Copper–zirconia catalysts for methanol synthesis from carbon dioxide: effect of ZnO addition to Cu–ZrO_2 catalysts

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Coprecipitated Cu–ZrO_2 catalysts were found to show higher selectivity to methanol in CO_2 hydrogenation than conventional Cu–ZnO catalysts. Addition of ZnO to Cu–ZrO_2 catalysts of Cu/ZrO_2 = 1 (weight ratio) greatly enhanced the activity at lower temperatures, while keeping the high methanol selectivity of Cu–ZrO_2 catalysts. A remarkable increase in the Cu dispersion with increased amount of added ZnO explains the increased activity at lower temperatures, while the reforming of methanol to CO is accelerated by ZnO at higher temperatures, leading to a lowered yield of methanol. It is suggested that ZrO_2 rather than ZnO in the ternary systems plays a more effective role for the selective formation of methanol.

Keywords: CO_2 hydrogenation; copper–zirconia catalyst; Cu–ZrO_2–ZnO; methanol synthesis

1. Introduction

The synthesis of methanol from carbon dioxide and hydrogen over Cu–ZnO catalysts and the effect of supports or additives on the properties of the Cu–ZnO catalysts have been the subject of considerable investigations [1–9]. Addition of ZrO_2 as well as Al_2O_3 has been found to be very effective for this reaction [6,7]. In many studies, however, the active site in these copper-based catalysts has been believed to require ZnO as an essential component.

On the other hand, Cu–ZrO_2 catalysts have been reported to be active and selective for methanol synthesis in spite of a lack of ZnO [6,10–18]. While the addition of ZnO to Cu–ZrO_2 catalysts was reported to increase the conversion to methanol slightly [11], detailed information is missing in the literature on the effect of ZnO as the third component and on the role of ZnO or ZrO_2 in Cu–ZrO_2–ZnO catalysts. It is still subject to considerable controversy that ZnO plays an essential role in the copper-based binary or ternary catalysts for methanol synthesis from carbon dioxide and hydrogen [19–21].

In most investigations reported so far, both Cu–ZrO_2 and Cu–ZnO catalysts have been prepared from nitrates as the starting salts. However, it is well known in the preparation of supported metal catalysts that starting materials strongly affect the performance of the resulting catalysts. As a matter of fact, we have perviously shown that the choice of the starting materials in the preparation of Cu–ZrO_2 catalysts has marked influence on the properties of the resulting catalysts and that a simultaneous use of copper chloride and zirconium sulfate significantly improves both the activity and selectivity for methanol formation [18]. The enhanced activity of the Cu–ZrO_2 catalyst coprecipitated at lower temperatures (<ca. 320 K) by using zirconium sulfate was attributed to the increased dispersions of not only Cu but also Zr species in the catalysts. Therefore, the use of similar starting salts in the preparation of Cu–ZrO_2–ZnO catalysts is expected to improve the catalytic performance and give additional information on the role of ZnO and ZrO_2 in these catalysts.

In the present work, we have prepared a variety of Cu–ZrO_2–ZnO catalysts with varying compositions using different starting salts, and examined the catalytic behavior in the methanol synthesis at different reaction temperatures.

2. Experimental

Two series of Cu–ZrO_2–ZnO catalysts, one containing 50 wt% of copper and another keeping the weight ratio of Cu to ZrO_2 at unity, were prepared by a coprecipitation method using different starting salts and 10% excess of Na_2CO_3 as listed in table 1. A typical procedure to prepare a precursor CSN-x was as follows: An aqueous solution (25 cm^3) of Na_2CO_3 was rapidly added to a mixed solution of copper chloride, zirconium sulfate, and zinc nitrate in 150 cm^3 of deionized water at 293 K while vigorously stirring. The precipitate was aged at 348 K for 15 min under gentle stirring, and then filtered and thoroughly washed with hot water. The final pH values were 8.2–8.4 for all preparations. The precipitate was dried at 383 K for 20 h and crushed into a powder. Precursors from nitrates (NNN-x) were similarly prepared for comparison by using copper nitrate, zirconyl nitrate and zinc nitrate.

