An Optimization of catalytic performance on hydrogenation of CO_2 to DME

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Abstract

Chemical utilization of carbon dioxide obtained from large scale stationary sources such as coal, oil and natural gas industries is one possible pathway to decrease the rate of carbon emissions. Catalysis plays a crucial role in these carbon dioxide utilization reactions. In this research, the synthesis of a clean fuel such as, Dimethyl Ether (DME) via CO_2 hydrogenation has been investigated on bifunctional catalysts composed of Cu-ZnO-Al_2O_3-ZrO_2 as hydrogenation component and Na-Mordenite as dehydration component with different ZrO_2 and Al_2O_3 contents. The samples were synthesized by co-precipitating sedimentation and characterized by BET surface area measurements and X-ray diffraction. Results show that both ZrO_2 and Al_2O_3 have similar effect on conversion for all catalysts, but Al_2O_3 profoundly increased selectivity of the DME. Besides, when the total contents of Al_2O_3 and ZrO_2 was increased above 16 wt%, the conversion and selectivity toward DME formation were remarkably decreased which may be related to lowering of the amount of active sites of copper on hybrid catalysts.

Keywords: Carbon dioxide, hydrogenation, Dimethyl ether, bifunctional catalyst.

1. Introduction

The utilization of CO_2 as a feedstock for producing chemicals is appealing not only because it may contribute to mitigation of greenhouse gas emissions, but also due to it being an interesting challenge in exploring new concepts and opportunities for catalysis and industrial chemistry[1]. In addition, pure resources may be saved when secondary CO_2 is used as a raw material to replace them. Remarkably, also are the cheap price and non-toxicity of CO_2, and the potential to discover entirely new materials and novel routes to existing chemical intermediates and products, which are more efficient and economical than current methods. This provides strong motivations to utilize CO_2 as a feedstock whenever possible [2].

Dimethyl ether as a suitable clean fuel for diesel engines has attracted a good deal of attention in industry due to its higher cetane number, lower concentration of particulates, NO_x emission, near zero smoke and less engine noise compared to traditional diesel fuels[3]. Hydrogenation of CO_2 to DME has attracted more attention as one of the most promising methods to mitigate the global warming and reduction of greenhouse gases [4,5]. However, there are unfavourable thermodynamic conditions on methanol formation from hydrogenation of CO_2 [6]. Direct synthesis of the DME by using hybrid catalyst may overcome equilibrium restrictions as follows

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[7]:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H^0_{298} = -49.5 \frac{Kj}{mol} \tag{1}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H^0_{298} = 41.2 \frac{Kj}{mol} \tag{2}$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \Delta H^0_{298} = -23.4 \frac{Kj}{mol} \tag{3}$$

Simultaneous occurrence of these reactions results in a synergistic effect, that may relieve unfavorable thermodynamics for methanol synthesis since the product of each step is a reactant for the next step. Therefore, this creates a strong driving force for the overall reaction, which allows for a very high CO_2 conversion in one single pass.

Reactions (1) and (2) are catalyzed by methanol synthesis catalyst and reaction (3) is catalyzed by the solid acid catalyst. Most common components of hybrid catalysts reported in the literature are Cu/ ZnO/Al_2O_3 or $Cu/ZnO/ZrO_2$ for methanol synthesis [8,9] and zeolites such as, HZSM-5, HY, H-Mordenite or Na-Mordenite for methanol dehydration [10-12]. In this research, the influence of ZrO_2 and Al_2O_3 contents on production of the DME from CO_2 hydrogenation was investigated. In this direction, Cu-ZnO-ZrO_2-Al_2O_3/Na-Mordenite catalyst with different contents of ZrO_2 and Al_2O_3 was prepared by co-precipitating sedimentation method and evaluated in a three phase slurry reactor.

2. Experimental

2.1. Catalyst preparation

Bifunctional catalyst with different ZrO_2 and Al_2O_3 contents (Cu/ZnO = 1:1 wt%) were prepared by co-precipitating sedimentation method [11]. For this purpose, a solution of metal nitrate and sodium carbonate were prepared and added simultaneously and drop-wise to de-ionized water over a period of 30 min at 70ºC and pH=7, under continuous stirring. The precipitates formed were aged for an hour, under continuous stirring at 70ºC. Resulting precipitates were filtered and washed several times with de-ionized water to remove residual sodium ions. This was then added to the suspended liquid containing the dehydration component of the catalyst (Na-Mordenite, Si/Al=13, S_{BET}=425m^2/g) and water. The weight ratio of hydrogenation catalyst to dehydration catalyst was 4:1 according to the reference [13]. The mixture was stirred then filtered and dried at 120ºC for 12 hrs. Next, it was calcined in air at 450 ºC for 3 hrs. Specifications of six hybrid catalysts prepared are shown in Table 1.

