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Effect of Ultrasonic During Preparation on Cu-Based Catalyst Performance for Hydrogenation of CO_2 to Methanol

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Indonesia is rich in natural gas resources. These resources contain hydrocarbons and impurities such as CO_2. CO_2 creates a difficulty in further gas treatment and also becomes an environmental problem. Therefore, it is needed to develop a concept to recover this kind of gas and to convert it into more useful chemicals. Catalytic hydrogenation to methanol is one of the technologies that can be considered.

Conversion of CO_2 to methanol can be catalyzed by Cu-based catalyst. Reported to be the best catalyst, this catalyst is selected as a catalyst for a pilot plant that is operated at a high pressure and a high temperature. However, further development is needed to rearrange the synthesis to be operated both at lower pressure and temperature. For this system, it is needed to increase its catalytic activity. One of the alternatives is to apply a catalyst preparation method using ultrasonic effect.

In this research work, $CuO/ZnO/Al_2O_3$ catalyst with Cr as a promoter was prepared by co-precipitation method. The effect of ultrasonic on catalyst performance, which was irradiated to the catalyst during preparation, was investigated. Co-precipitation was conducted by using carbonate salt for respective metal cations added to the catalyst. Ultrasonic wave was irradiated to the catalyst preparation chamber with 40kHZ and time variable. The characteristics of the catalyst were analyzed by BET method for surface area, while SEM and H_2 chemical adsorption were conducted to determine active site dispersion. A high-pressure continuous flow reactor was used for catalyst activity and stability test. The test was conducted at an operation condition of 30 bars and 200–300°C.

The effect of ultrasonic on the $CuO/ZnO/Al_2O_3$ catalyst shows that ultrasonic irradiation enhances the catalyst surface from 23 to 50 m^2/g. SEM analysis shows the change of catalyst morphology to be more uniform and the catalyst particle becomes smaller. The activity test shows that the catalyst with 60 min irradiation time has the highest activity in the hydrogenation of CO_2 to methanol at 30 bars and at 275°C.

Keywords: Hydrogenation, dispersion, methanol, *and* ultrasonic.

INTRODUCTION

Alfred L. Loomis a chemist introduced that sound wave has effect to properties of materials. This knowledge was then called *sonochemistry*. Since 1980, ultrasonic has been used in several sectors of research because it has significant chemical and physical effects on a material (Suslick 1994). Ultrasonic has a frequency higher than the audible sound wave >16 kHz (Chang 1994). Ultrasonic irradiation results in very high energy that relates to the formation, growth, and destruction of a bubble in a liquid.

Ultrasonic shows a unique energy that can transfer a high energy to other materials in a short time and at a high intensity. This phenomenon unique to ultrasonic is known as *insonation* (Suslick 1994, Suslick et al. 1999, Suslick and Price, 1999). *Sonocatalysis* is the use of ultrasonic in catalysis technology to improve the performance of catalysts (Lii and Inui 1996). The application of ultrasonic in catalyst preparation can result in better solution mixing to give high catalyst surface area and metal active dispersion, among others.

The development of a CO_2 conversion system for methanol synthesis by catalytic hydrogenation has been considered in recent years with the need for methanol as an alternative fuel and for the environmental reason that CO_2 leads to global warming. This synthesis is thermodynamically exothermic and needs a high pressure to increase methanol yield.

A pilot plant has been established to utilize $CuO/ZnO/Al_2O_3$-based catalyst (*Mitsubishi Juko Giho* 1986). This kind of catalyst, with some modifications, has been reported by many researchers to have both high activity and selectivity to the synthesis. For the pilot plant, the reaction was operated at around 130 bars and 300°C in order to obtain the maximum yield of methanol (Morikawa et al. 1986, Fujitani et al. 1993, Rasmussen et al. 1994, Chichen 1988). Considering the thermodynamic calculation, the conversion of CO_2 can reach as high as 50% at lower pressure, which is 30 bars and 250°C with low ratio of CO_2/H_2. Consequently, a higher activity catalyst is needed. Fujita et al. (1995) reported the possibility of synthesis at atmospheric pressure.

To operate the synthesis at low pressure, improvement of catalyst activity has been conducted by adding promoters, such as Zr, Cr, Mn, and Ga. In this research, the catalyst improvement was done by using ultrasonic effect on catalyst characteristics during catalyst preparation. The catalyst prepared was $CuO/ZnO/Al_2O_3$ and precipitation method was conducted. The improvement of catalyst characteristics, such as surface area and metal active dispersion, were expected to enhance the conversion of CO_2 and the selectivity to methanol.

EXPERIMENTAL

Catalyst was prepared by precipitation method with weight percentage ratio of $CuO:ZnO:Al_2O_3 = 50\%:45\%:5\%$. Ultrasonic was being irradiated to catalyst during preparation with variation of time. U-30, U-60 and U-90 are catalysts with irradiation time 30, 60 and 90 min respectively. Ultrasonic generator (Benson 200 ultrasonic, see Figure 1) was utilized to generate a wave at 40 kHz.