The hydrogenation of CO_2 was carried out at a pressure of 0.9 MPa using a continuous tubular flow fixed-bed microreactor. The catalyst sample (0.5 g) was mounted in a stainless steel reactor (i.d. = 6 mm) and pre-reduced at 523 K for 1 h in a hydrogen flow of 100 cm^3 min^{-1} (NTP). After cooling to 413 K the hydrogen flow was replaced with a reactant gas ($H_2/CO_2 = 3$) flow of 40 cm^3 min^{-1} (NTP) and then the pressure was increased gradually to 0.9 MPa. The reaction temperature was raised stepwise (30 min per step of 20 K) to 533 K. The product gas was analyzed at each reaction temperature by using on-line gas chromatographs. Conversion of CO_2, typically in the range 0–20%, is defined as: (mol carbon dioxide converted to all products) / (mol carbon dioxide in the feed gas). The methanol selectivity is defined as: (mol methanol) / (mol carbon dioxide converted to all products).

Table 1
Chemical and physical properties of Cu–ZrO_2–ZnO catalysts

Catalyst	Composition Cu : ZrO : ZnO (wt%)	Starting salt Cu/Zr/Zn	S(BET) (m^2/g)	D_c(XRD) Cu (nm)	Conv.[a] CO_2 (%)	Selec.[a] MeOH (%)	Formation rate[a] (mmol/g h)	
							MeOH	CO
CSN-1	50 : 50 : 0	chloride/sulfate/–	25.6	26	1.75	77.5	0.73	0.21
CSN-2	45 : 45 : 10	chloride/sulfate/nitrate	27.6	14	4.13	56.6	1.25	0.96
CSN-3	35 : 35 : 30	chloride/sulfate/nitrate	48.7	5	5.86	47.5	1.49	1.65
CSN-4	25 : 25 : 50	chloride/sulfate/nitrate	65.2	5	10.19	20.9	1.14	4.32
CSN-5	10 : 10 : 80	chloride/sulfate/nitrate	113.2	5	9.04	13.2	0.64	4.21
CSN-6	50 : 40 : 10	chloride/sulfate/nitrate	34.2	15	7.36	36.1	1.38	2.44
CSN-7	50 : 25 : 25	chloride/sulfate/nitrate	55.2	8	4.29	29.3	0.79	1.91
CSN-8	50 : 10 : 40	chloride/sulfate/nitrate	75.6	8	4.00	22.9	0.51	1.71
CSN-9	50 : 0 : 50	chloride/–/nitrate	70.6	9	3.00	19.4	0.33	1.37
NNN-1	50 : 50 : 0	nitrate/nitrate/–	47.2	23	1.67	45.2	0.40	0.49
NNN-2	45 : 45 : 10	nitrate/nitrate/nitrate	63.2	13	3.86	48.6	1.00	1.06
NNN-3	35 : 35 : 30	nitrate/nitrate/nitrate	115.1	6	13.21	10.7	0.76	6.31
CSS-9	50 : 0 : 50	chloride/–/sulfate	75.9	10	1.86	50.6	0.50	0.49
NNN-9	50 : 0 : 50	nitrate/–/nitrate	55.3	11	5.78	9.6	0.30	2.83

[a] Reaction after 3 h on stream (0.5 g precursor, 473 K, 0.9 MPa, 40 $cm^3\ min^{-1}$ (NTP), $H_2/CO_2 = 3$).

The catalyst samples were characterized by nitrogen physisorption measurements (BET), X-ray powder diffraction (XRD), and thermal analysis (TGA/DTA). Mean crystallite sizes of copper (D_c) in H_2-reduced catalysts were calculated from the half-width of the (111) reflection of Cu metal in XRD patterns using the Scherrer equation after correction of the peak width for the contribution by instrumental broadening [22].

3. Results and discussion

Methanol and carbon monoxide were the only carbon-containing products found in this study, except for trace amounts of methane and higher hydrocarbons in the reactions at higher temperatures. Preliminary experiments showed that a $Cu-ZrO_2$ catalyst calcined at 633 K for 3 h has a higher conversion but a lower selectivity to methanol and so a lower rate of methanol formation than the catalyst used without calcination. Therefore, all the catalysts examined in this study were used without calcination prior to the hydrogen reduction.

