SHORT PAPER

Methanol synthesis from CO_2 hydrogenation over a novel titanium-modified γ-Al_2O_3 supported copper catalyst[†]

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A titanium-modified γ-Al_2O_3 supported CuO catalyst prepared by impregnation method shows high activity of methanol synthesis from CO_2 hydrogenation.

Conversion of CO_2 into useful chemicals is widely investigated by many workers from the viewpoint of finding technologies for suppressing the green house effect caused by CO_2 emission. The utilisation of an industrial $Cu/ZnO/Al_2O_3$ catalyst, which exhibited a high activity for methanol synthesis from CO/H_2, has not been successful[1] in CO_2 hydrogenation. Therefore, it is important to synthesise and develop new catalysts with a higher activity and better selectivity to methanol. Recently, great efforts have put into preparing an ideal catalyst for the hydrogenation of CO_2.[2-7] Arakawa *et al.*[8] have reported that methanol synthesis from CO_2 hydrogenation over Cu/TiO_2 shows high turnover frequency because the rate of hydrogenation of formate hydrogenation is enhanced by the synergetic effect between Cu and TiO_2. The titania support, however, presents the disadvantage of a low surface area ($Sg≈50m^2/g$) and poor thermal stability compared to their alumina counterparts ($Sg≈200m^2/g$). To date, there have no reports about CO_2 hydrogenation over Cu-based catalysts supported on titanium-modified γ-alumina. In this paper, it is found that the addition of titania on $Cu/γ-Al_2O_3$ catalyst enhances the catalytic performance.

Experimental

Preparation of catalysts: A solution of titanium isopropoxide in ethanol was added to dry γ-alumina (γ-Al_2O_3, 20-40 mesh) and kept under argon for 24h. The solids were washed with ethanol before drying, dried at 393K and calcined at air flow at 773K for 5h. The solids prepared were named Al–Ti(x), where $x = 100 × (Ti)/(n(Ti)+n(Al))$. A series of copper catalysts containing 12wt%Cu were prepared by impregnating the above supports using the appropriate amount of an

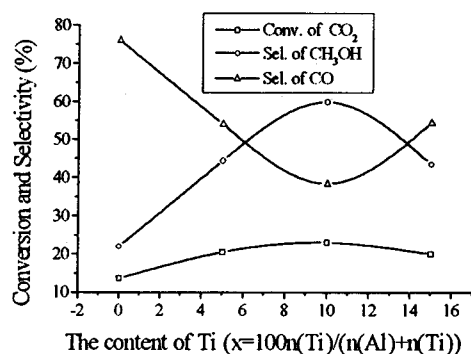**Fig. 1** Effect of Ti loading on conversion and selectivity of CO_2 hydrogenation. Reaction condition: P=3.0MPa; GHSV=3600h^{-1}; CO_2/H_2=1/3; T=513K
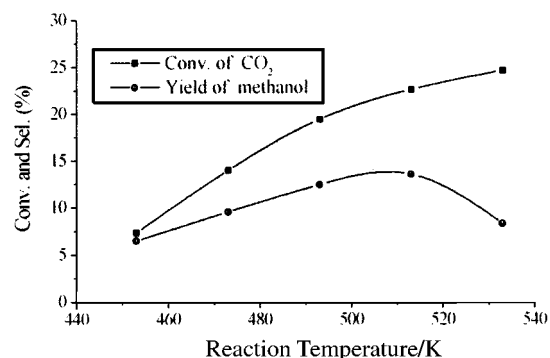

Fig. 2 The effect of reaction temperature on activity of CO_2 hydrogenation. Reaction condition: GHSV=3600h-1; CO_2/H_2 =1/3; P=3.0MPa. Catalyst: 12Cu/Al–Ti(10).

aqueous solution of $Cu(NO_3)_2$. The impregnated samples were dried at 373K and later calcined at 673K for 4h; hereafter the catalysts will be referred as Cu/Al–Ti(x).

Catalytic activity measurements: Catalytic activity measurements were carried out by using high pressure micro reactor after introducing pretreatment gas (H_2) at 300°C for 3h, the reactant gas was passed through the catalyst bed (2ml, 20–40mesh) under a total pressure of 3.0MPa and a space velocity of 3600h^{-1}, at a certain temperature. The tubing from the catalyst bed to the gas chromatograph was heated at 393K in order to avoid any condensation of the products. All experimental data were obtained under steady-state conditions that were usually maintained for several hours before changing the reaction conditions to obtain another set of data. The products were analysed by on-line gas chromatograph with a thermal detector, in which columns Porapak-Q was used to separate reaction products
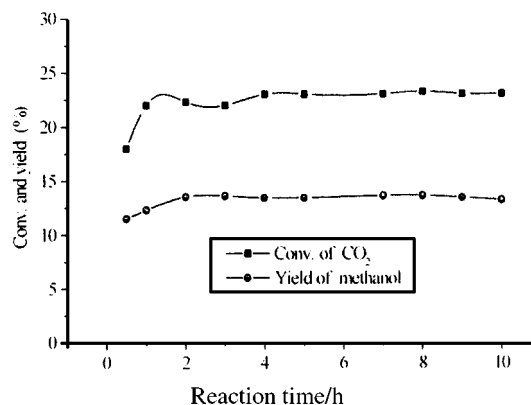

