50.3, 73.3 and 142.3 h by using Equation (3.4) and deactivation rates were determined by using Equation (3.5).

$$CO\ to\ Methanol\ Conversion = C_i = \left(\frac{Moles\ of\ methanol\ produced}{Moles\ of\ CO\ fed\ to\ system} \right)_i \times 100 \quad (3.4)$$

$$Deactivation\ rate = \frac{(C_i - C_{i-1}) \times 100}{t_i - t_{i-1}} \quad (3.5)$$

where, t_i is the time point of interest, t_{i-1} is the time point before t_i , C_i is the CO to methanol conversion ratio at t_i , and C_{i-1} is the CO to methanol conversion ratio at t_{i-1} .

Cr containing catalysts have lower deactivation rate than the others (Figure 3.10b). The catalysts which contain no Cr deactivated rapidly during the first 50 h activity test. Deactivation rate of CZAM-50Cr was the lowest and it nearly continue to give same amount of methanol during 142.3 h. This finding is in good agreement with the literature which reported that Cr could prevent the sintering of the catalyst by providing considerably larger surface area and improving the dispersion of CuO [13], [20]. Cr was also reported as an active component for methanol generation in the literature [13]. The catalysts, CZAM-10Cr and CZAM-50Cr, had larger surface area than CZA and CZAM (Table 3.6). Cr containing compounds can promote activities of skeletal Cu catalysts for methanol synthesis, yet overloading the Cu surface with Cr can decrease Cu surface area, and thereby reduce catalytic activity [62]. Cr may cause partial blockage of the pores in the catalyst, but the presence of suitable amount of Cr containing compounds can provide high BET surface areas and retard the deactivation [72]. The highest methanol production activity can be evaluated by adjusting the Cr content in the catalysts.

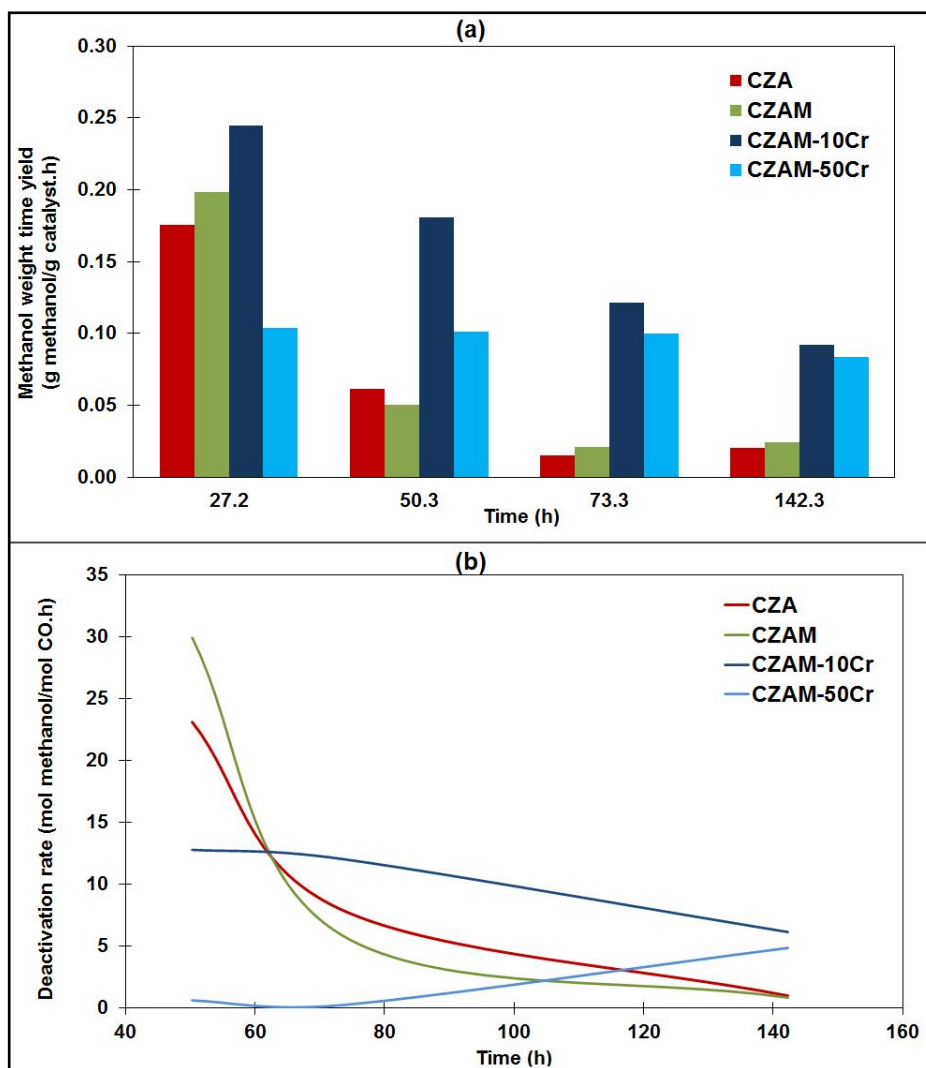


Figure 3.10: Change in (a) methanol weight time yield and (b) deactivation rate by time for different catalysts.

Table 3.6: BET surface area, methanol selectivity, total methanol production and methanol weight time yield of the catalysts.

Catalyst Name	BET Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Methanol Selectivity (%)	Total Methanol Production (g)	Methanol Weight Time Yield ($\text{g}_{\text{total methanol}} \cdot \text{g}_{\text{catalyst}}^{-1} \cdot \text{h}^{-1}$)
CZA	33.826	80.450	6.261	0.175
CZAM	39.720	79.590	7.107	0.199
CZAM-10Cr	84.397	83.530	14.210	0.245
CZAM-50Cr	93.127	81.930	7.928	0.104

The BET surface area of CZAM-10Cr was higher than CZAM and CZA (Figure 3.11a). The total methanol production activity, methanol weight time yield and prevention against deactivation of CZAM-10Cr was also higher than CZAM and CZA (Figure 3.10a, Figure 3.10b and Figure 3.11a). CZAM-50Cr had the highest surface area, but the activity of this catalyst was not high enough. This was due to the high Cr loading which resulted in blockage of pores [72]. Analysis of CZA and CZAM catalysts showed that addition of small amounts of Mg can increase surface area and methanol production activity. CO consumption of the catalysts except for CZA was similar to each other (Figure 3.11b). The lowest CO conversion was attained by CZA. CZAM-10Cr gave the highest methanol production activity, but CO conversion of this catalyst was similar to CZAM and CZAM-50Cr. This could be attributed to Cr addition which promoted methanol production via hydrogenation of CO₂ [62]. This means that both CO and CO₂ can be utilized as a carbon source for methanol generation for Cr containing catalysts.

Cu/M_xO_y binary catalysts where M is Mg, Zn, Mn or Ce and the molar ratio of Cu/M_xO_y was 70:30 had been previously synthesized by co-precipitation method in which Cu/Mg catalysts had higher Cu surface area and lower methanol activity [27]. CuO formation took place in precursor phase due to high Mg ratio and high pH during aging [27]. In our study, no CuO formation was detected in the precursor phase because addition of small amount of Mg and relatively lower pH values during aging improved catalyst stability, and increased surface area and catalytic activity. Addition of small amounts of Mg to CZA, which was converted to CZAM, increased the surface area and methanol generation from 33.8 to 39.7 m²·g⁻¹ and 6.2 to 7.1 g, respectively. The CZAM-50Cr catalyst had the highest surface area of 93.1 m²·g⁻¹. CZAM-10Cr catalyst, which had a surface area of 84.4 m²·g⁻¹, gave the highest methanol generation value of 14.2 g. This was almost twice that of others. The highest methanol selectivity was obtained for CZAM-10Cr as 83.5%. These differences between methanol generation and selectivity could be attributed to the inhibitory effect of Cr against deactivation and enlargement of the surface areas. Higher Cr loadings can cause blockage of the catalytic pores and reduce activity as suggested by CZAM-50Cr results (Figure 3.11a).

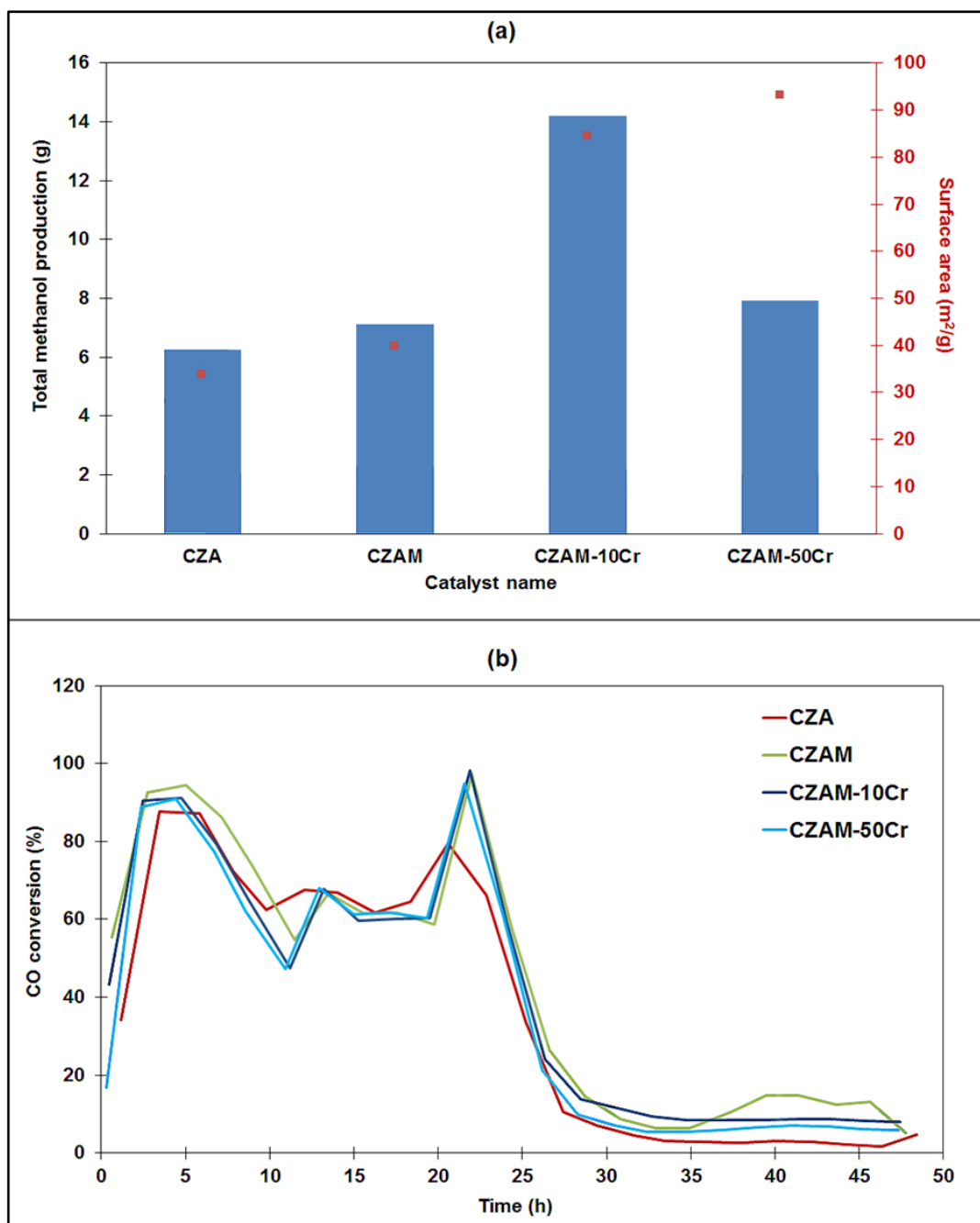


Figure 3.11: (a) Comparison of methanol generation and BET surface areas of different catalysts and (b) CO conversion curves for catalysts.

