

Effects of calcination temperature on the catalyst performance in a CO₂ hydrogenation reaction

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Abstract: Cu/ZnO catalysts were synthesized on Al₂O₃-ZrO₂ support via impregnation method with addition of manganese and niobium promoters. Samples were calcined at 181, 350 and 518 °C. Different characterization techniques such as H₂-TPR and CO₂-TPD were used to study the catalytic reduction behavior and catalytic basicity, respectively. H₂-TPR studies shows that all the catalysts reduction occurred on the range of temperature between 237 °C and 265 °C. The CO₂-TPD profiles showed that the calcination temperature significantly influences the basicity of the catalyst and the catalyst calcined at 350 °C was proved to contain the highest amount of the basic sites. Furthermore, the characterization results were validated through analyzing of the catalyst performance during CO₂ hydrogenation reaction and the results indicate that highest methanol yield of 12.2 % were obtained from the catalyst that calcined 350 °C.

Keywords: Methanol, CO₂ Hydrogenation, calcination temperature

1. Introduction

Methanol, also known as wood alcohol was commercially obtained from destructive distillation of wood before mainly produced by hydrogenation of carbon monoxide (Equation 1). At room temperature, methanol exists as a polar colorless, volatile, and flammable liquid form. Methanol, being the simplest type of alcohol, has a distinctive odor similar to the drinking alcohol, ethanol but far more toxic than ethanol [1]. Despite that, methanol has been identified as a precursor to other commodity chemicals such as acetic acid, dimethyl ether, and methane, hence, more than 20 million tons of methanol is being produced annually for these industrial demands[2]–[4].



In this era, the significant increase of CO₂ content in the earth's atmosphere develops researchers' interests to produce valuable chemicals from CO₂, such as methanol, as shown in equation 2 [5]–[7]. This process is one of the best options for storing energy in a most convenient form of liquid fuels with sufficiently high energy density in comparison to all the existing methods of energy storage [8]. However, this process is also very challenging due to the high stability of the CO₂.

Commercially, methanol is synthesized from syngas feedstock using Cu/ZnO/Al₂O₃ catalyst [9]. Besides the commercialized alumina support, zirconia (ZrO₂) is utilized as one of main catalyst components because of its strength and thermal-resistant property. Findings by Witoon et al. suggests that CO₂ hydrogenation is highly influenced by the zirconia phase, Cu-ZrO₂ interaction of amorphous-ZrO₂ and tetragonal-ZrO₂ is stronger than monoclinic-ZrO₂[10]. A study conducted by Zhang et al. proved that the presence of ZrO₂ in the commercial CO₂ hydrogenation catalyst has increased the CO₂ conversion up to 25.9–24.7% at 250 °C and 5 MPa using 10% of alumina sol in a slurry bed reactor [11]. Recently, ZrO₂ also found to reduce weak basic sites which resulted in high methanol selectivity (75%) over the CuO-ZnO catalyst which was calcined at temperature >600°C [12].

Besides ZrO₂, manganese (Mn), zirconium (Zr), titanium (Ti), lead (Pb), etc. also exhibit ability to fine-tune interfaces between their oxides and active copper which promote methanol selectivity and the stability of the catalyst[13]–[17]. For instance, TiO₂, ZrO₂, and TiO₂-ZrO₂ mixed-oxide on CuO-ZnO catalyst have been reported to improve the CuO dispersion and increase the Cu surface area and adsorption capacities of CO₂ and H₂ [18] - [19]

This study investigated the roles of calcination temperatures on physiochemical properties of Mn and Nb-

promoted Cu/ZnO/Al₂O₃-ZrO₂ catalyst and their performance in CO₂ hydrogenation reaction into methanol. The synthesized catalysts were characterized with field emission scanning electron microscope (FESEM), hydrogen temperature-programmed reduction, H₂-TPR, and carbon dioxide temperature-programmed desorption (CO₂-TPD) techniques.