Table 1: Specifications of The hybrid catalysts prepared

Catalyst No	Al_2O_3 content (wt%)	ZrO_2 content (wt%)
1	*0*	8
2	*8*	0
3	*4*	4
4	*8*	8
5	*10*	8
6	*16*	8

2.2. Catalyst characterization

The BET surface area of prepared catalysts was determined by the N_2- physi-sorption at 77 K in Bel- Sorb mini (Japan) apparatus. X-ray diffraction (XRD) data of these materials were obtained by a Rigaku Dmax-B diffractometer (with Cu Kα radiation, 50 kV and 60 mA).

2.3. Catalytic activity test

DME synthesis reaction was carried out in a 500 ml mechanically agitated slurry reactor. In each experiment, 3 g of hybrid catalyst was slurred into 250 ml of kerosene as solvent. A feed gas containing the composition of $H_2/CO_2=1$ molar ratio, was utilized for all experiments. The reaction was performed under conditions of 20 bar, $250^{\circ}C$, the feed rate of 4000 ml / (g_{cat}.hr) and stirring rate of 1000 rpm. Prior to reaction, the hybrid catalyst was reduced under 20 bar pressure by pure hydrogen *in situ* at $250^{\circ}C$ for 1 hr. Effluent gas from reactor was analyzed, by an on-line gas chromatograph PERICHROM (PR2100) equipped with Porapak-Q column connected to a thermal conductivity detector (TCD) for the CO_2 and CO, and HP- PONA column connected to a flame ionization detector (FID) for the methanol and DME.

3. Results and discussion

3.1. Characterization of catalysts

To investigate effect of additives of Al_2O_3 and ZrO_2 on surface area of catalyst, the BET analysis was carried out. Table 2 shows the BET surface area of samples 1, 2 and 4. These results show ZrO_2 and Al_2O_3 enhance surface area of methanol synthesis catalyst (Cu/ZnO). However, the Al_2O_3 addition exhibits larger surface area and pore volume than ZrO_2, possibly due to introducing of Al_2O_3 with a higher surface area. A slight increase in surface area was observed when Al_2O_3 and ZrO_2 contents increased to 16 wt% (i.e.; sample 4).

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Table 2: The results of physical specification of the catalysts

Sample	**Surface area (m^2/g)**	**Total pore volume (cm^3/gr)**	**Mean pore diameter (nm)**
1	***19***	**0.1204**	**25.500**
2	***61***	**0.3253**	**21.372**
4	***67***	**0.2989**	**17.902**

From these results, it may be deduced that no dramatic surface area change is obtained upon ZrO_2 addition. On the other hand, a noticeable decrease in the mean pore diameter of particles might be an indicative of mass transfer restriction imposed upon catalysts with Al_2O_3 addition, leading one to conclude that ZrO_2 lowers the internal mass transfer resistance. XRD spectra of catalysts 1, 2, 3 and 4 are shown in Figure 1. Except CuO and ZnO peaks, no diffraction peaks of other metals might be detected in the range of 20-50 ° (2θ). This indicates no new species were formed upon these additions. The diffraction intensity of CuO and ZnO peaks decreased obviously with increasing of ZrO_2 and Al_2O_3 contents in catalysts. Thus, it may be concluded Al_2O_3 and ZrO_2 increase dispersion of active sites on catalyst. Nonetheless, effect of Al_2O_3 is more pronounced than ZrO_2.