4. EFFECTS OF METAL PROMOTION ON THE PERFORMANCE, CATALYTIC ACTIVITY, SELECTIVITY AND DEACTIVATION RATES OF CU/ZNO/AL₂O₃ CATALYSTS FOR METHANOL SYNTHESIS

Methanol is used worldwide in various chemical processes and industrial products. Its importance in the global market continuously increases due to the depletion of fossil fuels [73]. Nearly, 85% of methanol generated is utilized in the chemical and energy sectors [3]–[5], [74]. Synthesis gas (syngas), which is a mixture of carbon monoxide (CO), carbon dioxide (CO₂) and H₂, is converted to methanol via copper (Cu)-based catalysts. Three fundamental reactions involved in methanol synthesis can be given as hydrogenation of CO (Equation 4.1), hydrogenation of CO₂ (Equation 4.2) and reverse water gas shift reaction (Equation 4.3) [75]:



Methanol is commercially produced via catalytic reaction of CO and H₂. CO₂ also exists in the reaction mixture in small concentrations (2-6%) to prevent deactivation of Cu-based methanol synthesis catalysts [29]. Catalysts containing zinc oxide/chromium oxide (ZnO/Cr₂O₃) have been used to produce methanol from syngas at high temperatures (350-450 °C) and high pressures (25-35 MPa) since 1920's [6], [20]. This process was improved in 1960's with copper/zinc oxide/aluminum oxide (Cu/ZnO/Al₂O₃)-based catalysts that are able to operate at lower temperatures (230-280 °C) and pressures (5-12 MPa) [6]. However, low thermal stability, low structural characteristics and textural properties, poor tolerance to poisoning and short lifetime are still important drawbacks of Cu-based catalysts [7].

A great deal of research has been carried out to overcome the drawbacks of Cu-based methanol synthesis catalysts. One approach is to use different catalyst preparation methods such as co-precipitation [34], [42], sol-gel [76] and impregnation [77] among which, co-precipitation is the most extensively used industrial method [78]. Many catalysts for methanol synthesis have also been investigated including Cu/ZnO-based catalysts [79]–[82], Pd-based catalysts [83]–[85] and bimetallic catalysts [86]–[88]. Cu/ZnO-based catalysts are the most widely used catalysts for methanol synthesis because ZnO prevents agglomeration of Cu particles and induces a synergistic effect between Cu and ZnO interface, thus leading to large Cu surface area needed for methanol synthesis, resulting in improved performance and catalytic activity of the Cu/ZnO-based catalysts [86], [89], [90]. Cu/ZnO-based catalysts for methanol synthesis need mild operating temperatures and pressures, and have better catalytic activity [28], [29].

Some researchers reported that addition of an appropriate promoter and/or support to the Cu/ZnO-based catalysts increased the catalyst activity and specific surface area [91]–[93]. Cu/ZnO/Al₂O₃ catalysts are the most commonly used methanol synthesis catalysts in the industrial methanol production processes [78], [94], [95]. Al₂O₃ is used in Cu/ZnO catalysts due to its promotional effect [23]. The addition of 10% Al₂O₃ into the Cu/Al₂O₃/(ZnO-Zn) ternary catalyst inhibited the reduction of Cu²⁺ to inactive Cu⁰, and stabilized Cu⁺ by retarding the reduction of Cu²⁺ and maintaining it in the form of active Cu⁺ [26]. Liang et al. [96] found that agglomeration of ZnO caused the deactivation of the Cu/ZnO/Al₂O₃ catalysts and proposed that addition of a suitable hydrophobic promoter could stabilize the ZnO species resulting in prolonged lifetime of the catalyst. Cr was reported to act similar to Al in increasing the thermal stability, catalytic activity and regenerability of Cu/ZnO/Cr₂O₃ catalysts where Cr improved the distribution of Cu in ZnO by decreasing the Cu particle size [22], [24].

Many efforts have been made to further enhance the catalytic activity, surface acidity and structural characteristics of Cu/ZnO/Al₂O₃ catalysts using different promoters [25], [28], [43], [54], [95]. ZnO in the catalyst composition due to its basic property increased the methanol activity by decreasing the surface acidity of catalysts [15]. Addition of metal oxides such as BaO, CaO, MgO and SrO into the Cu/ZnO/Al₂O₃ catalysts improved the methanol activity by forming strong basic sites

on the catalyst surface [14]. Cu/ZnO/Al₂O₃ catalysts doped by Ca, Sr and Mg having basic character yielded higher methanol activity [43]. Mg promoted Cu/ZnO/Al₂O₃ catalyst increased the methanol activity mainly owing to the enhancement of the catalyst surface area [28]. The addition of Cr as the promoter into Cu/ZnO/Al₂O₃ catalyst enhanced the stabilization of Cu⁺ during reduction and reaction processes by increasing the Cu⁺ concentration at the surface, and thereby improved the methanol productivity and lifetime [25]. However, these studies did not address the effect of simultaneous addition of two promoters on the catalytic activity and structural characteristics of Cu/ZnO/Al₂O₃ catalysts used for methanol production.

The novelty of this research lied on the fact that effects of simultaneous addition of Mg and Cr to Cu/ZnO/Al₂O₃ catalysts on the methanol activity and structural characteristics of Mg and Cr promoted Cu/ZnO/Al₂O₃ catalysts were investigated to obtain catalysts with higher methanol production activity and selectivity. Cr, Mg and Mg-Cr promoted Cu/ZnO/Al₂O₃ catalysts were synthesized using co-precipitation method, and characterized by H₂-temperature programmed reduction (H₂-TPR), X-ray diffraction (XRD), temperature programmed ammonia (NH₃) desorption (TPAD) method, Brunauer–Emmett–Teller (BET) and thermal gravimetric analyzer (TGA). Catalytic performance tests of the catalysts were also investigated.

4.1. Materials and Methods

4.1.1. Chemicals

Copper (II) nitrate trihydrate with the formula of Cu(NO₃)₂·3H₂O (>99%) and zinc nitrate hexahydrate with the formula of Zn(NO₃)₂·6H₂O (>98%) were obtained from Acros Organics. Aluminum nitrate nonahydrate with the formula of Al(NO₃)₃·9H₂O (>98%) and sodium carbonate anhydrous with the formula of Na₂CO₃ (>99.5%) were purchased from Carlo Erba. Magnesium nitrate hexahydrate with the formula of Mg(NO₃)₂·6H₂O (>99%) and chromium nitrate nonahydrate with the formula of Cr(NO₃)₃·9H₂O (>98%) were received from Merck and Carl Roth, respectively. Deionized water was used for the preparation of all solutions.

4.1.2. Preparation of Catalyst

Catalysts were synthesized using co-precipitation method [34]. Two aqueous solutions, metal salts solutions of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at a concentration of 1 molar (M) (metal solution) and an aqueous solution of Na_2CO_3 at a concentration of 1.6 M (base solution) were prepared. The metal component molar ratios of the metal solutions are given in Table 4.1.

Two hundred mL of deionized water placed in a glass reactor and heated up to 65 °C. One hundred mL's of metal solution and base solution were fed simultaneously into the preheated reaction medium at a flow rate of $10 \text{ mL} \cdot \text{min}^{-1}$ by a peristaltic pump (Cole-Parmer, Masterflex L/S Easy Load), and reactants were continuously stirred at a rate of 150 rpm. When the co-precipitation was over, precipitates were kept in mother liquor for 24 h at 65 °C with stirring at 150 rpm, and the pH value of the resulting suspension was adjusted to 8.1 ± 0.3 by an aqueous solution of Na_2CO_3 using an automated pH controller (Bluelab). After aging the precipitates for 24 h, the suspensions were filtered under vacuum and rinsed several times with deionized water until the pH value of the washing medium was 7. The precursors were obtained by drying the resultant filter cakes in an oven (Carbolite Gero Ltd., AX), at 105 °C overnight. The precursors were then calcined at 350 °C for 10 h at a heating rate of $1^\circ\text{C} \cdot \text{min}^{-1}$. The calcined catalysts were grinded by a grinder, and sieved through a mesh with Tyler mesh size of 150 (105 μm). The synthesized catalysts were denoted as CZA, CZAM, CZACr1, CZACr2, CZAMCr1 and CZAMCr2 which correspond to Cu/ZnO/ Al_2O_3 , Cu/ZnO/ Al_2O_3 -Mg (6%), Cu/ZnO/ Al_2O_3 -Cr (3%), Cu/ZnO/ Al_2O_3 -Cr (6%), Cu/ZnO/ Al_2O_3 -Mg (6%)-Cr (3%) and Cu/ZnO/ Al_2O_3 -Mg (6%)-Cr (6%), respectively, where percentages are in mole percent.

4.1.3. Characterization of Catalyst

Powder X-ray diffraction (XRD) patterns of precursors, and calcined, reduced and spent catalysts were recorded using an XRD diffractometer (Rigaku Corp., Miniflex 600) equipped with Cu-K α radiation at a scan rate of $1^\circ \cdot \text{min}^{-1}$ in the range of $5^\circ < 2\theta < 80^\circ$. The tube voltage and current were 40 kV and 15 mA, respectively.

Modified Scherrer equation, used for calculating CuO and Cu particle sizes from diffraction lines of XRD patterns, is given in Equation (4.4) [64]:

$$\ln(\beta) = \ln\left(\frac{1}{\cos\theta}\right) + \ln\left(\frac{K\lambda}{D}\right) \quad (4.4)$$

where β is full width at half maximum value of the diffraction peak in radian, θ is Bragg diffraction angle in degree, λ is X-ray wavelength (1.54 Å), K is the Scherrer constant (0.89), and D is mean particle size in nanometer (nm).

Thermal decomposition behavior of precursors (Air-TGA) and weight loss of calcined catalysts during the reduction process (H₂-TGA) were determined using a thermogravimetric analyzer (Shimadzu Corp., DTG-60H TG/DTA). In Air-TGA analyses, ~10 mg of precursor was placed into the sample holder, and weight loss was monitored up to 700 °C at a heating rate of 10 °C·min⁻¹ and an air flow rate of 300 mL·min⁻¹. In H₂-TGA analyses, ~10 mg of calcined catalyst was used, and the change in weight was recorded in the temperature range of 25-700 °C at a heating rate of 10 °C·min⁻¹ under 20% H₂/N₂ flow of 50 mL·min⁻¹.

BET surface areas and pore volumes of the calcined catalysts were determined by N₂ adsorption isotherms of the samples at -196 °C with Quadrasorb-S1 instrument (Quantachrome Instrument Corp.). Sample degassing was carried out under vacuum at 150 °C overnight before measurements.

H₂-TPR experiments were carried out using a continuous flow tubular fixed bed reactor. The samples (1 g) were placed into the reactor bed, purged with N₂ for 10 min and thereafter reduction was carried out with 10% H₂/N₂ flow (0.2 L·min⁻¹) at a heating rate of 5 °C·min⁻¹ up to 750 °C. The amount of H₂ in the reactor effluent was analyzed with an online mass spectrometry (HIDEN Analytical, HAL201 RC).

