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Effect of Titanium on Methanol Synthesis from CO_2 Hydrogenation over Cu/γ-Al_2O_3

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Abstract: Titanium-modified γ-alumina supported CuO catalyst has been prepared and used to methanol synthesis from CO_2 hydrogenation. The addition of Ti to the CuO/γ-Al_2O_3 catalyst made the copper in the catalyst exist in much smaller crystallites. The effect of the loading of Ti on the activity and selectivity to methanol from CO_2 hydrogenation was investigated. The activity was found to increase with the increasing of surface area of metallic copper, but it is not a linear relationship.

Keywords: CO_2 hydrogenation, CuO/γ-Al_2O_3-TiO_2, methanol synthesis.

Conversion of CO_2 to useful chemicals is widely investigated by many workers from the view point of finding technologies for suppressing the green house effect caused by CO_2 emission. The utilization of industrial Cu/ZnO/Al_2O_3 catalyst, which exhibited a high activity for methanol synthesis from syngas, was not successful[1] in CO_2 hydrogenation. Therefore, it is important to synthesize and develop new catalysts with a higher activity and better selectivity to methanol. Recently, great efforts have been put into preparing an ideal catalyst for the hydrogenation of CO_2[2-7]. Arakawa *et al*[8] have reported that the methanol synthesis from CO_2 hydrogenation over Cu/TiO_2 showed high turnover frequency because the rate of formate hydrogenation was enhanced by the synergetic effect between Cu and TiO_2. But the titania presents the disadvantage of a low surface area (Sg $\approx$ 50 m²/g) and poor thermal stability compared to their alumina counterparts (Sg $\approx$ 200 m²/g). To date, there have been no report on the characterization and activity on CO_2 hydrogenation of Cu-based catalysts supported on titanium-modified γ-alumina. In this paper, it is found that the adding of titania on Cu/γ-Al_2O_3 catalyst enhances remarkably the catalytic performance.

A non-aqueous solution of titanium isopropoxide in ethanol was added to dry γ-alumina (γ- Al_2O_3, 20-40 mesh) and kept under argon atmosphere for 24 h. The solids were washed with ethanol before drying, then dried at 393 K and calcined at air flow at 773 K for 5 h. The solids prepared were named Al-Ti(x), where x = 100×Ti/(Ti + Al). A series of copper catalysts containing 12 wt%Cu were prepared by impregnating the above supports using the appropriate amount of an aqueous solution of Cu(NO₃)₂. The impregnated samples were dried at 373 K and later calcined at 673 K for 4 h; hereafter the catalysts will be referred as Cu/Al-Ti(x).

Catalytic activity measurements were carried out by using high pressure micro reactor after introducing pretreatment gas (H_2) at 300℃ for 3 h, the reactant gas was passed through the catalyst bed (2 mL, 20-40 mesh) under a total pressure of 3.0 MPa and a space velocity of 3600 h^{-1}, at certain temperature.

The catalytic activity and selectivity results obtained in a microreactor (MRC8004) are shown in **Figure 1**. Carbon monoxide and methanol are the only carbon-containing products found under the reaction conditions (T = 180℃, P = 3.0 Mpa, GHSV = 3600 h^{-1}, H_2/CO_2 = 3/1). Comparing the Cu/Al-Ti(x) ternary catalysts with the Cu/γ-Al_2O_3 catalysts, it can be found that the former shows a higher conversion of CO_2 and higher yield of methanol. From **Figure 1**, it can be seen that although the CO_2 conversion of 12Cu/γ-Al_2O_3 is 13.6%, the 12 Cu/Al-Ti(10) is as high as 22.54%; the yield of Methanol on the 12Cu/Al-Ti(10) (13.48%) is four times more than that on 12Cu/γ-Al_2O_3 (2.98%). The yield of Methanol is in the order of 12Cu/Al-Ti(10) > 12Cu/Al-Ti(15) > 12Cu/Al-Ti(5) > 12Cu/γ-Al_2O_3.

The XRD results of the Cu catalysts supported on γ-Al_2O_3 and titania-modified alumina showed that for the Cu/Al-Ti(10) catalyst, the diffraction peaks of CuO were broadened remarkably. In contrast to the CuO/Al-Ti(10) catalyst, the CuO/γ-Al_2O_3 showed much narrower and sharper diffraction and two resolvable peaks at 2θ = 35° and 2θ = 38° respectively. **Table 1** reports the particles size and area of metallic copper of the reduced catalyst with different Ti content. It is found that the adding of titania decreases obviously the particle size of metallic copper, which may be related to the activity of CO_2 hydrogenation. It has been proposed that[9-12] the yield of methanol is directly proportional to the surface of metallic copper for Cu/ZnO/Al_2O_3 or supported copper catalysts in the synthesis of methanol from the hydrogenation of CO/CO_2. However, there are also conflicting reports[13-15] which suggest that the yield of methanol is not proportion to the surface area of metallic copper for the Cu/ZnO and Cu/ZnO/Al_2O_3 catalysts.

Table 1   Metallic copper size and area

Catalysts	Particles size (nm)		Metallic copper area m^2/g
	d^1	d^2	
12Cu/Al_2O_3	52.43		0.28
12Cu/Al-Ti(5)	22.95	9.31	1.60
12Cu/Al-Ti(10)	20.00	4.04	2.08
12Cu/Al-Ti(15)	18.96	3.05	2.81

In our experiment, the effect of the surface area of metallic copper on the activity of synthesis of methanol from CO_2 hydrogenation over Cu/Al-Ti(x) was studied and the results were shown in **Figure 2**. It can be seen that the catalytic activity increased with the increase of the surface area of metallic copper, but it was not a linear relationship. This indicates that the catalytic activity of the catalysts depends on both the metallic copper surface area and the powerful synergy between copper and titanium oxide, it is consistent with Arakawa *et al.*[8] have reported.