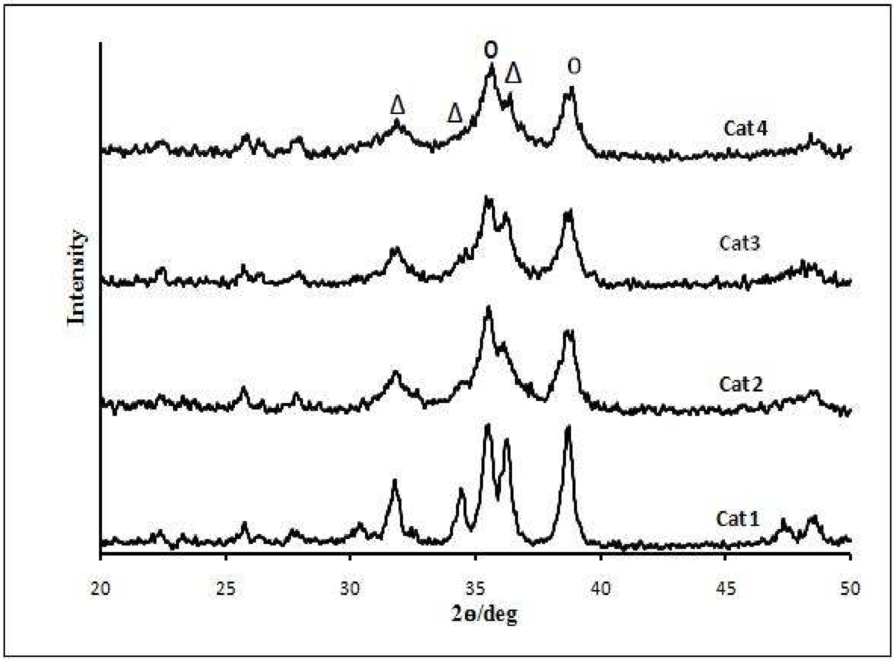

Fig. 1: XRD patterns of hybrid catalysts (**o** : CuO, Δ : ZnO)

3.2. Catalytic activity

The catalytic performance for direct synthesis of the DME from CO_2 hydrogenation is summarized in Table 3. As it may be seen, samples 1, 2, 3 and 4 gave similar conversions when ZrO_2 and Al_2O_3 contents increased up to 16 wt%, however, for more than that, due to a decrease of active sites of copper on hybrid catalyst, the CO_2 Conversion was lowered.

Table 3: Catalytic performance of the hybrid catalysts

Catalyst No.	Conv. of CO_2(mol%)	DME selectivity(mol%)
1	*14.87*	36.23
2	*15.92*	46.85
3	*14.71*	34.31
4	*15.12*	38.68
5	*13.43*	18.69
6	*8.36*	10.37

Reaction conditions: P=20bar, T=250 °C, GHSV=4000 mL/(g_{cat}h), H_2/CO_2=1.

Results of table 3 represent no noticeable difference in CO_2 conversion for samples 1, 2 and 3. Thus, one may conclude that conversion is relatively independent of amounts of Al_2O_3 and ZrO_2 present in the catalyst composition. However, comparison of results of these samples displays a higher selectivity toward DME for the sample 2. This leads one to conclude that Al_2O_3 might be a more effective component in enhancing of the DME selectivity. This in turn means that Al_2O_3 increases the dehydration of methanol to DME more than ZrO_2. In a more clear comparison, figure 2 represents the CO_2 conversion and the corresponding DME selectivity for all samples. These results indicate that sample 2 with 8 wt% of Al_2O_3 and no ZrO_2 was the best catalyst in terms of resulting in highest conversion and selectivity. Increasing of Al_2O_3 content to more than 8 wt% in samples 5 and 6 displayed a remarkable decrease in CO_2 conversion and DME selectivity, due to reduction in the amount of copper and zinc oxide active sites on hybrid catalysts. These results also confirmed those of BET surface area and XRD analyses.