Acid-base properties of catalysts were studied by temperature programmed ammonia desorption (TPAD) with TGA [65], [66]. Catalyst (~10 mg) was reduced under 20% H₂/N₂ flow (50 mL·min⁻¹) at 300 °C for 2 h. After the sample was cooled to 100 °C under N₂ flow, the sample was saturated with 5% NH₃ + 95% N₂ at a flow rate of 50 mL·min⁻¹ for 60 min followed by purging with N₂ at 100 °C to remove physically adsorbed molecules. Adsorbed catalysts containing NH₃ were then heated in the temperature range of 100-500 °C at a heating rate of 5 °C·min⁻¹ under N₂ flow

(50 mL·min⁻¹), and the change in the weight due to the desorption of adsorbed NH₃ was recorded. The surface acidity values of the catalysts were determined using Equation (4.5) [66].

$$\text{Surface acidity} = \frac{W(g) \times \left(\frac{1}{MW \text{ of } NH_3} \right) \times \left(\frac{1000 \text{ mg}}{1 \text{ g}} \right)}{\text{Mass of catalyst after pretreatment (g)}} \quad (4.5)$$

where W is the change in weight occurred by the desorption of adsorbed NH₃ and MW is the molecular weight of NH₃ (17 g·mol⁻¹).

4.1.4. Catalytic Performance Tests

Catalytic performance tests were evaluated using a stainless steel (316L) fixed-bed reactor (ID = 7 mm, L = 130 mm) as shown in Figure 4.1. The catalytic performance test setup has a gas feeding unit, a reactor oven, a liquid product collector at the exit of the reactor and a gas chromatography equipment for analyzing the composition of reactor effluents.

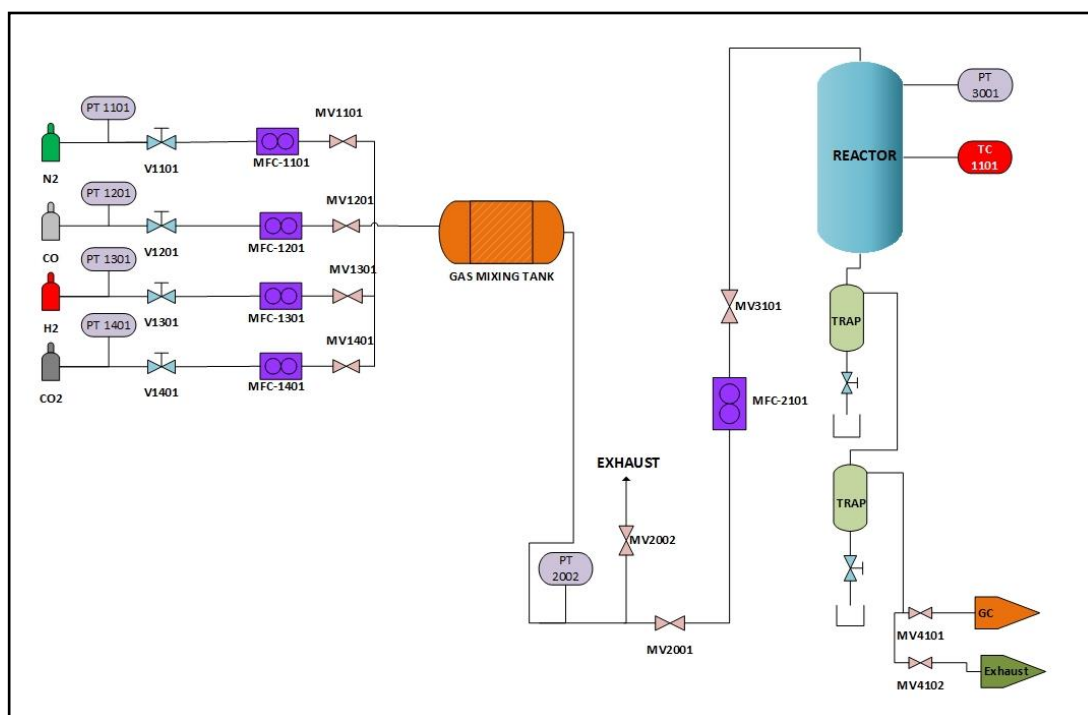


Figure 4.1: Flow diagram of the catalytic activity test reactor.

Prior to performance tests, the calcined catalyst (1000 mg) was mixed with 1000 mg quartz sand (between 100 and 200 mesh) and placed into the reactor bed where L/D ratio and volume of the catalytic bed were 1.3 and 3.5 cm³, respectively. Volume of 1000 mg of catalyst was ~1.5 mL, and it was diluted with 1000 mg quartz sand which had a volume of 2.9 mL. Apparent densities of the catalysts were 0.63 ± 0.05 g·mL⁻¹. Reduction of the catalysts in the catalytic bed was carried out at 250 °C under 10% H₂/N₂ flow (0.1 L·min⁻¹) for 15 h. After the reduced catalysts were cooled to 170 °C under N₂ flow, reactant gases of 65% H₂, 25% CO, 5% CO₂ and 5% N₂ (as an internal standard) were fed to the reactor. Total flow rate of the gases fed to the reactor was set to 0.11-0.12 L·min⁻¹ to maintain the gas hourly space velocity at 4500 h⁻¹. The reactor bed temperature and pressure were set to 270 °C and 3 MPa, respectively. The reactor bed temperature was monitored by a K-type thermocouple located at the center of the catalyst bed. Reactants and gaseous phase reactor effluents were analyzed online with a gas chromatography (Agilent Technologies Inc., 6890) equipped with a thermal conductivity detector (TCD) and three capillary columns of HP plotQ (L=30 m), HP plotQ (L=15 m) and HP Molsieve (L=30 m). Liquid phase condensed at -15 °C were collected in the cooling trap and analyzed offline with a gas chromatography-mass spectrometry (Agilent Technologies Inc., 6890N (G1540N)) equipped with a mass detector (MS) and a HP-5MS capillary column (L=30 m). Liquid products condensed in the trap were not detected in the gaseous reactor effluents because the temperature was low enough to condense all liquid products in the cooling trap. The products in the liquid phase were identified with NIST 98L library of the GC-MS instrument. Methanol selectivity was determined by quantifying the amount of methanol in the liquid phase by a gas chromatography (Agilent Technologies Inc., 7890A) equipped with a flame ionization detector (FID) and a DB wax capillary column (L=30 m). Methanol selectivities, CO to methanol conversions at 24, 48, 72, 96, 120 and 144 h, and deactivation rates were calculated with Equation's. (4.6) through (4.8) [11]:

$$\text{Methanol selectivity} = \frac{\text{Moles of methanol in liquid product}}{\text{Total moles of all liquid products}} \times 100 \quad (4.6)$$

$$\text{CO to methanol conversion} = C_i = \left(\frac{\text{Moles of methanol produced}}{\text{Moles of CO fed to system}} \right)_i \times 100 \quad (4.7)$$

$$Deactivation\ rate = \frac{(C_i - C_{i-1}) \times 100}{t_i - t_{i-1}} \quad (4.8)$$

4.2. Results and Discussion

4.2.1. Crystal Structure Analysis of Precursors

XRD patterns for CZA, CZAM, CZACr1, CZACr2, CZAMCr1 and CZAMCr2 precursors were examined, and diffraction peaks attributed to roasite ($((Cu,Zn)_2CO_3(OH)_2)$ at 14.64° , 17.47° , 24.08° , 29.59° , malachite ($(Cu_2(OH)_2CO_3)$ at 14.72° , 17.50° , 24.03° , 29.47° , aurichalcite ($(Zn_3Cu_2(OH)_6(CO_3)_2)$ at 13.03° , 24.03° , 27.86° , 32.66° , and copper aluminum hydrotalcite ($(Cu_{2.5}Al_2C_{1.7}O_{8.9} \cdot 5.2H_2O)$ at 11.75° , 23.58° , 35.62° , 39.26° were consistent with the 2θ values reported in previous studies [45], [46] (Figure 4.2).

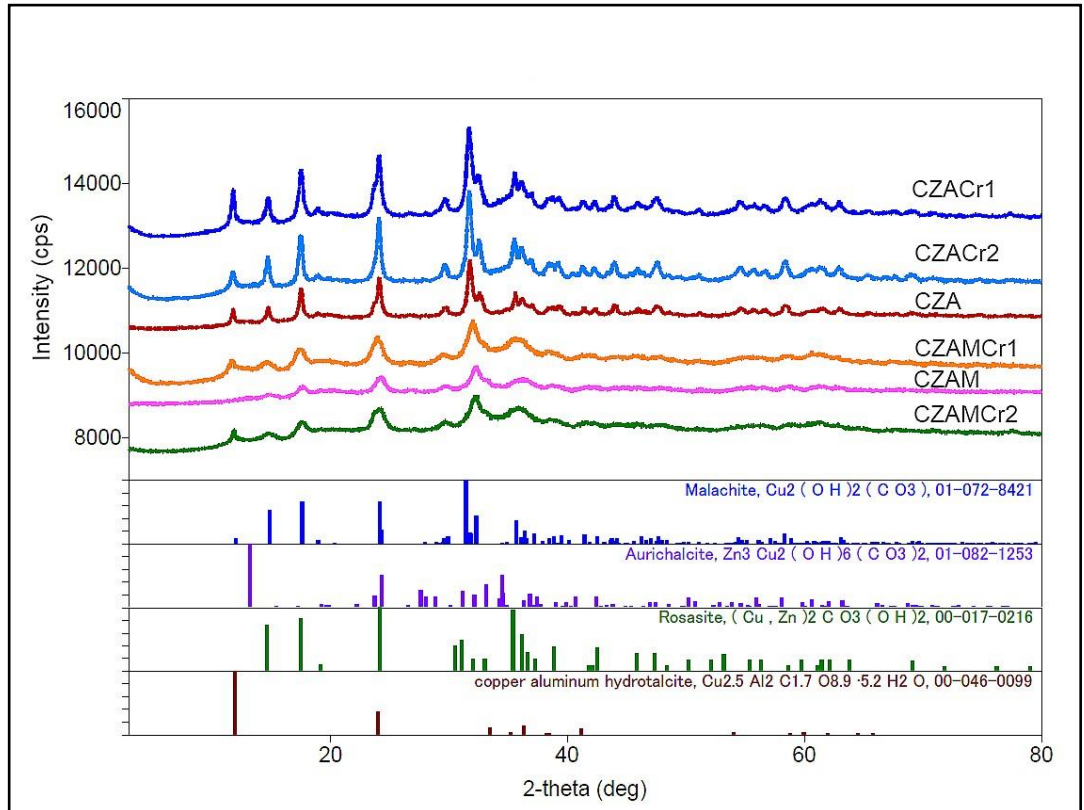


Figure 4.2: XRD diffractograms of precursors.

Intensities of the diffraction lines for the CZACr1 and CZACr2 precursors were sharper while intensities of the diffraction lines for the CZAM, CZAMCr1 and CZAMCr2 became smoother by the addition of Mg (Figure 4.2). Hydrotalcite-like phase was observed in all of the precursors except CZAM where the addition of only Mg to the CZA precursor inhibited the formation of hydrotalcite-like phase. The presence of hydrotalcite-like phase in the precursor enhances the relation between Cu and other phases by facilitating homogeneous dispersion of Cu^{2+} , Zn^{2+} and Mg^{2+} with Al^{3+} and Cr^{3+} [8], [12]. It was reported that malachite phase in the precursor improved Cu dispersion by escalating the interaction between Cu and ZnO, and thereby increased the Cu surface area in Cu-based catalysts [44], [61]. Aurichalcite and rosasite phases had an positive effect on increasing Cu dissolution in the catalyst composition [8], [46]. XRD diffractograms pertaining to the precursors showed that the intensity of the peaks belonging to malachite and rosasite phases weakened by simultaneous addition of Cr and Mg (Figure 4.2).

