Low-temperature methanol synthesis (LTMS) in liquid phase on novel copper-based catalysts

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Novel Cu-Cr based catalysts with alumina promotion have been prepared and studied in low-temperature methanol synthesis (LTMS) in a slurry reactor. The new method of co-precipitation from the sol state gave better results than those of three other preparation methods. From the results of temperature programmed desorption and XRD, there were more active sites in the presence of alumina.

KEY WORDS: methanol synthesis; low temperature; LTMS; catalyst; Cu-Cr-Al; co-precipitation from sol state; slurry; TPD characterization.

1. Introduction

In the chemical industries of coal and natural gas, methanol is a very useful and important product and raw material [1,2]; the world's annual production of methanol is 30×10^6 tons/year. In the ICI industrial process, the pressure was 40–200 atm and temperature 220–280 °C. In recent years, a new process has been reported with significant improvements in the low-temperature methanol synthesis in the slurry phase (LTMS) [3–14]. There were several advantages: higher conversion at single-pass (more than 90%, while conversion in the ICI process was only 20%), higher selectivity, and lower reaction temperature (100–150 °C against 230–280 °C), lower operation cost, etc. Typical results [4–12] have been presented on the nickel catalysts, on the copper catalysts, and also by Wu *et al.* using the Cu-Cr based catalysts. The reaction conditions are: $T = 90$–$150\,°\mathrm{C}$, $P = 20$–60 atm, the addition of CH_3ONa is imperative and promoting. The syngas conversion was more than 90%, the $CH_3OH + MF$ selectivity was higher than 95%. The catalysts developed by Wu *et al.* were operated at 110 °C and 50 atm; the yield was $97.8\ \mathrm{g\,l^{-1}\,h^{-1}}$.

The purposes of the present research consist of the preparation and characterization of novel supported Cu-Cr based catalysts in order to improve the catalytic performances in low-temperature methanol synthesis. The alumina presence promoted significantly the activity and selectivity.

2. Experimental

2.1. Preparation of catalysts

Three methods have been used for catalyst preparation: co-precipitation, impregnation, and co-precipitation from the sol state [12,15]. For the impregnation method, using the alumina powder, a solution of nitrate of copper ($C = 0.501$ mole/l) and nitrate of chromium ($C = 0.496$ mole/l) was impregnated; then the precursor was calcined by thermal decomposition. The copper content was 36% in the catalyst precursor. For the co-precipitation, a mixed solution of nitrate of copper, nitrate of chromium and nitrate of aluminium was reacted with the precipitation agent $NH_3{\cdot}H_2O$; then it was filtered, dried and calcined. There were the same components of equal molar content in the catalyst. For the co-precipitation from the sol state [12], two initial liquids were prepared (A, B); using an aqueous solution of $Al(NO_3)_3{\cdot}9H_2O$ (AR), the $Al(OH)_3$ sol (A) was prepared by adding the ammonia ($NH_3{\cdot}H_2O$). A solution of $Cu(NO_3)_2$ was mixed with the concentrated ammonia water solution, then a $Cu(NH_3)_4^{2+}$ complex solution of dark-blue colour was obtained; then a solution of $(NH_4)_2Cr_2O_7$ was added with good agitation, and the liquid (B) was prepared. The two liquids (A, B) were mixed together and kept at 60 °C for 1 h; the pH value was adjusted to 6.0 with the HNO_3 solution; the precipitation was obtained under continuous agitation. Then it was aged, filtered, washed, dried, ground and calcined to obtain the catalyst samples.

2.2. Test of catalytic reaction of LTMS in liquid phase

The activity of the catalyst was evaluated in a 500 ml stainless steel autoclave reactor in slurry phase with a

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magnetic stirrer [12–14]. The reaction proceeded at 115 °C and 5.0–6.0 MPa. The solvent xylene (170 ml) was dehydrated with a fresh 5 Å molecular sieve before reaction, and a catalyst sample of 6.0 g was used; 30 ml CH_3ONa solution ($C = 4.995$ mole/l) in methanol was added as the co-catalyst (the molar concentration of CH_3ONa in liquid reactant was 0.749 mole/l), the feed gas composition was $H_2:CO = 2.3:1$; the volume of the total reactant-mixture system was 200 ml. At 115 °C, the system was introduced to a pressure of 6.0 MPa and the initial time was recorded; when the pressure of the system decreased to 5.0 MPa, the time was also noted, and the feed gas was re-introduced quickly to a pressure of 6.0 MPa. The above processes were repeated many times, and the reaction was continued for several hours. The products in liquid phase of this batch reactor were analyzed by gas chromatograph (GC103) with a TCD detector. The catalytic activity was represented by the space time yield (STY) of methanol.