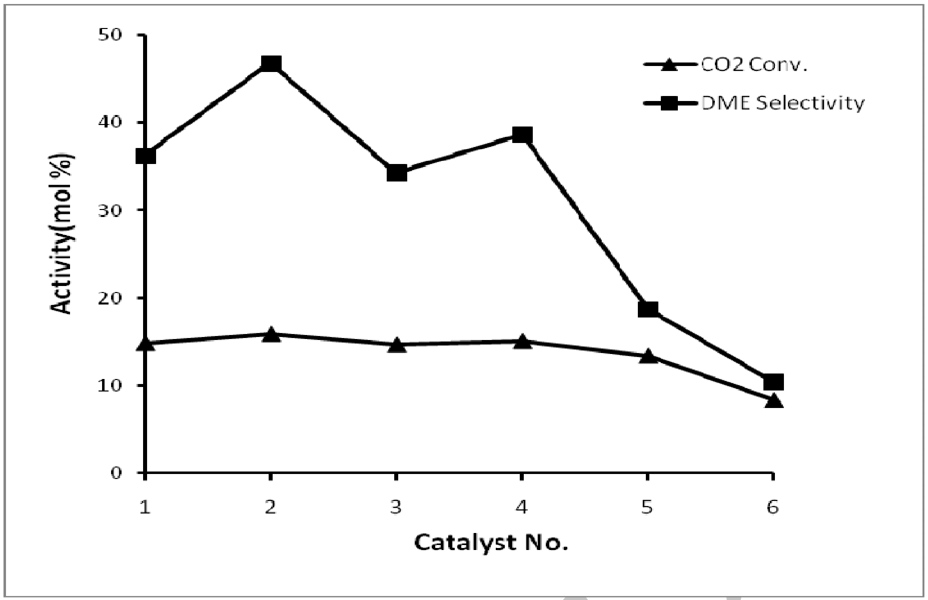

Fig2.CO_2 conversion and DME selectivity of hybrid catalysts at reaction conditions of P=20bar, T=250°C, GHSV=4000 mL/(g_{cat}hr) and H_2/CO_2=1

4. Conclusion

In this research, a series of hybrid catalysts with different Al_2O_3 and ZrO_2 contents were prepared by co-precipitating sedimentation method. Based upon results of the BET and XRD analyses, it might be concluded that Al_2O_3 containing catalysts had more surface area and dispersion compared to ZrO_2 ones. Results of activity tests showed that influence of Al_2O_3 and ZrO_2 on CO_2 conversion were similar, however, the former noticeably increased selectivity of the DME. Furthermore, increasing of Al_2O_3 and ZrO_2 contents up to 16 wt% was shown to lower the amount of copper active sites on the hybrid catalyst; hence decreased its CO_2 activity and DME selectivity. Ultimately, the best catalyst for the purpose at hand was determined to be the one with 8 wt% of Al_2O_3 and no ZrO_2. These results show CO_2 hydrogenation to DME may be a efficient approach to consume large amount of CO_2 produced in gas industry and reduce the greenhouse effects.

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بهینه سازی کارایی کاتالیست هیدروژناسیون دی اکسیدکربن به منظور تولید دی متیل اتر

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چکیده

کاربرد شیمیایی دی اکسیدکربن تولید شده از منابع انرژی همچون زغال سنگ، نفت خام و گازطبیعی یکی از راهکارهای ممکن جهت کاهش انتشار کربن می باشد. در این راستا، علم کاتالیست نقش اساسی در انجام واکنشهای شیمیایی دی اکسیدکربن ایفا می کند. بدین منظور، در این تحقیق سنتز یک سوخت پاک مانند دی متیل اتر، از طریق هیدروژناسیون دی اکسیدکربن برروی کاتالیست های دوعملگر متشکل از $Cu-ZnO-Al_2O_3-ZrO_2$ به عنوان جزء هیدروژناسیون و زئولیت Na-Mordenite به عنوان جزء آبگیری با ترکیب درصدوزنی های مختلف از Al_2O_3 و ZrO_2 مورد بررسی قرار گرفته است. نمونه ها با استفاده از روش همرسوبی- ته نشینی ساخته شده و آنالیزهای سطح مخصوص BET و XRD برروی نمونه ها انجام شده است. نتایج نشان می دهد، اکسید آلومینیم و اکسید زیرکونیوم اثر مشابه برروی میزان تبدیل داشته، حال آنکه اثر اکسید آلومینیم نسبت به اکسید زیرکونیوم برروی گزینش پذیری به سمت تولید دی متیل اتر به مراتب بیشتر بوده است. به علاوه، هنگامی که مقدار مجموع درصد وزنی اکسید آلومینیم و اکسید زیرکونیوم در ترکیب کاتالیست به بیش از ۱۶ درصد وزنی افزایش پیدا کرده، کاهش قابل توجهی در میزان تبدیل و گزینش پذیری به سمت تولید دی متیل اتر مشاهده شده است، که می توان علت آنرا کاهش سایت های فعال فلز مس (Cu) در ترکیب کاتالیست دوعملگر دانست.

کلمات کلیدی : دی اکسیدکربن، هیدروژناسیون، دی متیل اتر، کاتالیست دوعملگر