Catalysis Letters 7 (1990) 213–218

ON THE PROBLEM OF THE ACTIVITY IN METHANOL SYNTHESIS OF SUPPORTED, UNPROMOTED COPPER CATALYSTS

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Methanol synthesis, supported copper catalyst, unpromoted copper catalyst, promoted copper catalyst, alkali promoter, contaminated promoter, industrial catalyst production.

It is shown that a pure Cu catalyst is inactive in methanol synthesis. Activity can be invoked by small amounts of (alkali) promoters. Contaminations present in the current commercial supports are leached out during impregnation and promote Cu sufficiently to produce methanol. Contaminations-promoters slow down the reduction of Cu precursors.

1. Introduction

The synthesis of methanol from syngas is one of the technically very well developed industrial processes and there is also a lot of information available on its chemistry. However, on one particular point vivid discussions continue–it is the problem of active sites.

For a long time it has been tacitly accepted that the Cu-metal (Cu^0) is the locus of catalytic sites. The producers of the industrial catalysts tried to maximize the surface of Cu^0. However, some time ago a paper appeared [1], which collected important indications that for a reaction in the CO_2-free mixtures the active site is Cu^+ dissolved in ZnO. Others rejected this idea [2] referring to the linear relationship between the total activity and the Cu^0 surface area. However, the same authors [2] also mention that, when CO_2 is added to the reactants mixture, then at a given content of CO_2, a constant fraction of the Cu^0 surface is covered by products of oxidation (Cu^{2+}, Cu^+ in oxides or carbonates). Thus, the above mentioned linear relationship, which was observed with CO_2-containing mixtures, could equally represent a proportionality of the total activity to the content of ionic Cu. Then the Cu-ion(s) could be centre(s) of the methanol synthesis as well.

To resolve the problem, two pieces of evidence are necessary: (i) an independent (i.e. other than the mentioned linear relationship to the Cu^0–Cu^+ content) evidence that the activity is related to the Cu^{n+} content, and (ii) an evidence that

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pure Cu^0 is also inactive when Cu is on a carrier. The first evidence has been recently supplied by King et al. [3]. Out letter concerns point (ii).

Recently, experiments performed in our laboratory revealed the importance of minute contaminations in support for the activity and the selectivity of rhodium on silica catalysts [4]. This finding raised our suspicion against the claims that unpromoted Cu^0-catalysts (e.g. Cu/SiO_2) have an activity, which falls on the linear relationship "activity-Cu^0 surface area" mentioned above. If it were indeed so, that would represent a strong support of the idea that Cu^0 is the locus of catalytic activity, as it is widely claimed. For this reason, this short study has been performed.

2. Experimental

The catalysts were prepared here in the laboratory by conventional wet impregnation, using a solution of $Cu(NO_3)_2.3H_2O$. Promoted catalysts were prepared by co-impregnation of $Cu(NO_3)_2.3H_2O$ with $Zn(NO_3)_2$ or NH_4VO_3, or by post-impregnation of a prereduced copper catalyst with Na_2CO_3 or Cs_2CO_3. For reasons mentioned earlier [4] quartz-glassware and highly purified water (distilled, filtered) were used during the preparation of the samples.

Various carriers were used: Aerosil 200 (Degussa, 200 m^2/g) and Philips-silica (Philips NV, Eindhoven, 200 m^2/g, precursor of glasfibers, contaminations are in the low ppb range), as chemically "clean" supports. Kieselgel 60 reinst (Merck, 420 m^2/g), a commercial silica, which is known (see ref. [4]) to contain promoting compounds (Fe, Na) in several hundreds ppm. To remove these compounds, the Kieselgel 60 was washed with 12N HCl or 14N HNO_3 at 373 K. The nitric acid filtrate, containing the washed out impurities, was used for the preparation of one of the Cu/Aerosil 200 catalysts.

Experiments were performed in the same way as in earlier papers [4–6]. After impregnation and drying in air at 393 K, (about) 1.0 g catalyst was reduced in situ in H_2 (20 ml/min) at 523 K for 2 hours, heating rate 1 K/min. In one experiments with Cu/Aerosil 200, the final reduction temperature was 623 K. In another experiment with this catalyst, the reduction was preceded by calcination in technical air (20 ml/min) at 623 K for 1 hour, at a heating rate of 1 K/min. After reduction, the reaction was initiated under the following conditions: total flow of 30 ml/min, $H_2CO = 2$, $P = 0.1$ MPa. In some experiments CO_2, at the level indicated below, was added to CO/H_2, which led to a small increase of the total gas-flow. The method utilized for data gathering and evaluation was exactly the same as in the previous papers [5,6]. The detection limit for our apparatus is estimated to be $\leqslant 1$ nmol CH_3OH/min g.cat. The values in the tables refer to steady state conditions reached after at least 15 hours of the catalyst on stream.

Immediately after the reaction, the mean copper metal particle size was derived from XRD line broadening, using the simple Scherrer equation and estimated for all catalysts to be between 12 and 18 nm. The differences in the particle diameters in this region are thought to be unimportant.

For the temperature-programmed reduction experiments an all stainless steel apparatus with a quartz reactor was used. About 100 mg catalyst was loaded in the reactor. The TPR analysis started from 303 to 723 K at a heating rate of 5 K/min. The reducing gas mixture was 5% H_2/Ar and the flow rate 20 ml/min. The amount of hydrogen consumed and water produced were measured with a quadrupole mass spectrometer (Balzers). The temperature control and the data evaluation were performed with a Commodore PC-10.