4.2.2. Decomposition Characteristics of Precursors

Decomposition characteristics of the precursors were determined by considering Air-TGA (Figure 4.3a) and Air-DTG (Figure 4.3b) profiles. Weight losses observed for CZA, CZACr1, CZACr2, CZAMCr1 and CZAMCr2 precursors in the temperature range of 100-160 °C were attributed to the crystal water losses from hydrotalcite-like phase [45], [48]. The hydrotalcite-like phase was also observed in the XRD diffractograms of these precursors. The weight loss in the range of 100-160 °C was more pronounced in the Air-DTG profiles of CZA, CZACr1 and CZACr2, showing sharper hydrotalcite-like phase peaks than the other precursors in XRD diffractograms. Weight losses occurring in the temperature range of 160–400 °C were associated with the decomposition of hydroxycarbonates (rosasite, malachite and aurichalcite) and hydrotalcite-like species to metal oxide forms [48].

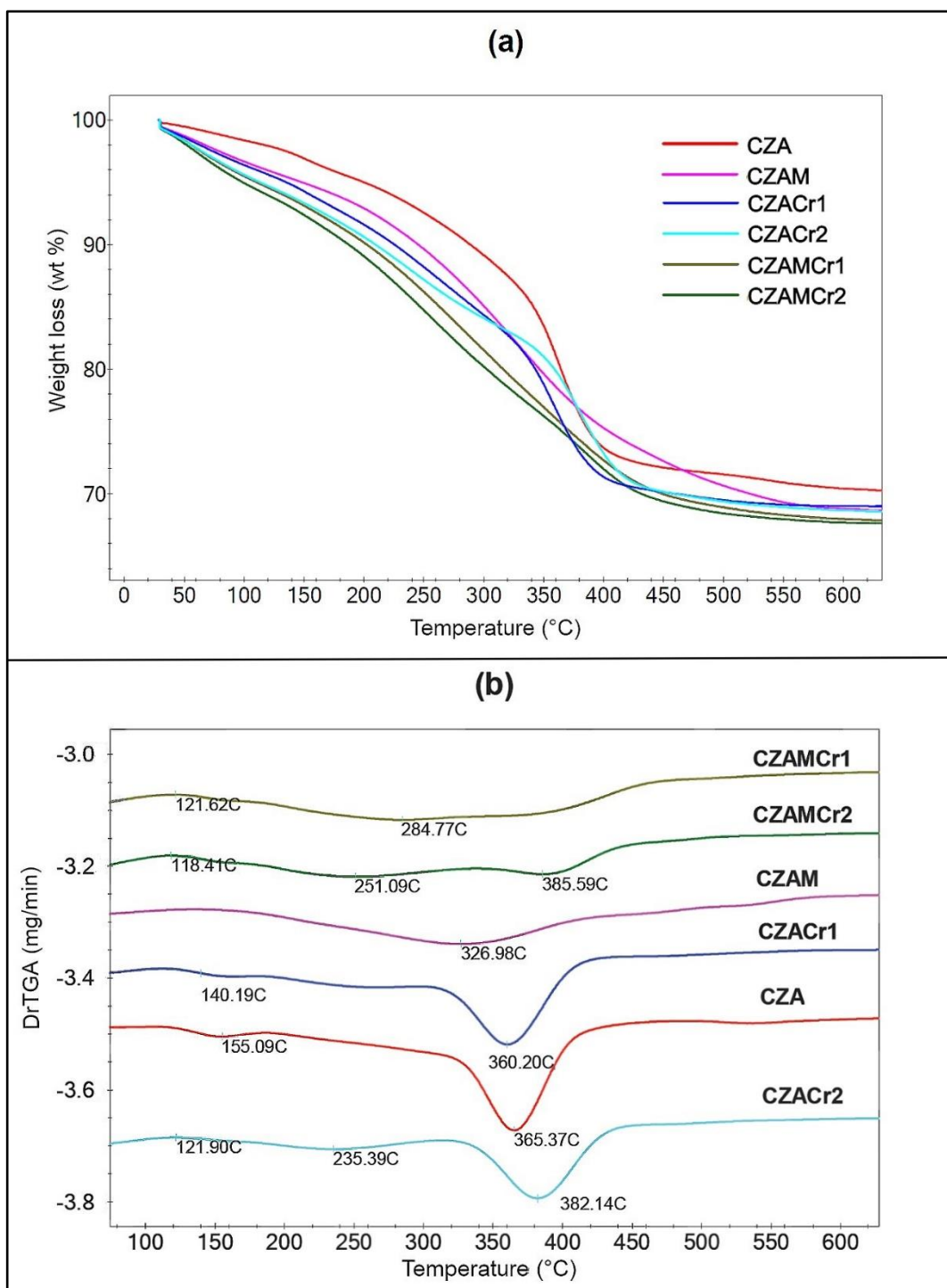


Figure 4.3: (a) Air-TGA and (b) Air-DTG curves of catalyst precursors.

The total percent weight losses of the six precursors in Air-TGA profiles were comparable (Figure 4.3a), pointing out the existence of similar hydrocarbonate precursors in different cationic species. Air-DTG curve of CZAM precursor was different from the other precursors (Figure 4.3b). There was only one weight loss in the Air-DTG curve of CZAM which did not show hydrotalcite-like phase formation in

XRD analysis. The weight loss observed between 160 and 400 °C was associated with the decomposition of hydroxycarbonate (rosasite, malachite and aurichalcite) phases existing in the CZAM precursor. The weight loss above 350 °C was associated with the sintering and formation of larger particle size metal oxides where the best calcination temperature for Cu/ZnO/Al₂O₃ catalysts was found to be 350 °C because higher calcination temperatures caused a decrease in BET surface area and poor reduction properties for the synthesized catalysts [16].

4.2.3. Crystal Structure, Particle Size and Surface Area Analysis of Calcined Catalysts

Tenorite and zincite phases present in the XRD diffractograms of the calcined catalysts revealed that CuO and ZnO phases were formed due to the decomposition of hydroxycarbonate phases during calcination (Figure 4.4). For the Cr and Mg-Cr promoted catalysts, in addition to the presence of CuO and ZnO phases, poor reflections were noticeable at 30.56°, 35.41°, 43.71°, 53.82°, 58.11°, 63.91°, 72.53° and 74.99° associated with zincochromite (ZnCr₂O₄). There was no Cr phase in the precursors due to the amorphous structure of ZnCr₂O₄ before calcination [67], but CuO, ZnO and weak ZnCr₂O₄ phases were detected for the Cr and Mg-Cr promoted catalysts after calcination (Figure 4.4). The intensity of CuO phase observed in the XRD diffractograms of the CZACr1 and CZACr2 catalysts was higher than the CuO peak intensities in the XRD diffractograms of the other catalysts which was the indication of larger CuO crystal formation, and these reflections became smoother in the XRD diffractograms of the CZAMCr1 and CZAMCr2 catalysts synthesized by the co-addition of Cr and Mg into the CZA catalyst. Cr₂O₃ phase was not observed in the Cr and Mg-Cr promoted catalysts due to its amorphous nature [59]. In the XRD diffractogram of the CZAM catalyst, periclase phase formation was observed, but this phase disappeared by the addition of Cr to the CZAM catalyst. The presence of MgO in the XRD diffractogram of the CZAM catalyst as a separate phase showed that MgO was not dispersed in the catalyst composition. The co-addition of Cr and Mg inhibited the MgO formation as a separate phase as shown in the XRD diffractograms of the CZAMCr1 and CZAMCr2 catalysts (Figure 4.4). This was attributed to the formation of MgCr₂O₄ phase by the co-addition of Cr and Mg where MgCr₂O₄ phase was in

amorphous nature in the CZAMCr1 and CZAMCr2 catalysts with Mg:Cr ratio of 2:1 and 1:1, respectively, calcined below 400 °C [97], [98]. Nayak et al. [99] observed the formation of MgCr_2O_4 crystallites in MgCr nanosheets for Mg:Cr ratios of 2:1, 3:1 and 4:1 calcined at 400 °C [99]. Hou et al. [100] reported that addition of 1.7% MgO into Cu-Al catalyst composition improved catalytic activity and stability, but higher amounts of MgO addition impaired catalytic activity and catalyst surface area [100].

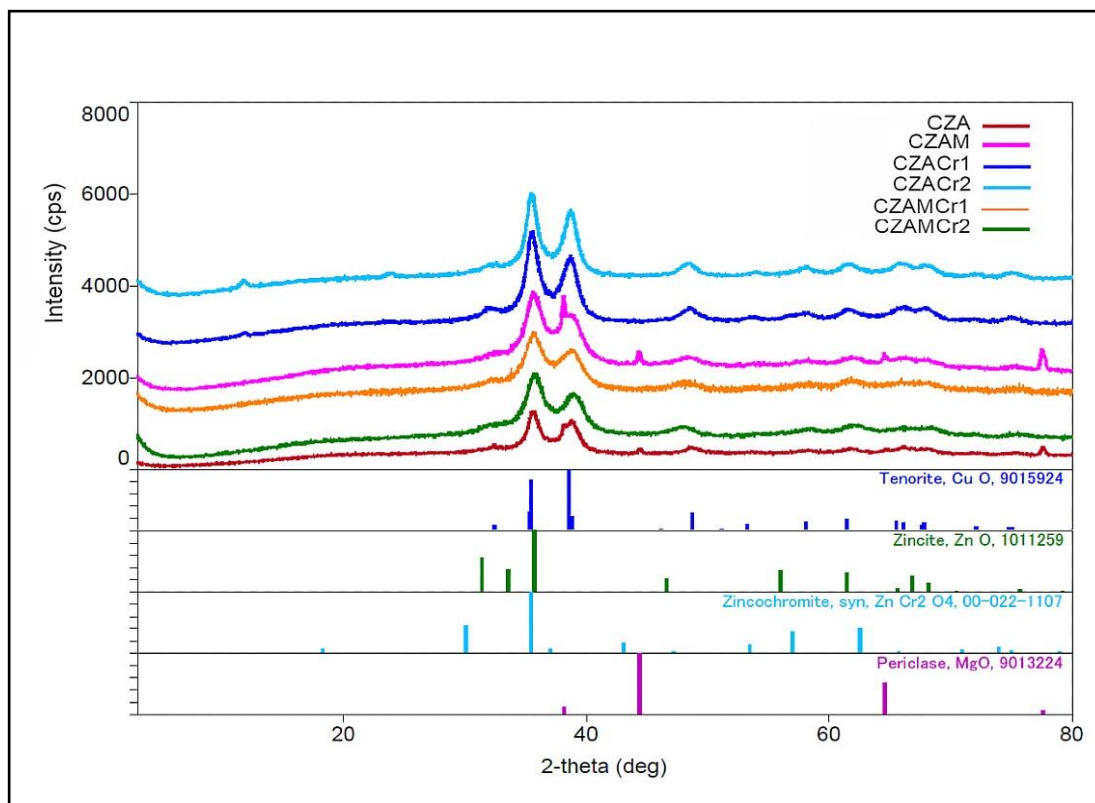


Figure 4.4: XRD diffractograms of calcined catalysts.