2. methodology (experimental)

2.1. Catalyst Synthesis

The catalyst was prepared using an impregnation method with 15 wt% metal loading at Cu to ZnO ratio of 7:3. A total of 0.09% of Mn and Nb metals were incorporated into the catalyst as promoters. For synthesis of 10g catalyst, 0.021g of Mn(NO₃)₂·4H₂O [Merck], 0.014g of C₄H₄NNbO₉ [Merck], 3.995g of Cu(NO₃)₂ [Merck], and 1.644g of Zn(NO₃)₂ [Sigma Aldrich], were dissolved in deionized water and stirred for 1 hour and then added dropwise onto the Al₂O₃-ZrO₂ [SASOL] powder. The mixture was continuously stirred for 24 hours and the pH was maintained at 7 using 10% ammonia solution, NH₄OH [Merck]. Then the mixture was filtered and the sample was washed using deionized water. The sample was dried at 120°C for 12 hours and then calcined statically at the presence of air for 4 hours under different range of temperature 181, 350 and 518 °C to study the effect of the calcination temperature on the catalytic performance.

2.2. Catalyst Evaluation

Catalyst evaluation was performed in a fixed-bed reactor (Microactivity Reference, PID Eng Tech). Prior to the reaction, a 0.2g of sample was treated in 5 vol% of H₂ in Argon gas at 20 mL min⁻¹ for 2 hours. The CO₂ hydrogenation reaction was performed at 22.5 bar, 250°C, and 1:3 of CO₂: H₂ with a total flow rate of 36 mL/min for 5 hours. The reactor effluents were analyzed using a gas chromatograph (Agilent 7890A) equipped with a TCD detector for H₂ and CO₂ analysis, and FID detector for analysis of alcohols and other hydrocarbons [20]. CO₂ conversion, alcohol selectivity and methanol yield were calculated using Equation 1, equation 2, and equation 3, respectively.

$$CO_2 \text{ conversion (\%)} = \frac{\text{Mole of } CO_2 \text{ in} - \text{Mole of } CO_2 \text{ out}}{\text{Mole of } CO_2 \text{ in}} \times 100 \quad (1)$$

$$\text{Methanol selectivity (\%)} = \frac{\text{mole of methanol produced}}{\text{total mole of product}} \times 100$$

$$\text{Methanol yield (\%)} = \frac{CO_2 \text{ conversion (\%)}}{100} \times \text{Methanol selectivity (\%)} \quad (2) \quad (3)$$

2.3. Catalyst Characterization

The morphology was observed on a Hitachi-8020 field emission scanning electron microscope (FESEM) at 5K magnification. The reduction profile of the catalyst was studied via the hydrogen temperature-programmed reduction (H₂-TPR) using a TPR equipment (1100 CE Instrument). 40-50 mg catalyst was placed in the quartz tube and was pre-treated at 250°C with a ramping rate of 10°C /min under the flow of pure N₂ for 1 hour. The analysis was then continued by flowing 5% H₂/Ar (20 mL/min) and heated to 990°C at 10°C/min for an hour. The carbon dioxide temperature-programmed desorption experiments (CO₂-TPD) were conducted using the same instrument as H₂-TPR experiments. The CO₂-TPD experiments were carried out by placing 40-50 mg of the calcined catalyst in the quartz tube and was pre-treated at 250°C with a ramping rate of 10°C /min under He flow (20 mL/min) for an hour. The CO₂ sorption then continued by continuous CO₂ flow at 10 mL/min for 30 minutes at 75°C.

3. Results And Discussion

3.1. Morphological Properties Of The Catalyst

FESEM images for catalyst samples calcined at different temperatures are shown in Fig. 1. All catalyst samples exhibit irregular morphology. Increasing the calcination temperature from 181 to 518 °C did not change the morphology of the samples.