2.3. Catalyst characterization (TPR, TPD) [13–16]

The apparatus for TPR experiments was homemade. The catalyst sample (50 mg) was placed in a quartz tube, pretreated *in situ* under pure Ar flow, then saturated with $H_2 + N_2$ (4.3%) mixture. The temperature was raised to 600 °C at a rate of 12 °C/min, while the TPR diagram was recorded on line by a thermal conductivity detector.

For the temperature programmed desorption (TPD) test, a 200 mg sample was charged; pre-reduced using $H_2 + N_2$ mixture (4.3%); then it was flushed by pure Ar gas and cooled to room temperature. The probe gas (H_2 or CO) was introduced for adsorption for 45 min; then flushed by Ar gas (more than 30 min) until the baseline was stabilized; the temperature increased to 600 °C at 12 °C/min, and the signal was measured.

3. Results and discussion

3.1. Effect of preparation method and parameters

The catalyst activity and structure could be very different while using different preparation methods and processes. The sol-gel method and plasma techniques were very useful for preparing effective catalytic materials [17,18]. In our previously reported work [18], the plasma technique was used for the preparation of the highly-active Ni/Al_2O_3 catalysts for the direct oxidation of methanol to form synthesis gas. The precursors were prepared by the conventional impregnation method. The plasma is a fourth state of material, other than in its solid, liquid, or gas state. The precursor was charged and treated in a plasma field activated from the discharge under high voltage for 30 min; the structure of this sample is very different from that treated conventionally at the higher temperature of 750 °C; high catalytic performance was obtained. In this work, three preparation techniques have been used, and the novel method of co-precipitation from the sol state is presented here. The performances are shown in figure 1; the activity and methanol selectivity of the catalyst from the co-precipitation method were slightly higher than those of the catalyst from the impregnation method; results of the catalyst issued from the novel method (co-precipitation from the sol state) are significantly better. The reason could be the different surface dispersion of active centers and the difference of their particle sizes.

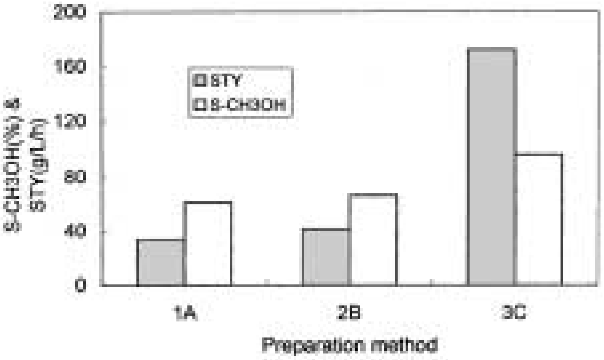

Figure 1. Effect of the preparation method on catalytic performances: $T = 115\,°C$, $P = 5.5$ MPa, $H_2:CO = 2.3:1$, Cat: Cu : Cr : Al = 1 : 1 : 0.5 (in mole). 1A: impregnation; 2B: co-precipitation; 3C: co-precipitation from the sol state.

During the preparation procedure, the temperature and the pH value of precipitation, the ageing, and the calcinations were also important for preparing a good catalyst. In figure 2, the influence of pH value on activity is shown. When pH value was changed from 5.4 to 7.0, there was a significant evolution of activity; the pH value should be controlled at 6.0 for the best activity. From the color of the catalyst precursor at different pH value, some general influence could be predicted; when the catalyst precursor was dark red, the activity was quite good.

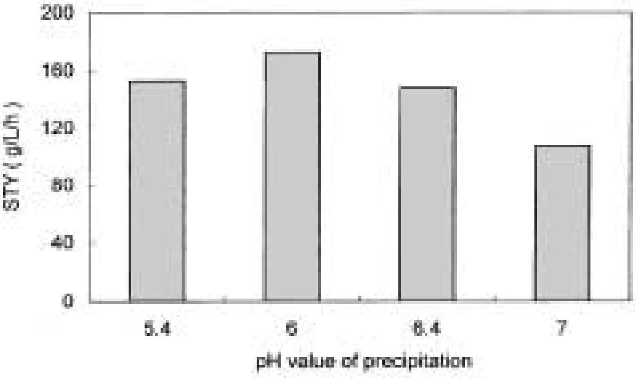

Figure 2. Influence of pH value of precipitation on STY of methanol. Conditions: as in figure 1 legend.

3.2. *Effect of alumina promotion*

In the same reaction conditions, the activity of Cu-Cr catalyst (Cu : Cr = 1 : 1, in mole) was compared to that of Cu-Cr-Al catalyst (Cu : Cr : Al = 1 : 1 : 0.5, in mole). It was observed that the activity of Cu-Cr-Al was significantly better than that of Cu-Cr catalyst. The STY of the Cu-Cr-Al catalyst increased to 172.5 $g\,l^{-1}\,h^{-1}$ and the methanol selectivity was 96%, while the STY of the Cu-Cr catalyst was just 117.5 $g\,l^{-1}\,h^{-1}$ and the methanol selectivity was only 79.5%. This indicated that the addition of alumina support could enhance the effective dispersion of active components in the catalyst, and the number of active sites on the surface increased; the hydrolysis activity of the catalyst was thus improved and resulted in the augmentation of catalytic activity and methanol selectivity. Compared with commercial methanol catalysts (*e.g.* Cu-Zn-Al), the turnover rates of the new catalysts were higher.