Growth in particle size could cause decrease in BET surface area as suggested by BET surface area and CuO particle size values for the catalysts (Table 4.1). CuO dispersion in catalyst composition could be enhanced by the formation of smaller CuO particle size where no separate metal oxide form of the promoter was observed. Therefore, higher BET surface areas can be obtained by smaller CuO particles [16], [48]. The formation of MgCr_2O_4 by the co-addition of Cr and Mg improved the dispersion of metal oxide mixture in the catalyst composition, resulting in the formation of higher pore volumes and BET surface areas, and smaller CuO particle sizes (Table 4.1). Simultaneous use of Cr and Mg caused a synergistic effect on

enhancement of the Cu surface area and the amount of dispersed Cu. Similar synergistic effect was also observed for simultaneous use of Mn and Zr in Cu/Zn/Al catalysts [40]. The CZAMCr2 catalyst having the minimum Cu/Zn ratio and equimolar Cr and Mg content gave the largest BET surface area and the smallest CuO particle size. Smaller Cu particles can be formed by the presence of ZnO, and the decrease in the Cu/Zn ratio causes a decrease in the CuO particle size [68]. The CZACr1 and CZACr2 catalysts had smaller BET surface areas than the BET surface area of CZAM, indicating that Mg addition was more effective than Cr addition for the enhancement of surface area. The CZAM catalyst had higher BET surface area and smaller particle size than those of the CZA, CZACr1 and CZACr2 catalysts (Table 4.1).

Table 4.1: Catalyst compositions, BET surface areas, pore volumes and CuO particle sizes of calcined catalysts.

Catalyst Name	Cu/Zn/Al/Mg/Cr (molar ratio)	BET Surface Area (m²·g⁻¹)	Total Pore Volume (cm³·g⁻¹)	d_{CuO}^a (nm)
CZA	66.2/24.1/9.7/0/0	62.0	0.45	8.24
CZAM	62.2/22.6/9.1/6/0	86.1	0.48	5.31
CZACr1	64.2/23.4/9.4/0/3	68.1	0.46	5.81
CZACr2	62.2/22.6/9.1/0/6	82.5	0.52	5.43
CZAMCr1	60.2/21.9/8.8/6/3	103.9	0.59	4.72
CZAMCr2	58.2/21.2/8.5/6/6	110.5	0.58	3.77

^a Particle size of CuO was determined by modified Scherrer equation

4.2.4. Crystal Structure and Particle Size Analysis of Reduced and Spent Catalysts

Cu phase formation was observed in all of the reduced catalysts as shown in the XRD diffractograms (Figure 4.5a). Cu peaks for the CZA, CZACr1 and CZACr2 reduced catalysts were more intense than the diffraction peaks for the CZAM, CZAMCr1 and CZAMCr2 reduced catalysts. The reduced CZAMCr2 catalyst gave the smallest Cu particle size of 17.76 nm (Table 4.2). The formation of smaller Cu particle size is the indication of good dispersion of Cu in the catalyst [16], [48].

Table 4.2: Cu particle size of reduced catalysts, and Cu and CuO particle sizes of spent catalysts^a.

Catalyst Name	d_{Cu} of Reduced Catalysts (nm)	d_{Cu} of Spent Catalysts (nm)	d_{CuO} of Spent Catalysts (nm)
CZA	31.05	8.12	-
CZAM	18.85	-	9.14
CZACr1	27.04	-	8.56
CZACr2	30.61	6.44	-
CZAMCr1	23.32	-	3.31
CZAMCr2	17.76	-	5.18

^a Particle sizes of Cu and CuO was determined by modified Scherrer equation

XRD diffractograms of the spent catalysts revealed that Cu formation was clearly noticeable only for the CZA and CZACr2 catalysts (Figure 4.5b). In CZACr1, CZAM, CZAMCr1 and CZAMCr2 spent catalysts, CuO phase was more pronounced than Cu phase. CuO formation was associated with the oxidation of Cu to CuO upon long term exposure to the syngas. The smallest CuO particle size (3.31 nm) formation observed for the CZAMCr1 spent catalyst (Table 4.2).

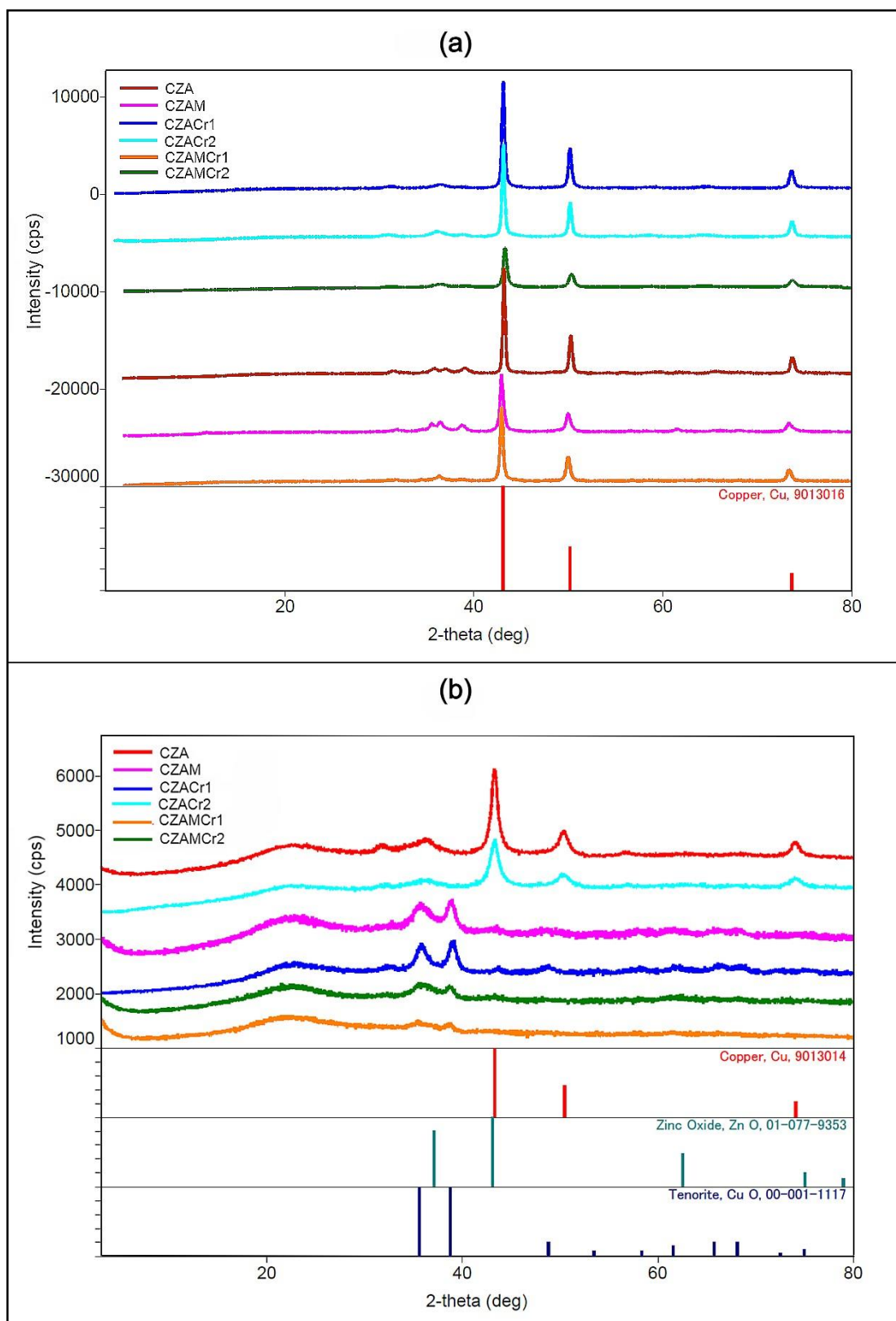


Figure 4.5: XRD diffractograms of (a) reduced catalysts after H₂-TPR studies and (b) spent catalysts after activity tests.

4.2.5. Evaluation of Reduction and Acid-Base Properties of Catalysts

Outlet H_2 concentration during H_2 -TPR experiments was continuously monitored to determine the reduction properties of the calcined catalysts, and the temperatures giving the lowest H_2 concentrations were assigned to catalyst reduction temperatures (Figure 4.6). All the catalysts exhibited similar H_2 -TPR profiles with one single and clear reduction peak. The reduction peak temperatures for the calcined catalysts changed between 253.4 and 270.9 °C. The CZAMCr2 catalyst had the lowest reduction peak temperature among the Cr and Mg-Cr promoted catalysts. The highest H_2 -DTG peak area was attained for the CZAMCr1 catalyst, and this finding was in good agreement with the previous studies [55], [56] where the methanol productivity increased by increasing the peak area. The H_2 -DTG peak area of the CZAMCr2 catalyst was comparable with the H_2 -DTG peak area of the CZAMCr1 catalyst (Table 4.3), suggesting that higher methanol productivity could be expected for the CZAMCr1 and CZAMCr2 catalysts [55], [56].

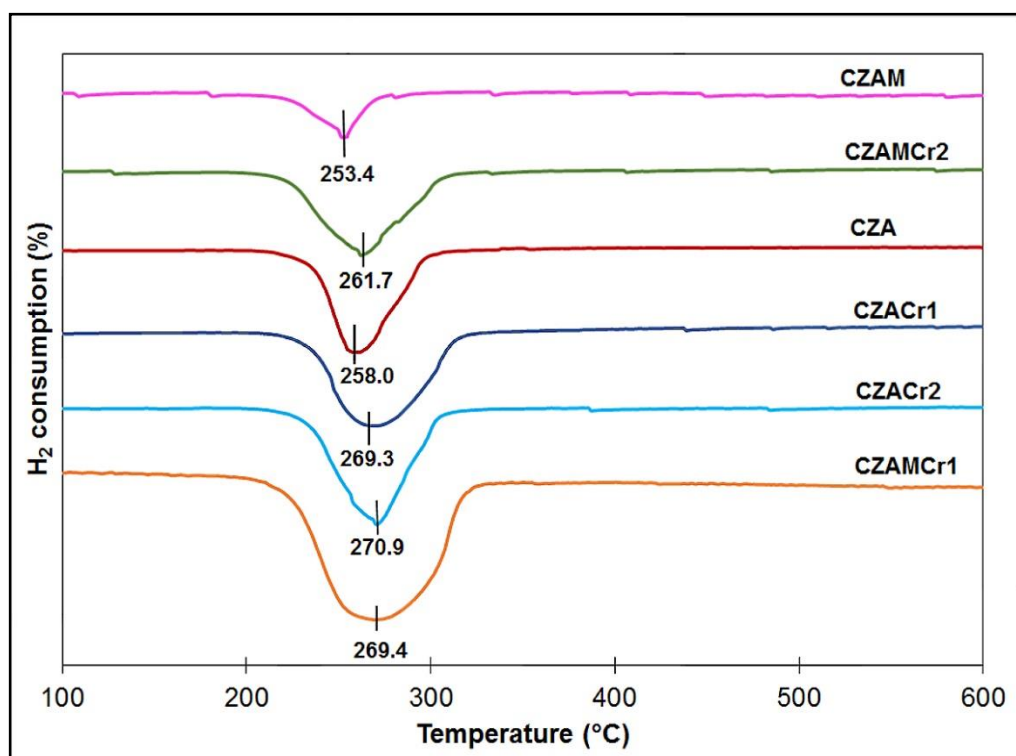


Figure 4.6: H_2 -TPR profiles of calcined catalysts.

Table 4.3: H₂-DTG peak areas and H₂-TPR peak temperatures of catalysts.