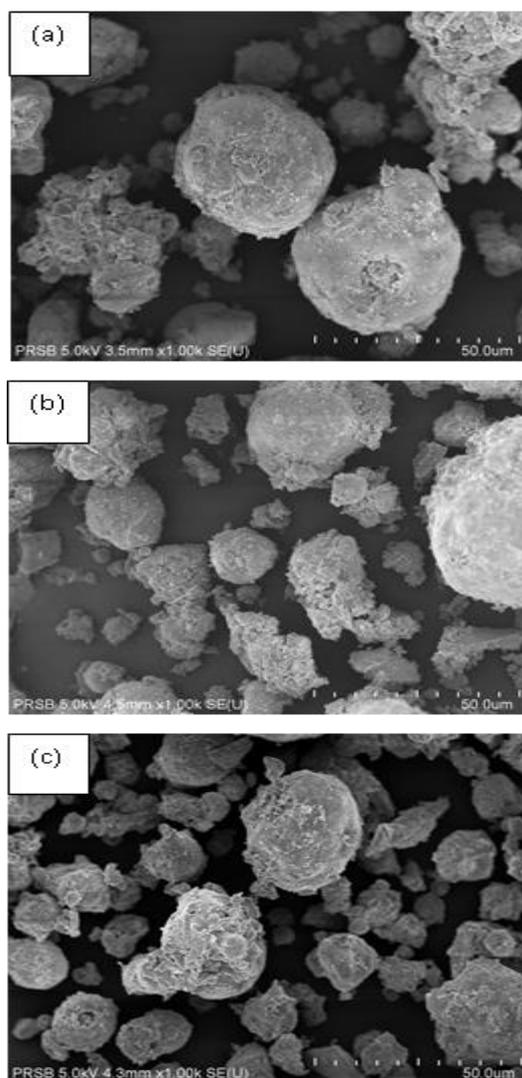


Fig. 1. FESEM images of catalysts calcined at (a) 181 °C(b) 350 °C, and (c) 518 °C

Fig. 2 shows the H₂-TPR profiles for catalyst samples calcined at 181, 350 and 518 °C. The amount of hydrogen consumed and the corresponding reduction temperature are shown in Table 1. Samples calcined at 181 and 350 °C exhibit two distinct TPR peaks, denoted as α and β , due to the stepwise reduction behavior of the Cu-based catalysts. The α peak resulted from the reduction of highly dispersed copper oxide species which are easier to reduce while the β peak is ascribed to the reduction of bulk-like CuO [7], [21]. The occurrence of reduction with shoulder peaks had also been reported previously in the literature[22]. The H₂-TPR profiles show that reduction for the catalysts occurred between 235 °C to 265 °C. For the sample calcined at 518 °C, only a single H₂-TPR peak was observed at 237 °C, which suggest that at high calcination temperature the bulk-like CuO was reduced directly to Cu⁰ instead of the stepwise reduction process which also consumed the least amount of hydrogen (1123 μ mol/g).