The evolution of activity versus reaction cycle-times is illustrated in figure 3. In the initial stage, the primary activity of the Cu-Cr catalyst was very close to that of Cu-Cr-Al. With the time going on or while the reaction cycle-times increased, the activity of the Cu-Cr catalyst decreased quite rapidly; however, the activity of the Cu-Cr-Al catalyst decreased quite smoothly and slowly. This indicated that the addition of alumina stabilized the catalyst active components [19] and improved the catalyst stability. From refs. [4,5], initial activities were usually reported; the evolution with time on stream was hardly discussed for the new process of low-temperature methanol synthesis (LTMS). In our previous work, we studied the deactivation of the catalyst system and the regeneration; the change of CH_3ONa and the coverage of copper catalyst were the principal factors. From the modification of catalyst design and the change of reactor design, the stability could be enhanced. Fast scanning of the activities of new catalysts could be obtained from the results in a batch reactor; however, much better stability was obtained in the continuously-flowing slurry reactor.

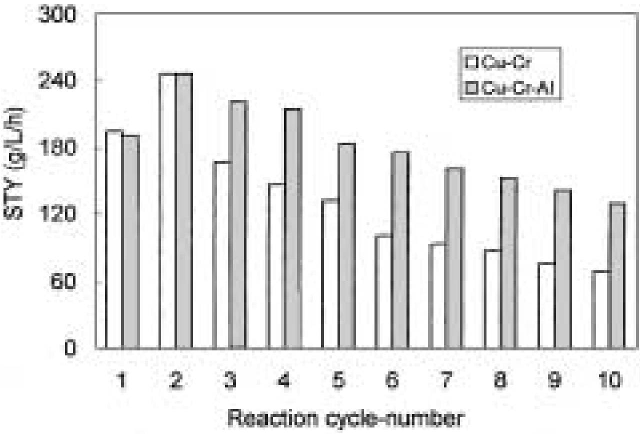

Figure 3. Effect of reaction cycle-times on catalytic performance. Conditions: as in figure 1 legend.

Table 1
Results of temperature programmed desorption (TPD-H_2)

Catalyst sample	Peak number	Peak temperature (°C)	Height (cm)	Width (cm) at mid-height	Peak area (a.u.)
Cu : Cr = 1 : 1	1	76	1.9	1.9	3.6
	2	170	1.2	1.6	1.9
Cu : Cr : Al = 1 : 1 : 0.5	1	105	5.1	3.3	16.8

3.3. *Temperature programmed characterization (TPR, TPD)*

For understanding the beneficial effect of alumina, several techniques such as XRD, TPR, and TPD-H_2 were used for the catalyst characterization. From XRD diagrams, there were both CuO and $CuCrO_2$ peaks for the Cu-Cr catalyst; however there were only $CuCrO_2$ for the Cu-Cr-Al catalyst, no longer the CuO peak. These data suggest that the alumina addition promoted the copper dispersion and stabilized the $CuCrO_2$ active phase.

The results of TPR were obtained and discussed. With the un-promoted Cu-Cr catalyst, there was only one reduction peak at 285 °C. For the Cu-Cr-Al catalyst with promotion, there was also one peak, shifted to a lower temperature at 240 °C; the peak area was only 46.2 a.u., compared with 108.8 a.u. for that of the Cu-Cr catalyst. Besides a lesser amount of copper in the catalyst, an important reason could be the interaction and better dispersion of the copper component in the Cu-Cr-Al catalyst (in contrast, there was a large amount of CuO crystal phase in the Cu-Cr catalyst).

The results of TPD-H_2 are reported in table 1. There were two peaks for the Cu-Cr catalyst at 76 °C and 170 °C; there was only one bigger peak for the Cu-Cr-Al catalyst at 105 °C; the area of the latter (Cu-Cr-Al) was three times the sum of the two peaks of the former (Cu-Cr); the spillover effect of H_2 [20–22] could be an explanation.

4. Conclusions

For the Cu-Cr catalyst, the alumina promotion was observed, both in the initial activity and the selectivity. The co-precipitation from the sol state was an efficient method for preparing highly active Cu-Cr-Al novel catalysts for LTMS. A good yield of 172 $g\,l^{-1}\,h^{-1}$ CH_3OH has been obtained at 115 °C, 5.5 MPa.

TPR, XRD, and TPD-H_2 were used for catalyst characterization, and promoting effects were illustrated. In the presence of alumina, the copper component was better dispersed; there were more active sites on the surface.

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