Catalyst Name	H ₂ -DTG	H ₂ -TPR Peak
	Peak Area (mg)	Temperature (°C)
CZA	0.98	258.0
CZAM	1.00	253.4
CZACr1	1.17	269.3
CZACr2	0.75	270.9
CZAMCr1	1.18	269.4
CZAMCr2	1.06	261.7

H₂-TGA analysis was also conducted to confirm the results determined in H₂-TPR analysis. The weight losses observed in the H₂-TGA analysis resulted from the desorption of water formed by the reduction reaction ($\text{CuO} + \text{H}_2 \rightarrow \text{Cu}^+/\text{Cu}^0 + \text{H}_2\text{O}$) and the existence of Cu⁺ and/or Cu⁰ in the catalysts can be determined from the total percentage weight loss of the catalyst. The CZAM catalyst gave the highest percentage weight loss while the CZAMCr1 and CZAMCr2 catalysts exhibited the lowest weight losses (Figure 4.7a). Two-step reduction was observed in the H₂-DTG curves of the CZA and CZAM catalysts (Figure 4.7b). The initial weight loss between 154.2 and 166.3 °C could be attributed to the reduction of smaller CuO particles and/or the reduction of CuO to Cu⁺ [7], [48], [70]. The weight losses at higher temperatures could be associated with the reduction of larger CuO particles and/or the reduction of Cu⁺ to inactive Cu⁰ [7], [48], [70]. In the present study, although the H₂-TPR peak temperature values of CZA and CZAM catalysts (258.0 and 253.4 °C) were lower than the CZACr1, CZACr2, CZAMCr1 and CZAMCr2 catalysts, two-step reduction ($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$) was observed in the H₂-DTG curves of these catalysts. Cu⁺ formation and sintering inhibitory effect of Cr was confirmed by the existence of only one weight loss peak in the H₂-DTG curves of the CZACr1, CZACr2, CZAMCr1 and CZAMCr2 catalysts (Figure 4.7b). The H₂-DTG peak areas of the CZACr1 and CZAMCr1 catalysts were almost similar, but Mg addition to the CZACr1 catalyst increased the BET surface area from 68.1 to 103.9 m²·g⁻¹ and reduced the CuO particle size from 5.81 to 4.72 nm (Table 4.1). Among the Cr and Mg-Cr promoted catalysts,

the CZACr2 catalyst had the minimum H₂-DTG peak area and the highest H₂-TPR peak temperature (Table 4.3).

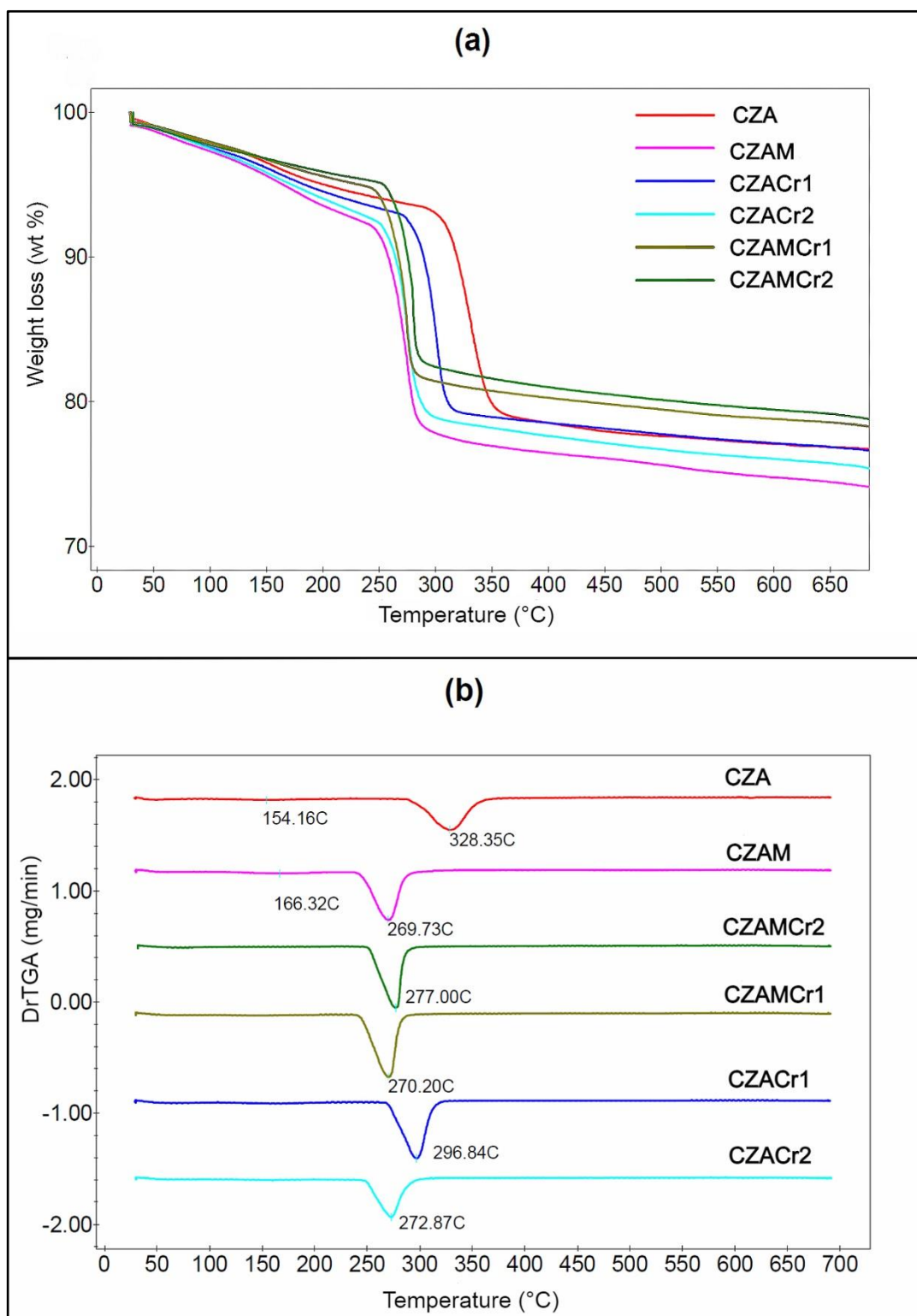


Figure 4.7: Comparison of (a) H₂-TGA and (b) H₂-DTG curves of calcined catalysts at a heating rate of 10 °C·min⁻¹.

Surface acidity is another parameter which has an effect on the methanol productivity [12]–[14]. Therefore, NH_3 adsorbed catalysts were analyzed by TPA-D-TGA (Figure 4.8a) and TPA-D-DTG (Figure 4.8b) to determine the acid-base properties of the catalysts. The CZA catalyst gave the highest weight loss, meaning that it had the maximum NH_3 adsorption and total surface acidity. The minimum weight loss was determined for the CZAMCr2 catalyst which had the lowest NH_3 adsorption and total surface acidity. The simultaneous addition of Cr and Mg reduced weight loss of the Cr and Mg promoted catalysts and their total surface acidities (Table 4.4). The total amount of adsorbed NH_3 decreased from $14.61 \text{ mmol NH}_3 \cdot \text{g}^{-1}$ catalyst for the CZA to $13.03 \text{ mmol NH}_3 \cdot \text{g}^{-1}$ catalyst for the CZAM, to $11.75 \text{ mmol NH}_3 \cdot \text{g}^{-1}$ catalyst for the CZACr1 and to $3.66 \text{ mmol NH}_3 \cdot \text{g}^{-1}$ catalyst for the CZAMCr2 catalyst. This indicated that the total number of basic sites increased following the simultaneous addition of Cr and Mg. As shown in Figure 4.8b, weight loss peaks for the catalysts due to the NH_3 desorption were detected within the temperature ranges of $100\text{--}250^\circ\text{C}$ and $250\text{--}500^\circ\text{C}$, which corresponded to weak and strong acid sites, respectively [66]. When only Mg added to the catalyst composition as the promoter, a slight decrease occurred in the total acidity, but a remarkable decrease in the total acidity took place when both Cr and Mg were used in the catalyst formulation (Table 4.4). The CZAMCr2 catalyst had lower total acidity than the CZAMCr1 catalyst, which had higher Cr content than the CZAMCr1 catalyst even if they contained the same amount of Mg. The CZACr2 catalyst gave higher total acidity than the CZACr1 catalyst which had lower Cr molar ratio than the CZACr2 catalyst. The increase in basic sites on the catalyst surface enhances the methanol selectivity and productivity of the Cu-based catalysts [12]–[14]. The decline in the surface acidity enhances the dispersion of metallic components and allows the formation of larger surface area [12].

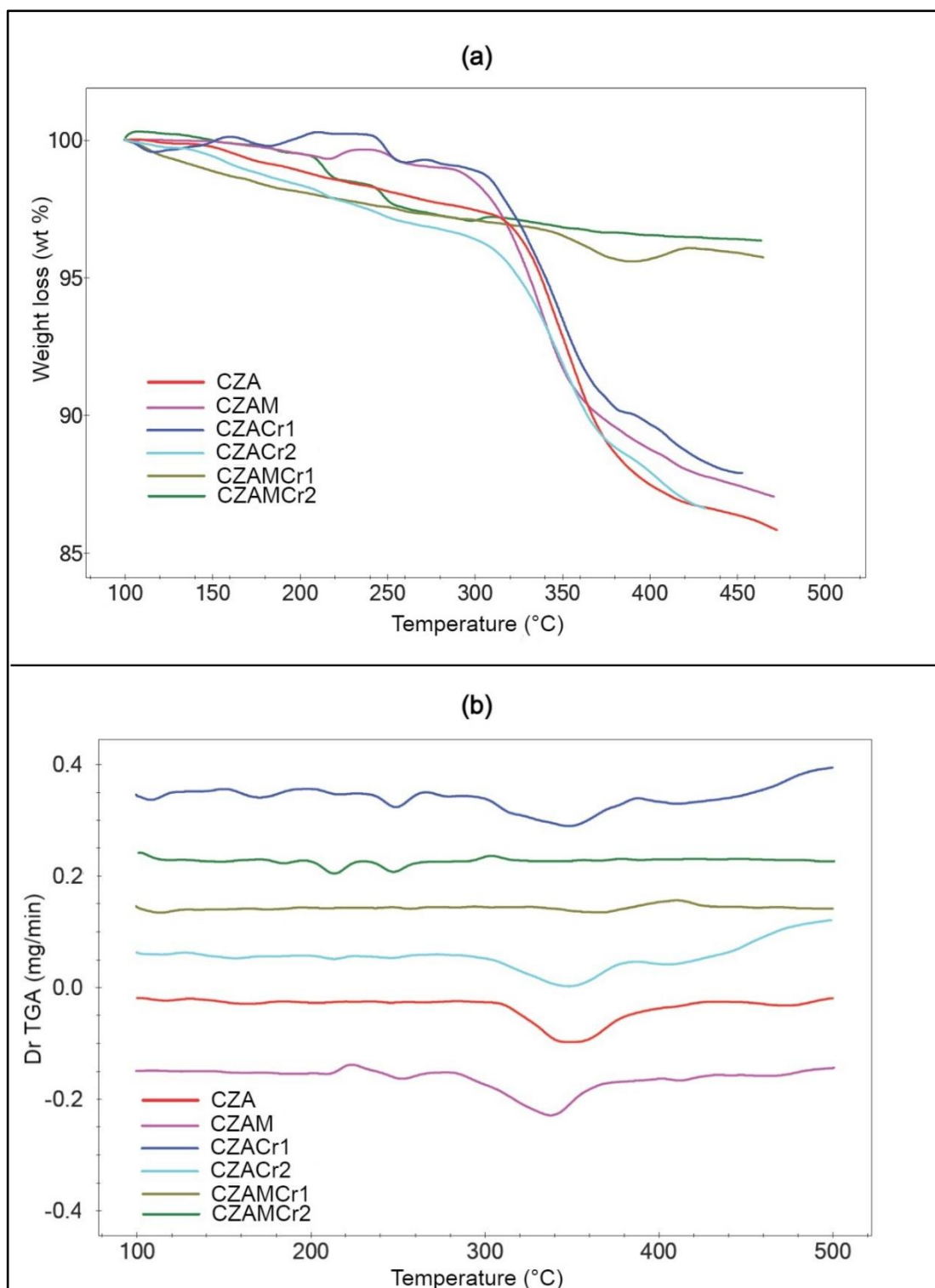


Figure 4.8: (a) TPAD-TGA and (b) TPAD-DTG curves of NH_3 adsorbed catalysts.

