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Modified $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from CO_2/H_2 and CO/H_2

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The effect of various modifiers on the performance of a commercial $Cu/ZnO/Al_2O_3$ catalyst in methanol synthesis from CO_2/H_2 and CO/H_2 at 523 K and 30 bar has been studied. Several modifiers improved significantly the rate of methanol formation from CO_2/H_2, while all modified catalysts showed decreased rates for the synthesis from CO/H_2 in comparison with the unmodified $Cu/ZnO/Al_2O_3$ catalyst. The synthesis rates from both CO_2/H_2 and CO/H_2 correlated with the oxygen coverage of copper surface measured after the reaction by N_2O titration.

Keywords: methanol synthesis; modifier effects; copper catalysts; oxygen coverage

1. Introduction

Conversion of CO_2 to methanol by catalytic hydrogenation has been recognized as a promising route to mitigate the global warming caused by the greenhouse gas [1]. The process is closely related to established methanol synthesis technology from CO/H_2 because current industrial feeds contain ca. 5 vol% of CO_2 in addition to CO/H_2 [2]. Catalysts composed of $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ are highly effective for the feed, yet may not necessarily be as effective for CO_2-rich feeds. Indeed, modified catalysts have been reported which are better than the current catalysts for CO_2/H_2 reactions although the majority of the new catalysts also contain copper as the main component together with various modifiers and supports [3–9].

Most of the previous studies on the effect of catalyst compositions involved the total catalyst preparation in which all catalyst components are processed in one

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step. Modifiers introduced into the preparation step usually affect the properties of prepared catalysts, particularly the state of copper. In an attempt to separate the modifier effects on reactivity from those on preparation, we employed a commercial $Cu/ZnO/Al_2O_3$ catalyst and modified it by adding a small amount of modifiers by incipient wetness impregnation. Thus the state of each component of $Cu/ZnO/Al_2O_3$ in the modified catalyst is not expected to be significantly changed from the one in the original catalyst.

2. Experimental

A commercial ICI catalyst $Cu/ZnO/Al_2O_3$ (39.8/23.5/6.7 wt%) was crushed and sieved to obtain 100/140 mesh powders. The catalyst was impregnated with an aqueous solution of the nitrate salt of each modifier in an amount that would give 2 wt% as metal. After drying at 390 K for 10 h, it was calcined at 623 K for 12 h in room air. Calcined catalyst was reduced in a $20\%H_2$–He flow (34 μmol s^{-1}) at atmospheric pressure and 523 K for 4 h.

Specific surface area was determined by the N_2 BET method on a Micromeritics constant-volume adsorption system (Accusorb 2100E). Exposed copper surface area was measured by N_2O titration at 333 K following the procedure described by Chinchen et al. [10].

The detailed procedure for the methanol synthesis reaction has been described elsewhere [11]. The reaction was carried out at 523 K, 3.0 MPa, and gas hourly space velocity (GHSV = feed gas volume at STP/catalyst volume h) of H_2/CO_x ($x = 1$ or 2) gas mixture of 54000. Reaction products were analyzed by an on-line gas chromatograph (Hewlett-Packard 5890) equipped with a 2.5 m long Porapak T column and a thermal conductivity detector. After the synthesis reaction, the reactor was depressurized and flushed with He near ambient temperature. The exposed copper surface after 4 h of the synthesis reaction (Cu_{rxn}) was determined by the N_2O titration assuming the copper atom density of 1.46×10^{19} m^{-2} [10]. The used catalyst was reduced (post-reduction) under the same condition as for the initial reduction in order to clean the copper surface, and then the N_2O titration was performed again to obtain the total copper surface area (Cu_{tot}) after the reaction. The oxygen coverage of the catalyst (θ_O) was defined as $\theta_O = (Cu_{tot} - Cu_{rxn})/2Cu_{tot}$. The definition reflected the assumption that an oxygen atom would titrate two surface copper sites [10].