Fig. 1 compares the reaction temperature dependence of the activity and selectivity of $Cu-ZrO_2$ (NNN-1) and Cu–ZnO (NNN-9) catalysts prepared from copper nitrate and zirconyl or zinc nitrate. At every temperature, Cu–ZnO has a higher conversion of CO_2 but a much lower selectivity to methanol than $Cu-ZrO_2$ catalyst. The methanol selectivity of $Cu-ZrO_2$ was always close to the equilibrium value. As a consequence, the methanol formation rate on $Cu-ZrO_2$ catalyst was

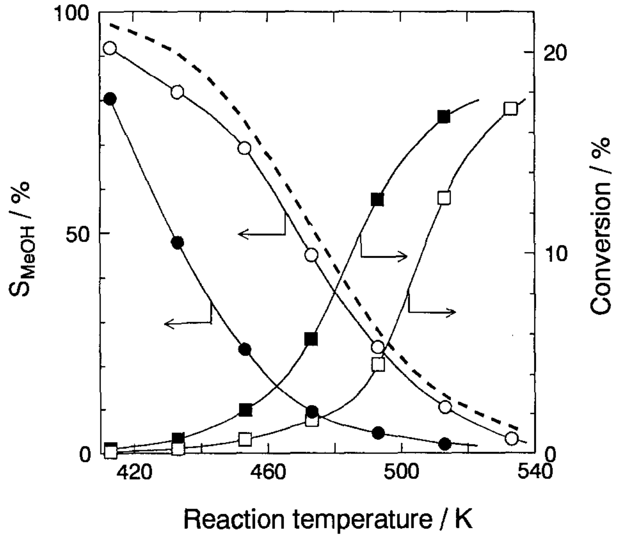

Fig. 1. Reaction temperature dependences of methanol selectivity and conversion on $Cu-ZrO_2$ (○, □) and Cu–ZnO (●, ■) catalysts prepared from nitrates (NNN-1 and NNN-9 in table 1, respectively). (- - -) Calculated selectivity based on thermodynamic equilibrium.

always higher than that on Cu–ZnO catalyst at every temperature (fig. 2). When these binary catalysts were prepared from copper chloride and zirconium or zinc sulfate, methanol formation rates increased considerably as compared to those prepared from nitrates, and the Cu–ZrO_2 (CSN-1) catalyst again had higher methanol formation rates than the Cu–ZnO (CSS-9) catalyst at all the reaction temperatures examined. The Cu–ZrO_2 (CSN-1) catalyst exhibited the highest yield of methanol at around 500 K. Therefore, ZrO_2 seems to play a more effective role than ZnO at least for methanol formation from CO_2. The basicity of ZrO_2 is considered to activate CO_2. It has been reported that the amount of CO_2 chemisorption on ZrO_2 is much larger than those on the other oxides such as Al_2O_3, TiO_2, MgO and SiO_2 [23]. Table 1 summarizes the catalyst composition and the chemical and physical properties of all binary and ternary catalysts examined in this study. Methanol formation rates on CSN and CSS catalysts were considerably high as compared to those on NNN catalysts of the same compositions. Therefore, we employed the catalysts of the CSN series for further experiments to clarify the effect of ZnO addition to Cu–ZrO_2 catalysts unless otherwise stated.

Fig. 3 shows the reaction temperature dependence of the methanol formation rate on Cu–ZrO_2–ZnO catalysts having various ZnO contents and the same weight loadings of Cu and ZrO_2. As the reaction temperature was raised, the methanol formation rate increased and reached a maximum at a varying temperature between 450 and 500 K depending on the catalyst composition, while the CO_2 conversion and CO formation rate increased remarkably with increasing reaction temperature for all the catalysts examined. The optimum temperature for methanol formation

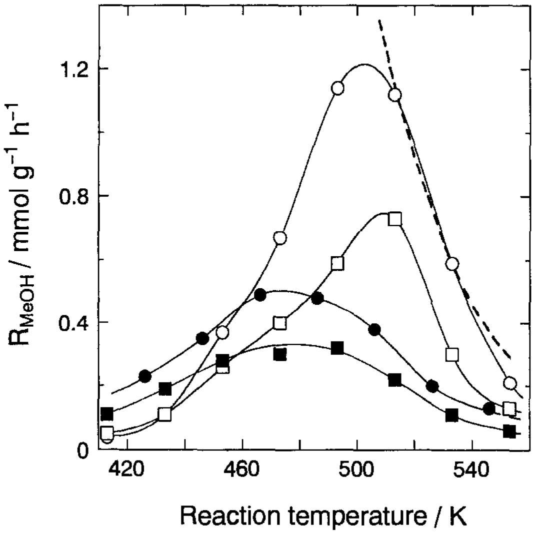

Fig. 2. Reaction temperature dependence of methanol formation rate on Cu–ZrO_2 (○, □) and Cu–ZnO (●, ■) catalysts prepared from different starting salts. (○) CSN-1, (□) NNN-1, (●) CSS-9, (■) NNN-9. (- - -) Calculated rate based on thermodynamic equilibrium.