For several catalysts, the copper metal surface area was determined by N_2O titration at 353 K, using the columetric-method. The catalysts were in situ treated with a 5% H_2/Ar mixture at 523 K (heating rate 1 K/min).

3. Results and discussion

The results in table 1 show that copper on chemically pure supports (Aerosil 200, Philips-silica) has at 493 K NO measurable activity with CO/H_2 mixtures. Occasionally increasing the reduction temperature to 623 K or calcining the catalyst in air at 623 K before reduction did not influence this behaviour. For comparison, a reference catalyst, prepared as 5% Cu/ZnO by the precipitation method [1], shows under the same test conditions a rate of 0.3×10^3 nmol/min g.cat ($S_{Cu} = 8.31$ m^2/g.cat). One can also notice from the table that the catalyst made with commercial Kieselgel 60 does show some activity, although the copper

Table 1
Copper supported on different silicas [a]

Silica	$Z(CH_3OH)$ [c] (nmol/min g.cat)	S(Cu) [d] (M^2/g.cat)
1. Aerosil 200	0	
2. Aerosil 200 [b]	0	
3. Aerosil 200	0	
4. Aerosil 200 + extract from K-60/14N HNO_3	9	
5. Philips-silica	0	1.99
6. Kieselgel 60	14	0.79
7. Kieselgel 60 12N HCl washed	5	
8. Kieselgel 60 14N HNO_3 washed	0	

[a] metal loading: 5 wt% Cu, except entries 3 and 7: 10 wt% Cu.
[b] calcined in air at 623 K before reduction.
[c] reaction conditions: $P = 0.1$ MPa, $T = 493$ K, $H_2/CO = 2$.
[d] total copper surface area after reduction measured by N_2O titration.

Table 2
Promoted copper/Aerosil 200 catalysts [a]

Promoter	Prom/Cu [b]	M CH_3OH [c] (Nmol/min g.cat)
1. ZnO	0.5	20
2. V_xO_y	0.5	27
3. Cs_2CO_3	0.5	4.5
4. Cs_2CO_3	0.1	18
5. Na_2CO_3	0.1	11
6. Na_2CO_3	0.02	3

[a] metal loading: 10 wt% Cu.
[b] atomic ratio of a cationic promoter to copper.
[c] reaction conditions: $P = 0.1$ MPa, $T = 493$ K, $H_2/CO = 2$, no CO_2 added.

surface area of this catalyst is about 2.5-times smaller than that of the Philips-silica supported catalyst (0.79 and 1.99 m^2/g.cat, respectively). Furthermore, the activity of the Kieselgel 60 supported catalysts is suppressed when the carrier prior to impregnation has been pretreated by acidic leaching: (compare line 6 with lines 7 and 8 of table 1). Using the acidic filtrate, obtained after washing the Kieselgel 60 for the impregnation of the copper nitrate. The precursor onto Aerosil 200 leads to a catalyst with a small but well measurable activity (9 nmol/min g.cat) in methanol formation. The behaviour of the different silicas as supports of copper in methanol synthesis is very similar to that observed with rhodium (in that case regarding the formation of ethanol and acetaldehyde [4]).

When potentially promoting compounds are added to the Cu/Aerosil 200 (10 wt% Cu) catalyst, the activity can be enhanced to the values shown in table 2. Adding CO_2 to the syngas mixture further increases the activity. These effects are well known in the literature [2]. For example, with Cu promoted by ZnO, the rate of 20 nmol/min g.cat is enhanced to 700 nmol/min g.cat, when the mixture CO/H_2 (1/2) is replaced by the mixture $CO_2/CO/H_2$ (3/5/10). In contrast, the unpromoted Cu/Aerosil 200 catalyst stays inactive even when CO_2 is added in varying amounts to the feed.

It is also apparent from table 2 that the addition of a very small amount of sodium promoter is sufficient to activate copper on Aerosil 200 (an amount which is about equal to that present in Kieselgel 60). This result could explain why some authors report an activity for unsupported or silica-supported copper (see e.g. ref. [2]), since they admit the presence of Na in their silica.

The conclusions from the work reported here are straightforward: unpromoted copper catalysts prepared by classical impregnation from small volumes of liquids and supported on chemically pure silicas are inactive in the methanol synthesis from CO/H_2 and $CO_2/CO/H_2$ mixtures. As our results clearly show, the activity can be induced by promoters. Furthermore, it is known of some of the promoters (e.g. ZnO, ref. [7]), that they retard the reduction of Cu-ions. With our

TPR-experiments is has been observed that addition of for example Cs_2CO_3 to a calcined Cu/Aerosil 200 catalyst ($Cs/Cu = 0.1$) leads to a shift of the peak maximum of hydrogen consumption from 453 K to 513 K. This is an additional indication that promoters stabilize Cu^{n+} centres.

This short letter does not address experimentally the problem of the mechanism of promotion. However, on the basis of our earlier papers [8–10] we conclude that the promoters primarily stabilize Cu^+ on the surface of Cu^0-metal, creating in this way active centres, which are supplied by H_{ads} from the Cu-metal surface. An alternative is that the added cations activate CO_{ads} or other surface intermediate for hydrogenation. Future studies should disclose which of these alternatives operate or whether they operate simultaneously.

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