Table 4.4: Weak, strong and total acidity of catalysts (mmol NH₃·g⁻¹ catalyst).

Catalyst Name	Weak Acidity	Strong Acidity	Total Acidity
CZA	1.83	12.77	14.61
CZAM	0.41	12.62	13.03
CZACr1	0.67	11.08	11.75
CZACr2	2.94	9.76	12.70
CZAMCr1	2.34	2.18	4.51
CZAMCr2	2.10	1.55	3.66

4.2.6. Catalytic Activities of Catalysts

Liquid phases produced by the CZA, CZAM, CZACr1, CZACr2, CZAMCr1 and CZAMCr2 catalysts were accumulated in the trap and examined at 24, 48, 72, 96, 120 and 144 h. Methanol, ethanol, propanol, higher alcohols and trace amounts of C₉-C₁₄ hydrocarbons were determined in the condensed liquid phases (Table 4.5). The CZAMCr2 catalyst gave the highest methanol selectivity of 98.3% and the lowest C₉-C₁₄ hydrocarbon formation of 0.6%.

Table 4.5: Liquid phase composition produced by the catalysts.

Catalyst Name	Methanol (%)	Ethanol (%)	Propanol (%)	Higher Alcohols (%)	Higher Hydrocarbons (C₉ – C₁₄) (%)
CZA	93.5	2.6	-	-	3.9
CZAM	78.5	-	-	3.7	17.8
CZACr1	96.5	-	-	1.7	1.8
CZACr2	82.2	5.1	5.5	6.0	1.2
CZAMCr1	97.7	-	0.1	0.3	1.9
CZAMCr2	98.3	-	-	1.1	0.6

Gaseous reactor effluents were analyzed, and small amounts of ethane and methane were detected as byproducts. Activity tests revealed that the CZAMCr2 catalyst gave the maximum percentage CO conversion (~ 20%) at the end of 144 h

while the CZA, CZAM, CZACr1, CZACr2 and CZAMCr1 catalysts gave percentage CO conversions of approximately 12, 0.5, 15, 7 and 10.5%, respectively (Figure 4.9a). Percentage CO₂ conversion values of all the catalysts varied between 90 and 95% except the CZAM catalyst (Figure 4.9b). These results showed that both CO₂ and CO were used as carbon sources for the methanol production by all of the catalysts. Four parallel reactions occur on Cu-based catalysts, which are (i) CO hydrogenation to methanol, (ii) CO₂ hydrogenation to methanol, (iii) reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$) and (iv) Boudouard reaction ($2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$) [27], [77], [101]. No water was detected in the liquid phase, which indicated that the reverse water gas shift reaction did not take place on the catalysts. The reactor effluent gas of the CZAM catalyst had an increase in its CO₂ content, which indicated that the Boudouard reaction occurred on this catalyst. The CZAM catalyst had the lowest activity due to the carbon deposition effect of the Boudouard reaction.

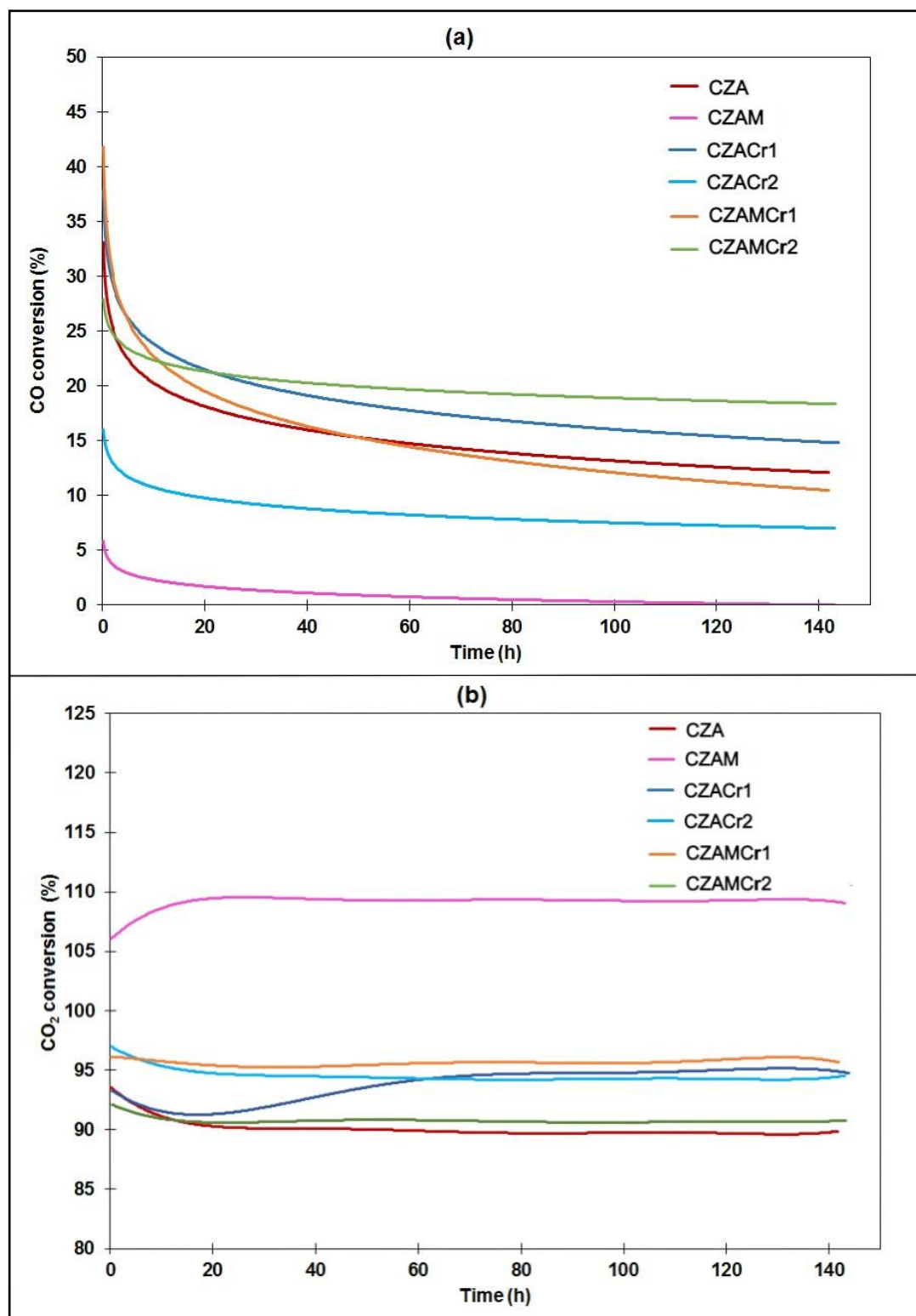


Figure 4.9: (a) CO conversion and (b) CO₂ conversion curves for catalysts during activity tests.

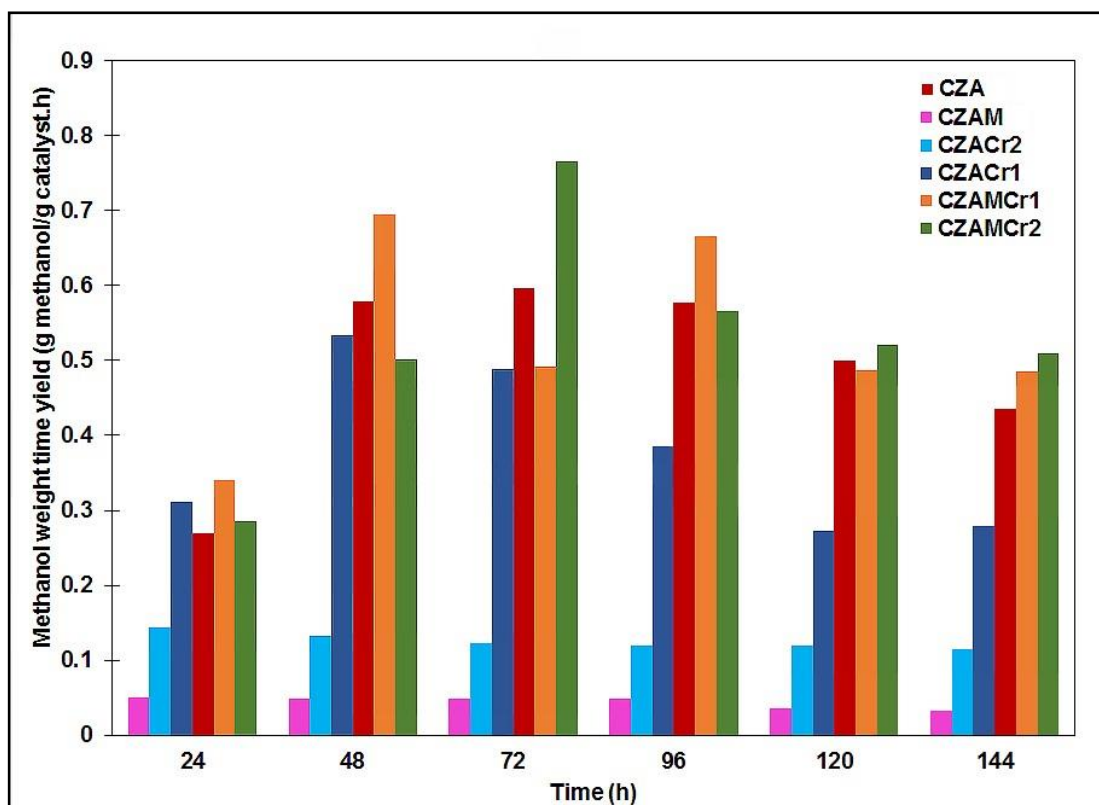


Figure 4.10: Change in methanol weight time yield by time for different catalysts.

The CZAM catalyst gave the lowest methanol weight time yield (MWTY) ($0.04 \text{ g methanol} \cdot \text{g catalyst}^{-1} \cdot \text{h}^{-1}$) while the CZAMCr1 or CZAMCr2 catalyst gave the highest MWTY during 144 h of testing period (Figure 4.10). The simultaneous addition of Cr and Mg promoters to the CZA catalyst increased the MWTY values of CZAMCr1 and CZAMCr2 catalysts up to $0.75 \text{ g methanol} \cdot \text{g catalyst}^{-1} \cdot \text{h}^{-1}$. The MWTY values of the CZAMCr1 and CZAMCr2 catalysts were almost 12-fold higher than the MWTY of the CZAM catalyst at 144 h. At 72 h, the highest MWTY of $0.58 \text{ g methanol} \cdot \text{g catalyst}^{-1} \cdot \text{h}^{-1}$ was attained for the conventional CZA catalyst whereas the highest MWTY of $0.75 \text{ g methanol} \cdot \text{g catalyst}^{-1} \cdot \text{h}^{-1}$ was obtained for the CZAMCr2 catalyst.