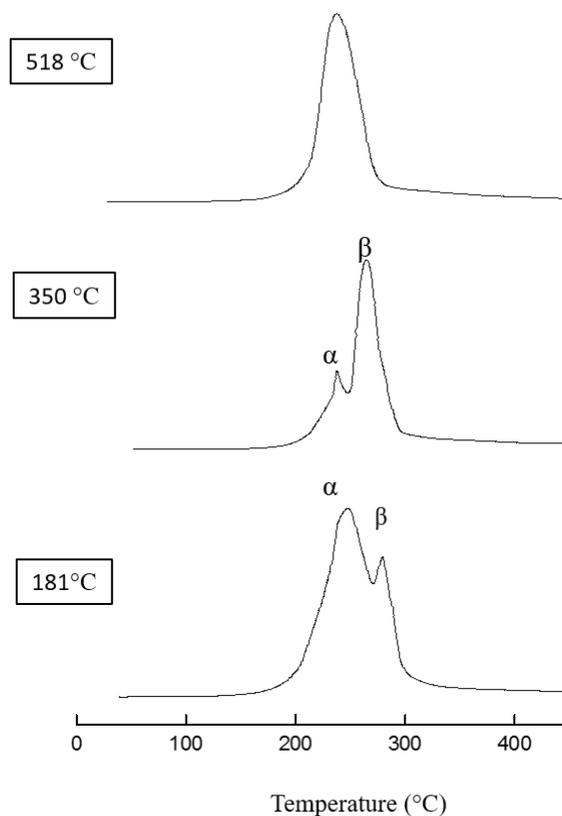

Fig. 2. H₂-TPR profiles of the catalysts

Table 1. H₂-TPR data of catalysts

Calcination temperature (°C)	H ₂ consumption (μmol/g) peak	Reduction temperature (°C)		H ₂ consumption (μmol/g) peak	
		<i>α</i>	<i>β</i>	<i>α</i>	<i>β</i>
181	1403	238	265	322	1081
350	2875	248	260	1881	994
518	1123	237		1123	

Fig. 3. shows the CO₂-TPD profiles of the catalysts and the data are shown in Table 2. The TPD peak at temperature <200°C is related to the weak basic sites which were contributed by the weakly-held surface hydroxyl groups (-OH). The medium basic sites (200 °C - 500 °C) were attributed to metal oxygen pairs i.e. Cu-O Al-O, Zn-O, Mn-O, Nb-O and Zr-O [23] - [24]. The high temperature desorption peaks (above 500°C) represent the strong basic sites that are associated with coordinatively unsaturated O₂⁻ ions (low coordination oxygen atoms) from partial breakup of metal-oxygen pairs [25]. The sample that was calcined at the lowest temperature (181 °C) contained mostly medium basic sites (β). However, the sample that was calcined at 350 °C exhibited weak, medium and strong basic sites and had the highest amount of basic sites (574 μmol/g). Nevertheless, the medium-strength basic sites disappeared when the calcination temperature was increased to 518 °C and the total amount of basic sites also decreased significantly to 88 μmol/g.

Table 2. CO₂-TPD data for the catalysts

Calcination temperature (°C)	Total basic sites (μmol/g)	Peak Temperature (°C)			CO ₂ consumption (μmol/g) peak		
		T ₁	T ₂	T ₃	α	β	γ
181	268	-	451	825	-	209	59
350	574	152	440	870	75	392	107
518	88	154	-	899	26	-	62

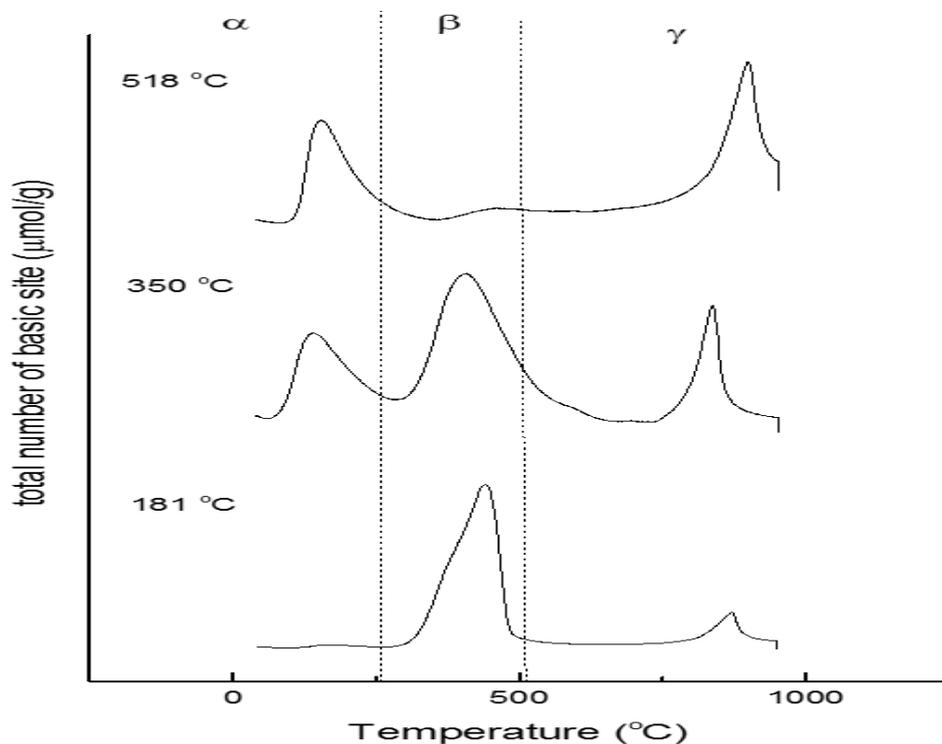
**Fig. 3.** CO₂-TPD profiles of the catalysts