3. Results and discussion

Table 1 lists characteristics of modified and unmodified $Cu/ZnO/Al_2O_3$ catalysts after reduction. Modification with 2 wt% modifiers exerts a minor effect on the total surface area measured by the BET method. A significant decrease in total

Table 1
Characteristics of modified Cu/ZnO/Al_2O_3 catalysts

Modifier[a]	BET area (m^2 g^{-1})	Initial Cu surface area (m^2Cu g^{-1})
none	64.3	19.3
Ag	61.5	19.2
Ag (10 wt%)	51.3	16.9
Pt	61.0	16.2
Rh	–	15.3
Ru	–	5.1
Co	–	18.1
Mn	71.5	18.8
Mo	70.5	18.3
Ti	69.2	18.3
Zr	66.4	20.0

[a] 2 wt% unless otherwise specified.

surface area was observed when the Ag loading was increased to 10 wt%. The initial copper surface area was a little more affected, particularly for the three noble metals Pt, Rh, and Ru.

Results of methanol synthesis from CO_2/H_2 are summarized in table 2. It also shows the copper surface area (Cu_{tot}) after the reaction and post-reduction, and oxygen coverage θ_O. In all cases, the copper area decreased during the reaction and the extent of the decrease was greater for modified catalysts. All the modified catalysts had lower copper areas than the unmodified catalyst. This is important to

Table 2
Effect of modifiers on methanol synthesis from CO_2/H_2 [a]

Modifier[b]	Cu area[c] (m^2 g^{-1}) / % of initial area	θ_O (%)	CO_2 conv. (%)	Selectivity (%)			H_2O content (%)
				CH_3OH	CO	CH_4	
none	17.9 / 93	11.8	7.0	65.2	33.8	1.0	9.2
Ag	14.6 / 76	19.0	7.0	53.0	46.3	0.6	10.6
Ag (10%)	13.7 / 81	16.9	8.1	50.9	47.4	1.6	12.5
Pt	12.1 / 75	22.7	4.7	44.7	52.6	2.7	8.0
Rh	12.4 / 81	23.6	10.6	59.6	40.1	0.3	7.2
Ru	4.7 / 92	18.8	7.4	64.8	35.2	0	6.3
Co	15.2 / 84	23.2	3.7	56.3	35.2	8.5	7.3
Mn	15.2 / 81	29.2	11.0	40.3	59.1	0.6	11.7
Mo	12.5 / 68	24.5	9.0	46.6	53.0	0.4	10.8
Ti	11.3 / 62	24.1	11.7	46.1	53.2	0.7	11.3
Zr	15.8 / 79	21.7	10.1	52.4	46.8	0.9	10.8

[a] $T = 523$ K, $P = 3.0$ MPa, $H_2/CO_2 = 4.0$, GHSV $= 54000$ h^{-1}.
[b] 2 wt% unless otherwise specified.
[c] Copper surface area after synthesis reaction.

note because any positive modifier effects in reactivity would not be due to increase in copper surface area. Significant variations of oxygen coverage were observed. In catalytic reactions, most modifiers increased CO_2 conversions but reduced CH_3OH selectivity. The product mixture contained ca. 10 vol% of moisture. The results are pictorially represented in fig. 1. In addition to CO_2 conversion, methanol yield (CO_2 conversion × CH_3OH selectivity) and methanol productivity (mol of CH_3OH produced per kg of catalyst per h) are also shown. Improvement in catalytic performance for methanol synthesis from CO_2/H_2 was observed when $Cu/ZnO/Al_2O_3$ was modified by Rh, Ru, Ti, and Zr.

Table 3 shows the results of methanol synthesis from CO/H_2 over the same series of modified and unmodified catalysts. There were a number of differences between methanol synthesis from CO_2/H_2 and CO/H_2. First, copper surface area of most catalysts was not decreased in CO/H_2. Instead, some catalysts showed increase in copper area after the reaction, probably due to further reduction during the reaction. Second, very small or near-zero oxygen coverages were measured. Third, the reactivity in CO/H_2 was characterized in comparison with CO_2/H_2 reactions by decreased CO conversions, increased selectivity to hydrocarbons particularly for modified catalysts, and very small water content in the reaction products. All these represent a more reducing atmosphere of CO/H_2 reaction than of CO_2/H_2 reaction. The results are presented pictorially in fig. 2. In no case, modifiers played a positive role in methanol synthesis from CO/H_2. Only Rh increased the CO conversion, yet not enough to compensate for the decreased CH_3OH selectivity.