Fig. 3 Conversion of CO_2 and yield of methanol on stream of time over 12Cu/Al–Ti(10) catalyst. Reaction condition: P=3.0MPa; T=513K; GHSV=3600h^{-1}.
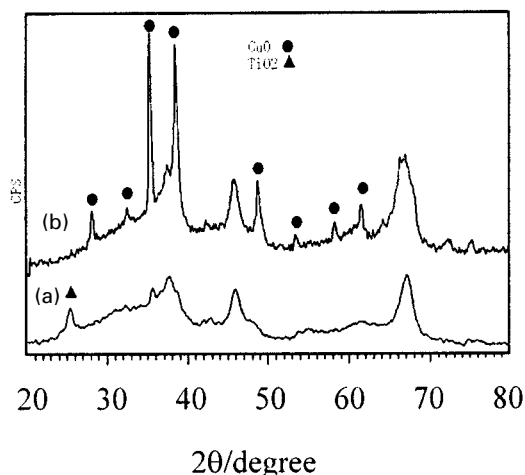

Fig. 4   XRD profiles of CuO/Al$_2$O$_3$ and CuO/Al–Ti(10) catalysts (a) 12CuO/Al–Ti(10); (b) 12CuO/Al$_2$O$_3$

Table 1   Metallic copper particle size for Cu/Al–Ti(x) catalysts

Catalysts	Metallic copper particle size (nm)	
12Cu/γ–Al$_2$O$_3$	52	
12Cu/Al–Ti(5)	231	92
12Cu/Al–Ti(10)	201	42
12Cu/Al–Ti(15)	191	32

* 1,2 refer to two kinds of particle size.

The XRD (Fig. 4.) results of the Cu catalysts supported on γ-Al$_2$O$_3$ and titania-modified γ-Al$_2$O$_3$ 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$_2$O$_3$ showed much narrower and sharper diffraction and two resolvable peaks at 2θ=35° and 2θ=38° respectively. Table 1 reports the particle size of metallic copper of the reduced catalyst with different Ti content. The mean crystallites size were determined using the Scherrer equation, d=κλ/βcosθ. This shows that the crystalline size of Cu decreases with the increasing of the content of TiO$_2$. Furthermore, it is interesting that there exist two kinds of metallic copper particles with different crystalline size on the reduced CuO/Al–Ti(x) catalysts. It is found that the adding of titania clearly decreases the particle size of metallic copper, which may be related to the activity of CO$_2$ hydrogenation.

Results and discussion

The catalytic activity and selectivity results obtained in a microreactor are shown in Fig.1. Carbon monoxide and methanol are the mainly carbon-containing products found under the reaction conditions (T=240°C, P=3.0MPa, GHSV=3600h^{-1}, H$_2$/CO$_2$=3/1). Comparing the Cu/Al–Ti(x) ternary catalysts with the Cu/γ-Al$_2$O$_3$ catalysts, it can be found that the former shows a higher conversion of CO$_2$ and higher yield of methanol. From Fig.1, it can be seen that although the CO$_2$ conversion of Cu/γ-Al$_2$O$_3$ is 13.6%, the Cu/Al–Ti(10) is as high as 22.54%; the yield of methanol on the 12Cu/Al–Ti(10) (13.48%) is four time more than that on 12Cu/γ-Al$_2$O$_3$ (2.98%).The yield of methanol is in the order of Cu/Al–Ti(10)>Cu/Al–Ti(15)>Cu/Al–Ti(5)> Cu/γ-Al$_2$O$_3$.

Figure 2 shows the effect of reaction temperature on the activity of CO$_2$ hydrogenation. According to this result, the conversion of CO$_2$ increases with increasing reaction temperature and the highest methanol yield is obtained at 513K.

Furthermore, we used the 12Cu/Al–Ti(10) catalyst to perform a long-term test at 513K. The change of carbon dioxide conversion and selectivity of methanol as a function of reaction time is displayed in Fig.3. It clearly shows that both the CO$_2$ conversion and selectivity of methanol are almost stable during the reaction for 10h, which indicates that no significant deactivation of the catalyst is occurring.

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