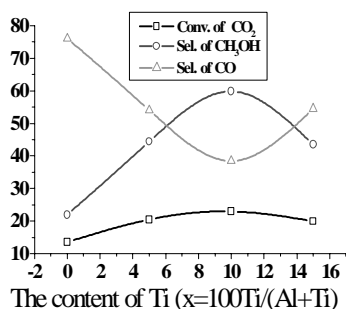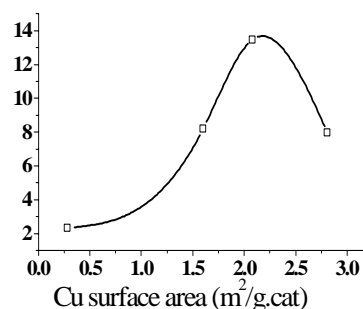**Figure 1** Effect of Ti content on the activity methanol synthesis (3.0 Mpa, 240℃ 3600 h^{-1}; CO_2/H$_2$=1/3)

Figure 2 The relationship between the yield of of methanol and Cu surface area(240℃ 3.0 Mpa, 3600 h^{-1}; CO_2/H$_2$=1/3)

The content of Ti (x=100Ti/(Al+Ti)

Cu surface area (m^2/g.cat)

The TPR profiles of the catalysts are displayed in **Figure 3**. Two reduction peaks can be observed in the TPR patterns of CuO/γ-Al$_2$O$_3$, According to Dow *et al.*[12], the low temperature peak (assigned as α) is due to the reduction of the high dispersed copper oxide species, The high temperature peak (assigned as β) has been ascribed to the reduction of bulk-like CuO phases. On the other hand, the CuO/Al-Ti(10) shows four peaks. The four peaks are designated by $\alpha_1, \alpha_2, \beta_1$ and β_2 in **Figure 3**. The positions of peaks shift to lower temperature in comparison with the CuO/γ-Al$_2$O$_3$ sample. It is well known that TiO$_2$ is partially reduction to TiO$_{2-x}$ under hydrogen at high temperature (above 773K)[13]. So the four TPR peaks on CuO/Al$_2$O$_3$-TiO$_2$ catalyst are contributed to CuO species. From the **Figure 3**, it can be seen that the reduction behavior of CuO/Al-Ti(x) catalyst is thus obviously different from that of CuO/γ-Al$_2$O$_3$ catalyst. The adding of Ti decreases obviously the area of the high temperature peak (β_1 and β_2) but enhances the area of the lower temperature peak (α_1 and α_2). Compared the XRD and TPR results, we believe that the lower temperature TPR peak (α_1 and α_2) is contributed to reduction of the dispersed copper oxide, while the high temperature TPR peak (β_1 and β_2) is the reduction of bulk CuO with different particle size which can be found in **Table 1**. Dow and huang[16] have reported that when copper oxide is supported on YSZ (Y$_2$O$_3$-stabilized ZrO$_2$), the interfacial oxygen ion of copper oxide can be removed at very low temperature to form third and forth TPR peaks, *i.e.* α_1 and α_2 peaks as well as β and γ peaks. Two TPR peaks with lower temperatures (namely α_1 and α_2) have been attributed to the hydrogen uptake of nested oxygen ions and temptable oxygen ions, respectively. We believe that the α_1 and α_2 peaks of our CuO/Al-Ti(10) catalyst correspond to the α_1 and α_2 peaks of the CuO/YSZ catalyst in the literature[16]. From **Figure 3**, it can be seen that there exists strong interaction between the support and metallic copper. These results above mentioned suggest that the adding of titanium affects greatly Cu/γ-Al$_2$O$_3$ catalyst in many ways such as dispersion, existence of copper species and support-metal interaction which led to a dramatic difference in catalytic performance between the Cu/γ-Al$_2$O$_3$ and Cu/Al$_2$O$_3$-TiO$_2$ catalyst.

Figure 3   TPR profiles of 12CuO/γ-Al₂O₃ and 12CuO/Al-Ti(10)
a) CuO/γ-Al₂O₃   b) CuO/Al-Ti(10)
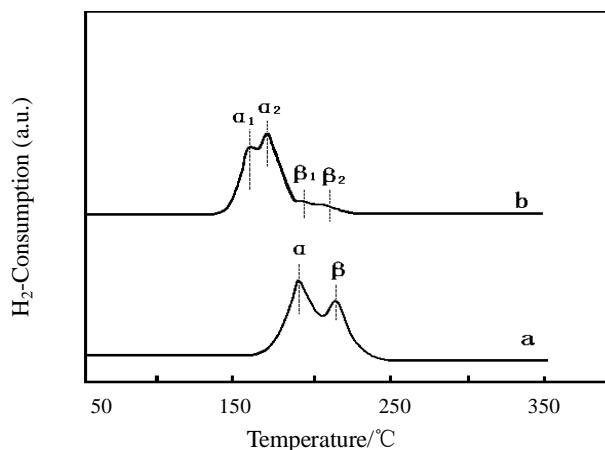
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