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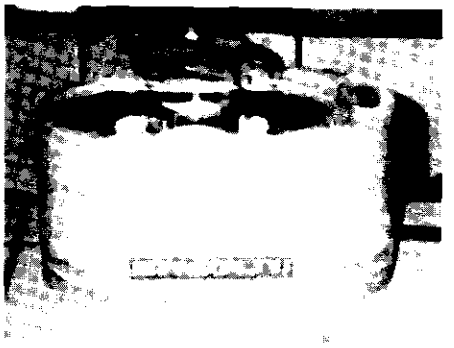

Figure 1. Ultrasonic Generator

Precipitation was done by mixing Cu, Zn, Cr, Al nitrates with NH_4OH as a *precipitating agent* at 50°C to give catalyst sediment. This step results blue color sediment then ultrasonic was introduced into. Centrifugation of this colloid and drying in *vacuum furnace* at 120 mbar and 120°C for 5h and calcination at 350°C for 5h was obtained a catalyst granular with black-brown color.

Surface area was determined by BET method using Quantachrome-Autosorb-6 and surface morphology was analyzed by TEM (LEO 401i), while H_2 isothermal adsorption was conducted for measuring metal active dispersion. Activity and selectivity of the catalyst were tested by using a high-pressure continuous tubular flow reactor (Vinci Technologies-MCB 890), with 6 mm ID of SS reactor and 0.5–1 ml. catalyst volume. The reactor was operated at 30 bars with a feed flow rate of 100–200 cc/min at 250–275°C. Reduction of catalyst was done before reaction by flowing 5%H_2/N_2 with flow rate of 200 cc/min at 220°C for 1 h. Reactants and products were analyzed continuously by gas chromatography (GC).

RESULT AND DISCUSSION

Table 1. Catalyst Surface Area (m^2/g)

Catalysts	$CuO/ZnO/Al_2O_3$	$CuO/ZnO/Al_2O_3/Cr_2O_3$
Non-U	23.1	50.0
U-30	46.4	102.4
U-60	50.1	125.2
U-90	34.7	104.4

Catalyst surface area

Table 1 shows the results of catalyst surface area measurement.

These results indicate that irradiation of ultrasonic to the catalyst increases its surface area; for instance, 30 min. of irradiation increases surface area by 100% from 23.13 to 46.4 m^2/g. The same phenomenon also occured in the catalyst with promoter, wherein surface area increased by more than 100%.

Ultrasonic energy that attached to the catalyst during its preparation obtained a more porous catalyst. However, U-90 had lower surface area than U-60. This difference was caused by the agglomeration of particles when irradiation attached too much to the catalyst (Lii and Inui 1996).

Metal active dispersion

Metal active dispersion is the ratio of metal exposed to the surface in comparison to the total metal in the catalyst. This dispersion was determined by H_2 isothermal adsorption. Table 2 shows the metal active dispersion of the catalyst.

Table 2. Active Site Dispersion

Catalyst	Dispersion, %
Non-U	1.9
U-60	18.9
U-90	15.7

Ultrasonic gives a very significant effect to the dispersion, although overdose of irradiation can also decrease the dispersion. Table 2 shows the effect that ultrasonic can increase metal dispersion tenfold compared to a non-ultrasonic catalyst.

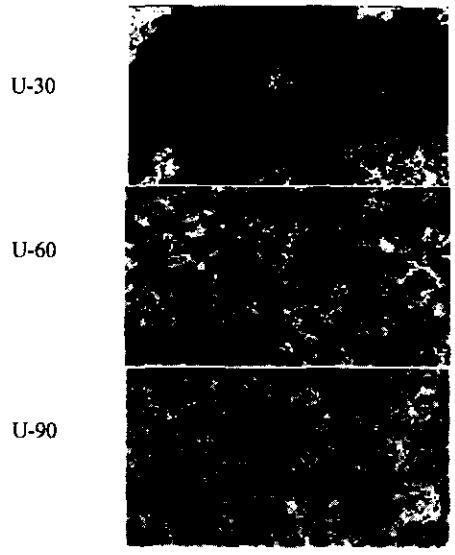

Figure 2. SEM Image of Catalysts (Magnitude x200, Scale 1 cm = 50 μm)

Ultrasonic has very high energy that causes more intense collisions between particles resulting in smaller particle size.

Surface morphology

High active metal dispersion indicates that a catalyst has a small particle size. In order to determine the particle size, SEM analysis was conducted for the catalyst with different irradiation times. Figure 2 shows the SEM images of the three irradiated catalysts.