Table 3 shows the catalytic activity in a CO₂ hydrogenation reaction performed at reaction temperature of 250 °C and reaction pressure of 22.5 bar. The values of CO₂ conversion ranged from 6.5 to 16% while the methanol selectivity varied from 19.5 and 75.9% using catalysts that were calcined at various temperatures. The highest methanol yield (12.2 %) was achieved using a catalyst that was calcined at 350 °C. The catalytic activity is proved to be affected by the presence and the amount of the basic sites. Compared to the other catalysts, the sample that was calcined at 350 °C contained the highest amount of basic sites (574 μmol/g) comprising weak, medium and strong basic sites which resulted in the highest catalytic activity. The sample that was calcined at high temperature (518 °C) might have been sintered and did not possess enough active sites to activate the CO₂ molecules, thus resulting in low CO₂ conversion. Our findings are in agreement with those of Shaharun et al. as they reported rapid catalyst weight loss starting below 200°C and continued up to 350°C for Cu/ZnO/Al₂O₃/ZrO₂ catalyst [26]. Fig. 4 shows effects of catalysts' calcination temperature on the yields of methanol in a CO₂ hydrogenation reaction. Based on this trend, 350 °C was found to be the suitable catalyst calcination temperature that results in higher conversion, selectivity and methanol yield.

Table 3. Catalysts performance in a CO₂ hydrogenation reaction at 22.5 bar, 250 °C for 5 hours.

Run	Calcination temperature (°C)	CO ₂ conversion (%)	Methanol selectivity (%)	Methanol yield (%)
1	181	6.5	19.5	1.3
2	350	16.0	75.9	12.2
3	518	7.2	58.4	4.2

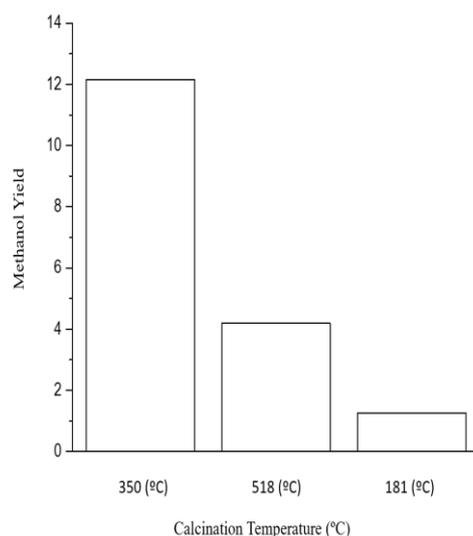


Fig. 4. Effect of catalysts' calcination temperature on methanol yields.

4. Conclusion

Effects of calcination temperature for Mn/Nb-promoted Cu/ZnO/Al₂O₃-ZrO₂ catalyst have been investigated. All the catalyst exhibits irregular shape and reduced below 300 °C. The catalyst that was calcined at 350 °C exhibited the highest amounts of basic sites (574 $\mu\text{mol/g}$) and resulted in the highest CO₂ conversion (16.0%), methanol selectivity (75.9%) and methanol yield (12.2%).