The $Cu/ZnO/Al_2O_3$ catalyst employed in the present study is one of those industrial catalysts proven to be highly efficient. It has been optimized over a long period of time for methanol synthesis from CO/H_2 feed containing a small amount of CO_2. When the major feed shifts to CO_2, it is clear that the $Cu/ZnO/Al_2O_3$ catalyst is no longer the best one. The catalytic performance could be improved by adding

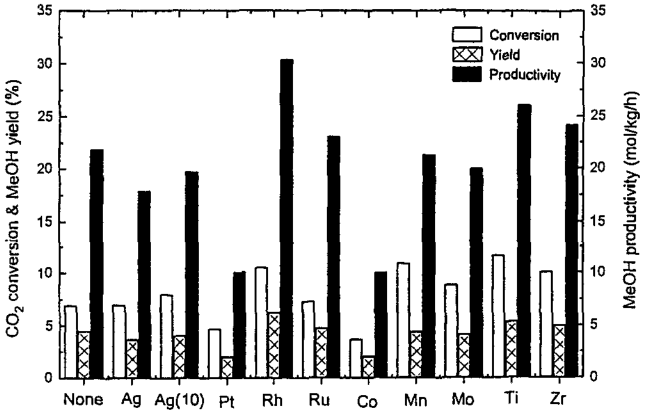

Fig. 1. Catalytic performance of modified $Cu/ZnO/Al_2O_3$ for methanol synthesis from CO_2/H_2. Reaction conditions: $T = 523$ K, $P = 3.0$ MPa, $H_2/CO_2 = 4$, GHSV = 54000 h^{-1}.

Table 3
Effect of modifiers on methanol synthesis from CO_2/H_2 [a]

Modifier [b]	Cu area [c] ($m^2\ g^{-1}$) / % of initial area	θ_O (%)	CO_2 conv. (%)	Selectivity (%) CH$_3$OH	Selectivity (%) CO_2	Selectivity (%) CH_4	H_2O content (%)
none	19.3 / 100	0	2.0	87.5	9.5	3.0	0.4
Ag	21.7 / 113	0.4	0.78	54.6	9.0	32.5	1.8
Pt	–	–	0.88	49.2	25.9	24.9	3.3
Rh	15.3 / 100	3.8	2.4	56.3	29.1	14.6	0.7
Ru	2.7 / 53	–	1.1	0	70.4	29.6	0.5
Co	14.5 / 80	–	0.34	47.6	16.9	32.3	0.8
Mn	19.9 / 105	0	1.4	83.6	3.7	12.7	0.5
Mo	17.9 / 98	7.8	0.39	57.2	17.5	25.3	0.01
Ti			1.1	71.4	8.3	20.3	–
Zr	21.3 / 106	1.6	1.1	91.9	1.9	6.2	0.0

[a] $T = 523$ K, $P = 3.0$ MPa, $H_2/CO = 4.0$, GHSV $= 54000\ h^{-1}$.
[b] 2 wt%.
[c] Copper surface area after synthesis reaction.

a number of promoters onto the catalyst. Unlike other studies on similar additive effects on copper-based methanol synthesis catalysts [3–9], the present study modified the preformed $Cu/ZnO/Al_2O_3$ by adding a small amount of modifiers. Hence, the physical state of each component is expected to have been changed to the minimum extent.