Although the images could not be used for distinguishing each active metal because of similarities in image properties, these SEM images at least can be used to analyze ultrasonic effect on particle size that can then be used to determine

metal dispersion. As shown in Figure 2, increasing the irradiation time results in smaller particle sizes of the catalyst. This is consistent with the increase of catalyst dispersion as a function of irradiation time. It can be estimated from Figure 2 that the particle size of catalysts U-30, U-60, and U-90 are 50, 15, and 50 mm. This is consistent with the fact that metal dispersion is inversely proportional to that of particle size. These data indicate again that ultrasonic can have significant effects on catalyst character, especially on particle size.

Catalyst activity

Just before reaction, the catalyst was reduced by a mixture of 5% H_2/N_2 at 220°C to obtain Cu as the active site. As was reported by other reseachers [4], there was no sintering of Cu site at the reduction temperature used.

The objective of this research is to develop a catalyst for lower pressures of methanol synthesis from CO_2. The catalyst obtained, which had higher surface area and metal dispersion, answered the research objective. In order to know the effect of catalyst characteristic improvement to the methanol synthesis, the activity of the catalysts were tested. Activity test was conducted at these conditions: P= 30 bars, T=250–275°C, and reaction time = 300 min.

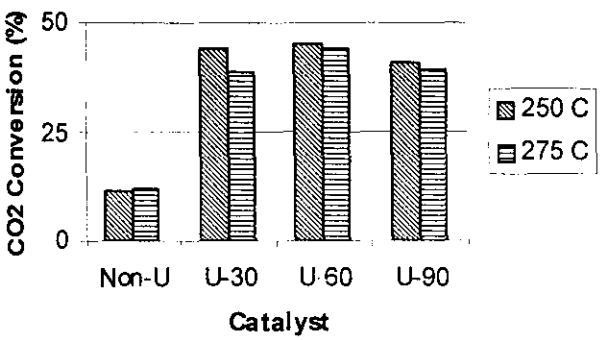

Figure 3. Effect of Irradiation Time on CO_2 Conversion

Figure 3 shows the result of the activity test. Non-U catalyst has very low activity compared to the irradiated catalysts. Irradiation to catalyst increases its activity more than 400% and degree of irradiation did not significantly affect their activity. As reported above, ultrasonic irradiation improved catalyst character, such as surface area and metal active dispersion. This improvement was the reason of the catalyst activity increase. As shown in Figure 4, the increase of reaction temperature affects the decrease of CO_2 conversion. This phenomenon is influenced by the thermodynamic properties of the reaction. Since the reaction is thermodynamically exothermic and the conversion obtained in Figure 4 was near equilibrium conversion at this reaction condition, increasing reaction temperature would decrease CO_2 conversion to follow its equilibrium conversion. From Figure 4 it can be concluded that the most active catalyst is U-60 since it shows higher activity that is caused by catalyst character with the highest surface area and metal active dispersion.

Catalyst selectivity

Figure 4 shows that the catalyst has very high selectivity to methanol in carbon-based calculation. This means that almost all the carbon atoms in CO_2 have been converted to methanol. The 30 minutes ultrasonic treatment increases methanol selectivity from about 95% (Non-U) to 100% (U-30). The irradiation time more than 30 minutes has no effect to the catalyst selectivity. This result shows that the ultrasonic irradiation is only has small effect to methanol selectivity. This confirmed the higher selectivity to methanol of Cu catalyst that has been reported by other workers (Mitsubishi Guko Jiho).

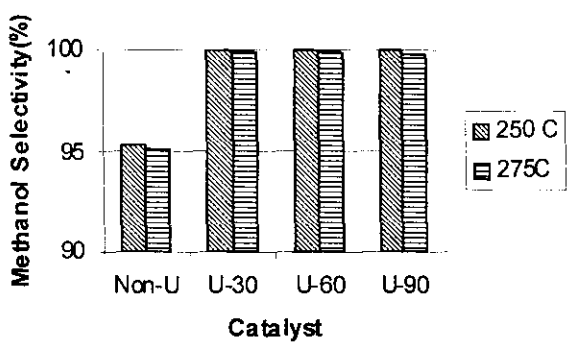

Figure 4. Effect of Reaction Temperature on Reaction Selectivity

CONCLUSIONS

1. Irradiation ultrasonic affected catalyst characteristics because intensive collision

occurs between molecules during catalyst preparation.

2. Ultrasonic irradiation increases catalyst surface area and metal active dispersion. Catalyst surface area increases up to 100% while metal active dispersion increased up to 1000%.

3. Higher metal dispersion was caused by smaller particle size. Irradiation ultrasonic for 60 min decreased particle size from 50 to 15 mm. 40 kHZ and 60 min is the optimum condition of ultrasonic irradiation.

4. Ultrasonic irradiation increased catalyst activity to convert CO_2 to methanol at 30 bars up to 400% but the irradiation did not show significantly effect to the catalyst selectivity to methanol.

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