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References

- E. Fiedler, G. Grossmann, D. B. Kersebohm, C. Witte, C. Deactivation, and O. C. Systems, "Methanol 1," 2005.
- A. Vita, C. Italiano, L. Pino, M. Laganà, M. Ferraro, and V. Antonucci, "High-temperature CO₂ methanation over structured Ni/GDC catalysts: Performance and scale-up for Power-to-Gas application," *Fuel Process. Technol.*, vol. 202, pp. 106365, 2020.
- P. S. Sai Prasad, J. W. Bae, S. H. Kang, Y. J. Lee, and K. W. Jun, "Single-step synthesis of DME from syngas on Cu-ZnO-Al₂O₃/zeolite bifunctional catalysts: The superiority of ferrierite over the other zeolites," *Fuel Process. Technol.*, vol. 89, no. 12, pp. 1281–1286, 2008.
- W. Huang, K. C. Xie, J. P. Wang, Z. H. Gao, L. H. Yin, and Q. M. Zhu, "Possibility of direct conversion of CH₄ and CO₂ to high-value products," *J. Catal.*, vol. 201, no. 1, pp. 100–104, 2001.
- O. Tursunov, L. Kustov, and Z. Tilyabaev, "Methanol synthesis from the catalytic hydrogenation of CO₂ over CuO-ZnO supported on aluminum and silicon oxides," *J. Taiwan Inst. Chem. Eng.*, vol. 78, pp. 416–422, 2017.
- A. Bansode, B. Tidona, P. R. Von Rohr, and A. Urakawa, "Impact of K and Ba promoters on CO₂ hydrogenation over Cu/Al₂O₃ catalysts at high pressure," *Catal. Sci. Technol.*, vol. 3, no. 3, pp. 767–778, 2013.
- M. K. Koh, Y. J. Wong, S. P. Chai, and A. R. Mohamed, "Carbon dioxide hydrogenation to methanol over multi-functional catalyst: Effects of reactants adsorption and metal-oxide(s) interfacial area," *J. Ind. Eng. Chem.*, vol. 62, pp. 156–165, 2018.
- . Ganesh, "Conversion of carbon dioxide into methanol - A potential liquid fuel: Fundamental challenges and opportunities (a review)," *Renew. Sustain. Energy Rev.*, vol. 31, pp. 221–257, 2014.
- P. S. S. Prasad, J. W. Bae, S. Kang, Y. Lee, and K. Jun, "Single-step synthesis of DME from syngas on Cu - ZnO - Al₂O₃/ zeolite bifunctional catalysts : The superiority of ferrierite over the other zeolites," *Fuel Process. Technol.*, vol. 89, no. 12, pp. 1281–1286, 2008.
- T. Wittoon, J. Chalorngham, and P. Dumrongbunditkul, "CO₂ hydrogenation to methanol over Cu/ ZrO₂ catalysts : Effects of zirconia phases," *Chem. Eng. J.*, vol. 293, pp. 327–336, 2016.
- Y. Zhang et al., "Catalytic performance of spray-dried Cu/ZnO/Al₂O₃/ZrO₂ catalysts for slurry methanol synthesis from CO₂ hydrogenation," *J. CO₂ Util.*, vol. 15, pp. 72–82, 2016.