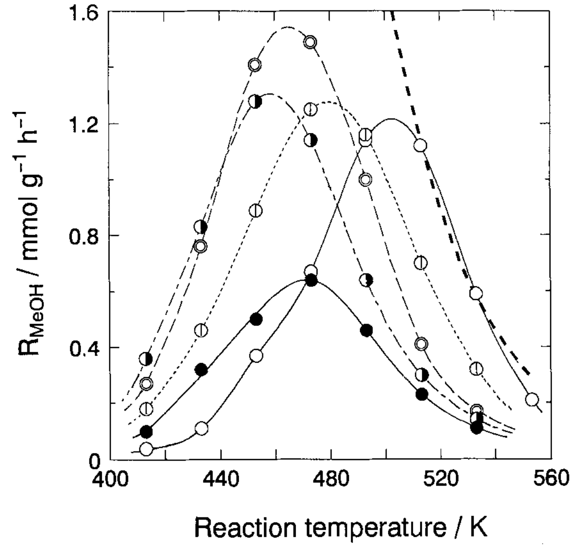

Fig. 3. Reaction temperature dependence of methanol formation rate on Cu–ZrO_2–ZnO catalysts prepared from copper chloride, zirconium sulfate, and zinc nitrate (Cu/ZrO_2 = 1 by weight). ZnO contents are as follows: (○) 0% (CSN-1), (⦶) 10% (CSN-2), (◎) 30% (CSN-3), (◐) 50% (CSN-4), and (●) 80% (CSN-5). (- - -) Calculated rate based on thermodynamic equilibrium.

decreased with increasing ZnO content in the catalyst except for CSN-5. The CSN-3 catalyst containing almost equimolar amounts of the three components exhibited the highest rate of methanol formation in all the catalysts prepared here, and the optimum temperature, 460–470 K, was lower by ca. 40 K than that for Cu–ZrO_2 (CSN-1) catalyst. The enhanced activities of the ZnO-containing catalysts at lower temperatures can be easily understood by taking into account the increases in the surface area and the dispersion of Cu in these catalysts as revealed by the decrease in the crystallite size of copper metal with increasing ZnO content as summarized in table 1. The decrease in the methanol formation rate on Cu–ZrO_2 (CSN-1) catalyst at higher temperatures is explained in terms of the thermodynamic equilibrium. However, the ZnO-containing catalysts lose the activity for methanol formation at much lower temperatures before reaching the thermodynamic equilibrium as shown in fig. 3. These observations suggest the detrimental effect of ZnO at a high temperature. The Cu–ZnO catalysts have been reported to accelerate the reforming of methanol to CO at a relatively low temperature [24].

Figs. 4 and 5 show the effects of ZnO content on the catalytic performance at 473 K of CSN catalysts prepared while keeping the weight ratio of Cu to ZrO_2 at unity and fixing the Cu content at 50 wt%, respectively. In both cases, the selectivity to methanol decreased considerably with increasing ZnO content. This can be explained by the decrease in the mean crystallite size of Cu in these ZnO-containing catalysts because it has been reported that methanol selectivity is favored on larger crystallites of Cu metal [8,18]. On the other hand, the addition of 10% ZrO_2 to