The conventional CZA catalyst gave high methanol productivity and selectivity, but it deactivated faster than the CZAMCr1 and CZAMCr2 catalysts (Figure 4.11). The results of long-term activity tests were used to calculate deactivation rates of the catalysts. The Cr and Mg-Cr promoted catalysts showed lower deactivation than the other catalysts (Figure 4.11). The catalysts without Cr promoter deactivated much rapidly. Cr promotes the formation of larger surface area and enhances CuO dispersion in the catalyst composition, thus providing resistance against sintering of the catalyst

[13], [20]. Deactivation curves of the CZAMCr1 and CZAMCr2 catalysts followed a sinusoidal trend. The regeneration process of the catalysts involved Cu oxidation and re-reduction cycles [75]. The deactivation curves of the CZAMCr1 and CZAMCr2 catalysts showed that they had self-regenerative characteristics. The CZACr1 and CZACr2 catalysts also exhibited a self-regenerative behavior, but not to the extent of the CZAMCr1 and CZAMCr2 catalysts (Figure 4.11).

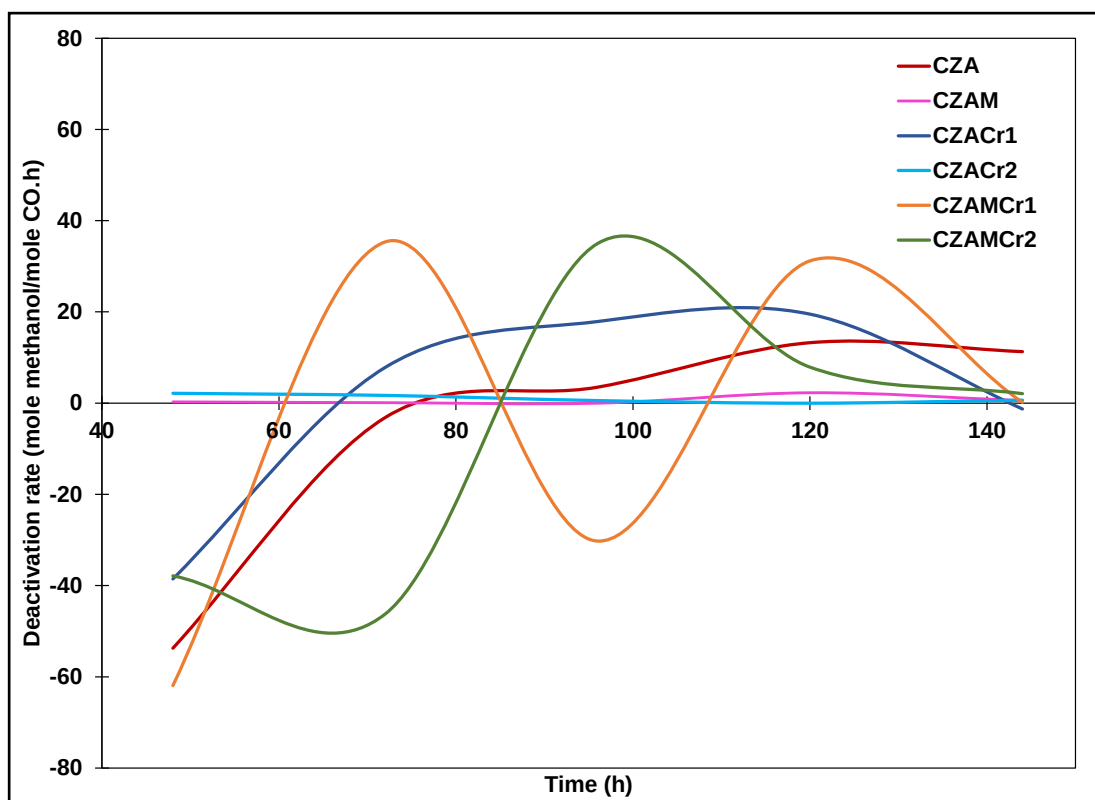


Figure 4.11: Change in deactivation rate of catalysts by time.

Although Cr can improve the catalytic activity of the Cu-based catalysts, higher Cr concentrations in the catalyst composition decrease catalytic activity by reducing the Cu surface area [62], [102]. This was the case for the CZACr2 catalyst where the methanol productivity dropped from 54.5 to 18.1 g when the Cr content in the catalyst was doubled (Table 4.6). The addition of appropriate amount of Cr into the catalyst composition provides higher BET surface area and prolongs lifetime of the catalyst, but higher Cr loadings may cause the closure of the pinholes in the catalyst and decrease the catalytic activity [72].

Table 4.6: BET surface area, methanol selectivity, total methanol production and methanol weight time yield of the catalysts.

Catalyst Name	BET Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)	Methanol Selectivity (%)	Total Methanol Production (g)	Methanol Weight Time Yield ($\text{g}_{\text{total methanol production}}\cdot\text{g}_{\text{catalyst}}^{-1}\cdot\text{h}^{-1}$)
CZA	62.0	93.5	71.0	0.49
CZAM	86.1	78.5	6.4	0.04
CZACr1	68.1	96.5	54.5	0.38
CZACr2	82.5	82.2	18.1	0.13
CZAMCr1	103.9	97.7	76.3	0.53
CZAMCr2	110.5	98.3	76.1	0.52

BET surface areas of the CZAMCr1 and CZAMCr2 catalysts were very close to each other and higher than the CZA, CZAM, CZACr1 and CZACr2 catalysts. Therefore, the methanol productivity and MWTY values of the CZAMCr1 and CZAMCr2 catalysts were very close to each other (Table 4.6). The CZAM catalyst had also higher BET surface area than the CZA, CZACr1 and CZACr2 catalysts, but its methanol productivity was the lowest. This could be attributed to the formation of separate MgO phase and a relatively poor dispersion of CuO [100]. Binary catalyst of Cu/Mg synthesized by the co-precipitation method possessed the highest Cu surface area, but it had lower methanol productivity [27]. The Mg-Cr promoted catalysts exhibited higher methanol productivities and MWTY values than only Cr or Mg promoted catalysts because the simultaneous addition of Cr and Mg caused the formation of MgCr_2O_4 in the CZAMCr1 and CZAMCr2 catalysts, thus increasing the catalytic activity [97]. The co-addition of Cr and Mg into the CZA (BET surface area of $62 \text{ m}^2\cdot\text{g}^{-1}$) catalyst increased the BET surface areas of the CZAMCr1 ($103.9 \text{ m}^2\cdot\text{g}^{-1}$) and CZAMCr2 ($110.5 \text{ m}^2\cdot\text{g}^{-1}$) catalysts. The MWTY of the CZA catalyst increased from $0.49 \text{ g}_{\text{total methanol production}}\cdot\text{g}_{\text{catalyst}}^{-1}\cdot\text{h}^{-1}$ to 0.53 and 0.52 $\text{g}_{\text{total methanol production}}\cdot\text{g}_{\text{catalyst}}^{-1}\cdot\text{h}^{-1}$, and the methanol selectivity increased from 93.5% to 97.7 and 98.3% for the CZAMCr1 and CZAMCr2 catalysts, respectively. Xiong et al. [103] prepared Cu/Zn and Cu/Cr methanol synthesis catalysts, and the highest MWTY value was found as

0.15 g_{total methanol production} · g_{catalyst}⁻¹ · h⁻¹, which was 3.5 times lower than the MWTY value of 0.53 g_{total methanol production} · g_{catalyst}⁻¹ · h⁻¹ for the CZAMCr1 catalyst in the current study. Song et al. [104] investigated the effect of lanthanum group promoters on the activity of conventional CZA catalyst, and the highest methanol selectivity of the best catalyst was found as 54%, which was almost half of the CZAMCr2 catalyst which had the highest methanol selectivity (98.3%) in the present study.

5. CONCLUSION

In the first part of the thesis, Air-TGA results revealed that the final weight losses for both Mn and Cr containing precursors were almost the same. Higher peak intensities in XRD diffractograms were obtained for K38-Mn precursor as compared with the K38-Cr precursor. The BET surface areas decreased by increasing crystallite size within each catalyst. H₂-TGA and H₂-DTG results indicated that peak temperatures of Mn containing catalysts were lower than those of Cr containing catalysts. The addition of Mn reduced the CuO particle size. The Cr promoted catalysts yielded higher surface area. At calcination temperatures below 350 °C, the formation of CuO phase was not completed. The highest H₂ consumption values were obtained for Mn containing catalysts calcined at 350 and 450 °C. The K38-Mn-350 catalyst had a peak temperature of ~255 °C whereas the peak temperature was 265 °C for the K38-Mn-450 catalyst. Lower peak temperature is a key parameter alongside with H₂ consumption. K38-Mn-350 catalyst, which exhibited the optimum H₂ consumption behavior, could have the best catalytic activity. The use of Mn-promoted catalyst in the present study could be an alternative to conventional Cu-based catalysts used in methanol production processes currently utilized in the industry.

In the second part of the thesis, XRD diffractograms of the precursors showed that Cr addition decreased malachite and rosasite formation and resulted in the disappearance of these phases by increasing the Cr content. Air-TGA profiles of the four precursors indicated that final weight losses were almost equal to each other. The smallest Cu crystallite size and highest BET surface area were observed for the reduced CZAM-50Cr catalyst. Mg in the catalyst increased the BET surface area, decreased the CuO crystal size and increased the amorphous phase. Addition of Mg also instigated methanol production activity. CuO crystallite sizes reduced by increasing the surface area and decreasing the surface acidity. The surface acidity values of the catalysts decreased by the addition of Mg and Cr. CZAM-50Cr had the highest BET surface area and the lowest surface acidity. CO consumption of the catalysts except for CZA was similar to each other. The lowest CO conversion was obtained by CZA. CZAM-10Cr resulted in the highest methanol production activity as compared with CZA, CZAM and CZAM-50Cr. Results showed that addition of 3 mol % Mg provided better dispersion of the catalysts. Deactivation rate of the catalysts

decreased, and methanol production activity increased by adjusting the Cu:Cr ratio (9:1). The methanol production activity decreased by increasing the Cu:Cr ratio (1:1), but the deactivation rate of the catalysts decreased drastically. Differences between methanol generation and selectivity was attributed to the inhibitory effect of Cr against deactivation and augmentation of the surface areas. Decreased catalytic activity in CZAM-50Cr may be attributed to lower Cu loading and/or partial blockage of pores caused by higher Cr loadings. Addition of Cr enhanced stability against moisture and CO₂ in the air and avoided carbonate and hydroxide formation. Increasing the Cr content in the catalysts considerably reduced deactivation rate. Finally, Cr content is said to be important for synthesizing more stable catalysts with the highest activity and prolonged shelf lives.

In the last part of the thesis, Cu/ZnO/Al₂O₃-Mg, Cr and Mg-Cr catalysts were synthesized using co-precipitation method. Methanol productivity, selectivity and deactivation rates of the synthesized catalysts were tested at a temperature of 270 °C and a pressure of 30 MPa for 144 h. Smaller CuO particles and higher BET surface areas were formed by the co-addition of Cr and Mg. The catalyst with a Mg:Cr molar ratio of 2:1, which had a BET surface area of 103.9 m²·g⁻¹, gave the highest methanol production activity of 76.3 g for 1 g of catalyst at 144 h reaction time, which corresponded to the MWTY of 0.53 g_{total methanol production}·g_{catalyst}⁻¹·h⁻¹. The catalyst with a Mg:Cr molar ratio of 1:1 yielded the highest methanol selectivity of 98.3%. The decrease in CO and CO₂ contents of the reactor effluent gases showed that both CO and CO₂ were acted as the carbon source for methanol synthesis reaction. The increase in the Cr content in the Cr promoted catalyst compositions remarkably reduced the methanol production activity and selectivity of the catalyst. The increase in the deactivation rate of the conventional CZA catalyst increased with time whereas the deactivation rates of the catalysts with Mg:Cr molar ratios of 2:1 and 1:1 exhibited a sinusoidal pattern which was the indication of self-regeneration. The co-addition of Cr and Mg into the catalysts increased methanol productivity and inhibited catalytic deactivation of the catalysts.

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