- C. Temvuttiroj et al., "Role of Calcination Temperatures of ZrO₂ Support on Methanol Synthesis from CO₂ Hydrogenation at High Reaction Temperatures over ZnO_x/ZrO₂ Catalysts," *Ind. Eng. Chem. Res.*, vol. 59, no. 13, pp. 5525–5535, 2020.
- S. F. H. Tasfy, N. A. Mohd Zabidi, M. S. Shaharun, and D. Subbarao, "Effect of Mn and Pb promoters on the performance of Cu/ZnO-catalyst in CO₂ hydrogenation to methanol," *Appl. Mech. Mater.*, vol. 625, pp. 289–292, 2014.
- M. K. Koh, M. M. Zain, and A. R. Mohamed, "Exploring transition metal (Cr, Mn, Fe, Co, Ni) promoted copper-catalyst for carbon dioxide hydrogenation to methanol," *AIP Conf. Proc.*, vol. 2124, no. July, 2019.
- S. F. H. Tasfy, N. A. M. Zabidi, M. S. Shaharun, and D. Subbarao, "The influence of Mn, Zr and Pb promoters on the performance of Cu/ZnO/SBA-15 catalyst for hydrogenation of CO₂ to methanol," *Defect Diffus. Forum*, vol. 365, pp. 178–182, 2015.
- F. Li, H. Zhan, N. Zhao, and F. Xiao, "CO₂ hydrogenation to methanol over La-Mn-Cu-Zn-O based catalysts derived from perovskite precursors," *Int. J. Hydrogen Energy*, vol. 42, no. 32, pp. 20649–20657, 2017.
- P. Gao et al., "Influence of modifier (Mn, La, Ce, Zr and Y) on the performance of Cu/Zn/Al catalysts via hydrotalcite-like precursors for CO₂ hydrogenation to methanol," *Appl. Catal. A Gen.*, vol. 468, pp. 442–452, 2013.
- J. Xiao, D. Mao, X. Guo, and J. Yu, "Effect of TiO₂, ZrO₂, and TiO₂-ZrO₂ on the performance of CuO-ZnO catalyst for CO₂ hydrogenation to methanol," *Appl. Surf. Sci.*, vol. 338, pp. 146–153, 2015.
- N. S. A. Halim, N. A. M. Zabidi, S. F. H. Tasfy, and M. S. Shaharun, "Morphology and performance of Cu/ZnO based catalyst: Comparison between Al₂O₃ and SiC support," *AIP Conf. Proc.*, vol. 1787, 2016.
- S. Faiz, H. Tasfy, N. Asmawati, M. Zabidi, M. S. Shaharun, and D. Subbarao, "Effect of Mn and Pb Promoters on the Performance of Cu / ZnO-Catalyst in CO₂ Hydrogenation to Methanol," vol. 625, pp. 289–292, 2014.
- F. E. López-Suárez, A. Bueno-López, and M. J. Illán-Gómez, "Cu/Al₂O₃ catalysts for soot oxidation: Copper loading effect," *Appl. Catal. B Environ.*, vol. 84, no. 3–4, pp. 651–658, 2008.
- I. U. Din, M. S. Shaharun, D. Subbarao, A. Naeem, and F. Hussain, "Influence of niobium on carbon nanofibres based Cu/ZrO₂ catalysts for liquid phase hydrogenation of CO₂ to methanol," *Catal. Today*, vol. 259, pp. 303–311, 2016.
- G. Wu, X. Wang, W. Wei, and Y. Sun, "Fluorine-modified Mg-Al mixed oxides: A solid base with variable basic sites and tunable basicity," *Appl. Catal. A Gen.*, vol. 377, no. 1–2, pp. 107–113, 2010.
- M. K. Koh, Y. J. Wong, S. P. Chai, and A. R. Mohamed, "Carbon dioxide hydrogenation to methanol over multi-functional catalyst: Effects of reactants adsorption and metal-oxide(s) interfacial area," *J. Ind. Eng. Chem.*, vol. 62, pp. 156–165, 2018.
- S. Ren et al., "Enhanced catalytic performance of Zr modified CuO/ZnO/Al₂O₃ catalyst for methanol and DME synthesis via CO₂ hydrogenation," *J. CO₂ Util.*, vol. 36, no. May 2019, pp. 82–95, 2020.
- S. Shaharun, M. S. Shaharun, D. Mohamad, and M. F. Taha, "The effect of Cu/Zn molar ratio on CO₂ hydrogenation over Cu/ZnO/ZrO₂/Al₂O₃ catalyst," vol. 1621, pp. 3–9, 2014.