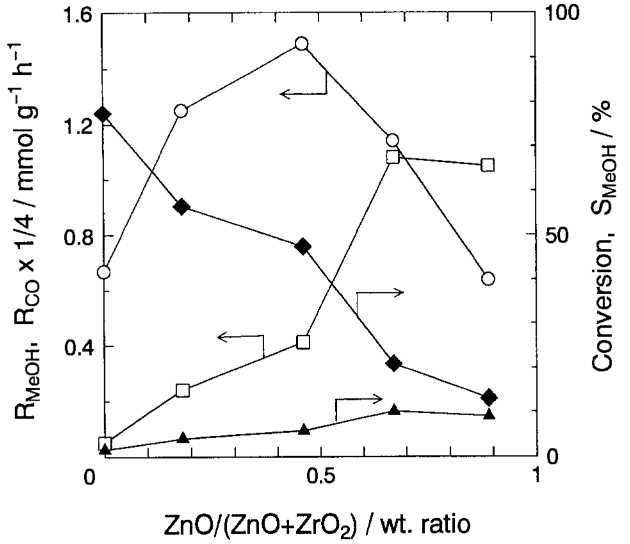

Fig. 4. Effect of ZnO content in Cu–ZrO_2–ZnO catalysts (Cu/ZrO_2 = 1 by weight) on the formation rates of methanol (○) and CO (□), conversion (▲), and methanol selectivity (◆) at 473 K.

Cu–ZnO catalyst resulted in an increase in the selectivity to methanol in spite of a slight decrease in the mean crystallite size of Cu (CSN-8 and CSN-9 in table 1). These observations indicate that ZnO content mainly affects the Cu dispersion while ZrO_2 has a favorite effect on methanol selectivity. Since the coprecipitation

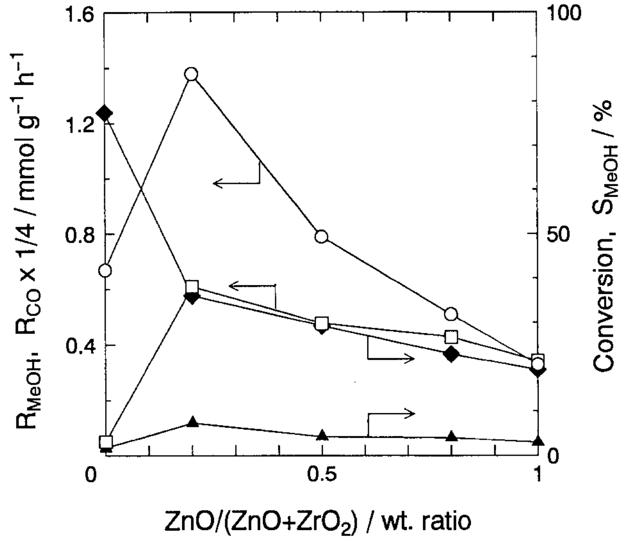

Fig. 5. Effect of ZnO content in Cu–ZrO_2–ZnO catalysts (Cu = 50 wt%) on the formation rates of methanol (○) and CO (□), conversion (▲), and methanol selectivity (◆) at 473 K.

of ZnO brought about a remarkable increase in the total conversion of the reaction, the formation rates of methanol on Cu–ZrO_2–ZnO catalysts were higher than those expected for the physical mixture of Cu–ZrO_2 and Cu–ZnO catalysts in spite of the decrease in the methanol selectivity. When the weight loadings of Cu and ZrO_2 were almost equal, the increase in the methanol formation rate caused by the ZnO addition was very large in a wide range of ZnO content (fig. 4, and CSN-6 in table 1). The ternary catalyst with a relatively low content of ZrO_2, however, did not exhibit such a large increase in the methanol formation rate (fig. 5). These findings strongly suggest that ZrO_2 plays a more important role than ZnO for the selective hydrogenation of CO_2 to methanol and that the synergy between Cu and ZrO_2 and/or ZnO becomes most effective when the weight ratio of Cu to ZrO_2 is around unity.

Fig. 6 shows the dependence of the BET surface area upon the ZnO content in the reduced catalyst. For each series of the catalyst, the surface area increased almost linearly with increasing amount of ZnO. Accordingly, an important role of ZnO in the catalysts is in increasing the surface area of the catalyst and the dispersion of Cu, leading to an increase in the CO_2 conversion but to a lowered selectivity to methanol. The increase in the Cu dispersion is considered to be due partly to strong interactions between ZnO and Cu [25,26]. Part of copper may be involved in a Cu–ZnO phase as well as in a Cu–ZrO_2 phase although we do not have any direct evidence for the distinct Cu–ZnO and Cu–ZrO_2 phases. The ZnO phase was detected by XRD measurements for the ZnO-containing catalysts.