An attempt was made to correlate surface oxygen coverage with any reaction parameter in methanol synthesis from CO_2/H_2. A reasonable correlation was obtained for CO_2 conversion as shown in fig. 3. However, data for Pt- and Co-modified catalysts were far off the correlation line. Fig. 3 also contains some data

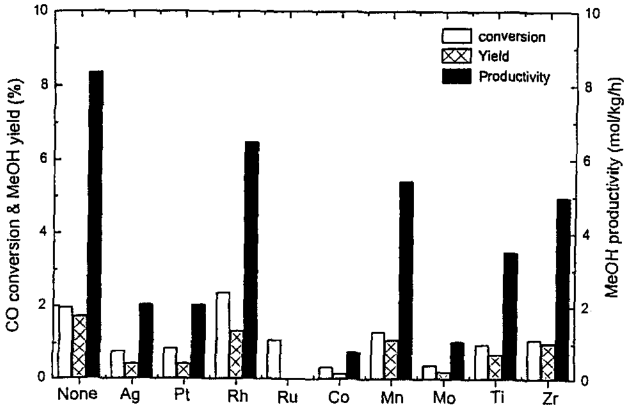

Fig. 2. Catalytic performance of modified $Cu/ZnO/Al_2O_3$ for methanol synthesis from CO/H_2. Reaction conditions: $T = 523$ K, $P = 3.0$ MPa, $H_2/CO = 4$, GHSV $= 54000\ h^{-1}$.

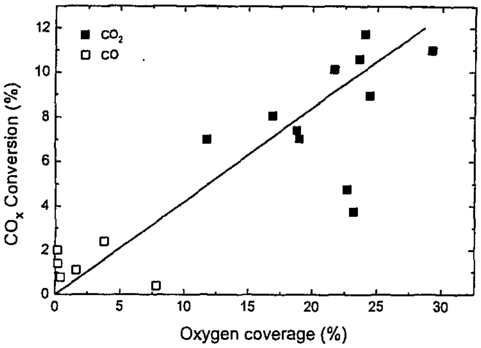

Fig. 3. Conversion of CO_2 or CO as a function of oxygen coverage of copper surface following the reaction. Reaction conditions: $T = 523K$, $P = 3.0$ MPa, $H_2/CO_x = 4$, GHSV = 54000 h^{-1}.

for methanol synthesis from CO/H_2. The correlation was not particularly good partly because of the limited accuracy of measurements of such low oxygen coverages. Yet, the general trend is clear.

Hence, the most important parameter that may be responsible for the modification effect is the surface oxygen coverage measured by N_2O titration. As mentioned, copper surface area itself did not contribute to the improvement of the catalyst performance because all the modified catalysts had reduced copper surface areas (table 2) compared to the unmodified catalyst. It is interesting that the methanol synthesis from CO/H_2 also follows the general trend followed by the synthesis from CO_2/H_2, as shown in fig. 3. Thus, one of the reasons that the rate of methanol synthesis from CO/H_2 is slower than that from CO_2/H_2 over the same catalyst may be the difficulty to maintain high surface oxygen coverages under the highly reducing CO/H_2 atmosphere.

There have been some controversies over the meaning of the "surface oxygen coverage" measured by the procedure described here. Surface atomic oxygen on copper derived from dissociative adsorption of CO_2 has been proposed to take part in the methanol synthesis both as reactant and as a promoter for the adsorption of CO_2, H_2O and H_2 [12]. Szanyi and Goodman [13] showed that methanol synthesis was faster over an oxidized Cu(100) than over a clean Cu(100). Recent transient experiments [14] and a DRIFT study [15] (both in situ) indicated that the actual oxygen coverage of copper surface under the industrial methanol synthesis conditions over $Cu/ZnO/Al_2O_3$ was less than 2%. Thus, Bailey et al. [15] proposed a new interpretation that the surface oxygen measured by N_2O probably derived from the thermal decomposition of adsorbed carbonate species which was the most abundant surface intermediate during the reaction.

Recently, Fujitani et al. [9] demonstrated an excellent correlation between the specific activity for methanol synthesis from CO_2/H_2 and the oxygen coverage for copper and various metal oxide supports. Our correlation is not as good as the one presented by Fujitani et al. probably because we employed a wider variety of modifiers including metals and metal oxides.

4. Conclusions

By adding several modifiers, the performance of commercial $Cu/ZnO/Al_2O_3$ could be improved for methanol synthesis from CO_2/H_2, but not for the synthesis from CO/H_2. The most important role of these modifiers appears to be to change the coverage of stable surface intermediates formed on copper during the reaction.

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