In order to confirm the detrimental effect of ZnO in the reactions at higher tem-

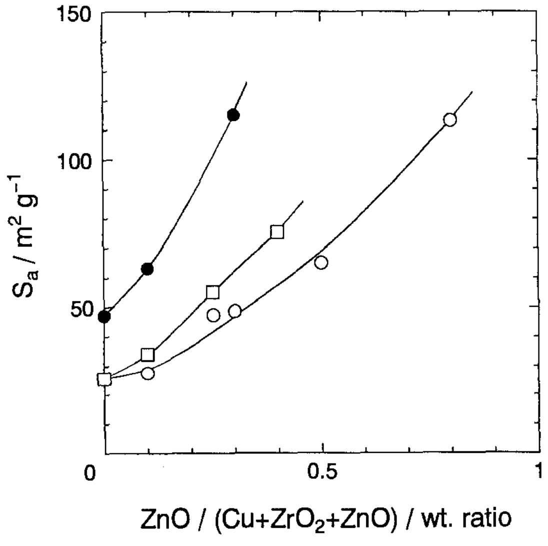

Fig. 6. Effect of ZnO content on the BET surface area of different series of Cu–ZrO_2–ZnO catalysts. (○) Cu/ZrO_2 = 1, (□) Cu = 50 wt%, (●) NNN catalysts.

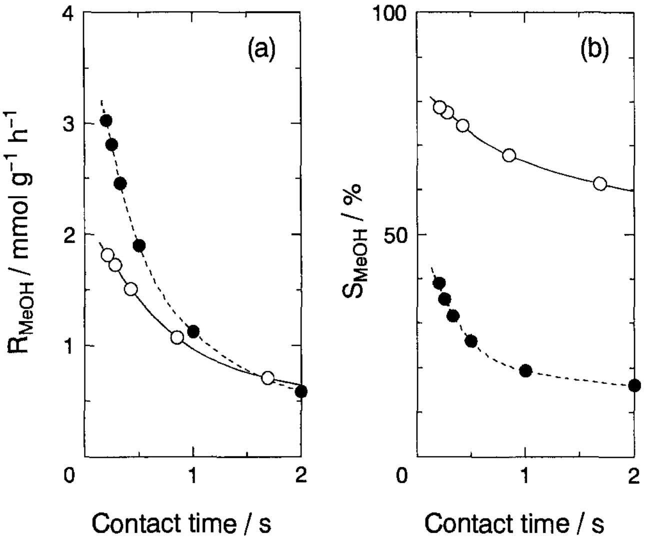

Fig. 7. Dependences of (a) the methanol formation rate and (b) the methanol selectivity over Cu–ZrO_2 (CSN-1) and Cu–ZrO_2–ZnO (CSN-4) catalysts on the contact time of the reaction at 473 K. (○) CSN-1; (●) CSN-4.

peratures as suggested above, the effect of contact time on the hydrogenation at 473 K was examined with two typical catalysts, CSN-1 and CSN-4 in table 1, by varying the flow rate of the mixed gas in the range of 10–200 cm^3 min^{-1}. As shown in fig. 7, the decreases in the methanol formation rate and selectivity with increasing contact time are much more remarkable with CSN-4 catalyst, containing 50 wt% ZnO, than with CSN-1 catalyst without ZnO. These observations indicate that the Cu–ZnO phase in CSN-4 catalyst, compared with the Cu–ZrO_2 phase, accelerates the reforming of once-produced methanol to CO, resulting in a lowered methanol yield at higher reaction temperatures. In fact, an increase in gas-phase CO with increasing contact time was observed for the reaction with CSN-4 catalyst at the contact time shorter than 0.5 s where the drop in the selectivity was remarkable.

In conclusion, Cu–ZrO_2 is more effective for methanol formation from CO_2 than Cu–ZnO irrespective of the starting salts for the catalyst preparation. The role of ZrO_2 in Cu–ZrO_2–ZnO catalysts is more essential than that of ZnO in selective formation of methanol. The main role of ZnO added to Cu–ZrO_2 is in remarkable increases in the surface area and the dispersion of Cu, leading to an enhanced activity of the catalyst at relatively low temperatures. The Cu–ZnO phase, however, accelerates the reforming of methanol to CO at high temperatures more extensively than the Cu–ZrO_2, leading to a much lower yield of methanol than that expected from thermodynamic equilibrium.

Further studies on the role of Zr species and on the detrimental effect of ZnO in the reactions at higher temperatures are now in progress.

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