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Reduction of carbon dioxide with hydrogen on a CuO–ZnO mixed catalyst under supercritical conditions

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Reduction of CO_2 with hydrogen into CO and CH_3OH on a conventional CuO–ZnO mixed catalyst of methanol synthesis under supercritical conditions provided comparable selectivities to methanol and CO with a quite good stability of the catalytic activity; no methanation reaction was observed.

The problem of CO_2 utilization can be solved by converting this green house gas into intermediates that can be further transformed into high value-added products. The simplest reaction seems to be the reduction of CO_2 with hydrogen. Among the primary products of this reduction, carbon monoxide, methane (synthetic natural gas) and methanol are the key intermediates that can be further transformed by the mature technologies into aldehydes, ketones, higher alcohols, liquid hydrocarbon fuels or energy. The methanation reaction is known to proceed quite efficiently on Ni- or Ru-containing catalysts, while Cu-based catalysts can transform CO_2 into methanol, with some other metals capable of converting carbon dioxide into CO.[1–3] Heterogeneous catalysts are more preferable compared to homogeneous ones in terms of stability, separation, handling, recyclization, reactor design to decrease CAPEX and OPEX costs for large-scale productions. Excellent reviews devoted to CO reactions have been published recently.[4–7]

The catalytic conversion of CO_2 to CO *via* reverse water gas shift reaction (1) is considered as the first stage of reduction of CO_2 with hydrogen, with the possibility of occurrence of methane (2) or methanol formation (3) as the second step.

$$CO_2 + H_2 = CO + H_2O, \quad \Delta H_{298} = 41.2 \text{ kJ mol}^{-1}, \qquad (1)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \quad \Delta H_{298} = -252.9 \text{ kJ mol}^{-1}, \qquad (2)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O, \quad \Delta H_{298} = -49.5 \text{ kJ mol}^{-1}. \qquad (3)$$

The catalysts for CO_2 methanation have been reviewed.[8] For instance, Ru-containing catalysts supported on a ceramic sponge (1 wt% Ru, Ru particle size of 5–20 nm) were studied.[9]

Martin *et al*. investigated Ni- and Ru-containing catalysts (5 wt%) in hydrogen reduction of CO_2 at 350–400 °C, 1–20 bar, molar ratio $H_2 : CO_2$ of 4 : 1, with a gas hourly space velocity 6000 h^{-1}.[10] The Ru/ZrO_2 catalysts with a Ru particle size of 4 nm were found to be much more active as compared to Ni/ZrO_2 catalysts with a Ni particle size of 20–30 nm. Yields of methane above 70% were achieved at ambient pressure, whereas at elevated pressures the yields increased to 93% for Ni and 96% for Ru with the methane selectivity exceeding 99.9%. A zirconia-based RuNi bimetallic nanoparticles (3–5 wt% of metals) were shown[11] to provide a complete CO_2 conversion at 300–400 °C, 10 bar, and space velocities up to 36000 h^{-1} with the selectivity to methane being 100%. Noteworthy that the gas mixture was significantly diluted with H_2 and N_2 (4–7 times excess over CO_2). Kwak *et al*. studied the Ru particle size effect on the catalytic behavior of Ru/Al_2O_3.[12] The bimetallic catalysts ($Ru–Ni/CeO_2–ZrO_2$) demonstrate enhanced performance in methane formation.[13] Copper catalysts were used in reduction $CO_2 \rightarrow CO$. Liu *et al*. developed bimetallic $Cu–Ni/Al_2O_3$ catalysts for hydrogenation of CO_2.[14] Whereas Cu is beneficial for CO formation, Ni is effective in CH_4 formation. Cu/ZnO and $Cu–Zn/Al_2O_3$ catalysts of methanol synthesis from CO and H_2 were also used for reduction of CO_2.[15] The highest activity was demonstrated by the system with the Cu : Zn ratio of 4 : 3 on alumina. Chen *et al*. found that Cu/SiO_2 promoted with potassium showed the CO_2 conversion of 12.8% at 600 °C.[16] It was also demonstrated that the activity is improved upon modification of the catalyst with iron.[17,18]

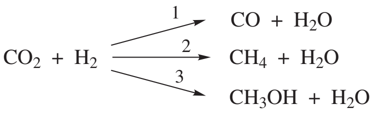
To the best of our knowledge, the use of supercritical CO_2 ($scCO_2$) in the hydrogenation of CO_2 was the focus of only a few recent publications.[19–21] Synthesis of *N*,*N*-dimethylformamide (DMF) from CO_2, H_2, and dimethylamine has been examined by several groups. Jessop *et al*. were the first who reported on the homogeneous $RuCl_2[PMe_3]_4$ catalyst for this reaction.[22]

The only publication related to supercritical studies with heterogeneous catalysts is focused on Pd/Al_2O_3 catalysts and supercritical mixture of CO_2 and H_2, with IR spectra indicating the formation of surface species such as carbonate, formate, and CO.[23] Earlier we have also studied this reaction in the gas phase using microwave activation of the catalysts (Fe- and Au-containing catalysts, $LaNi_5$ intermetallide).[24]

Here we report the first study of the CO_2 reduction with hydrogen on a typical methanol synthesis catalyst from synthesis gas (CO + H_2) under supercritical CO_2 conditions.[†]

Generally, the interaction between CO_2 and H_2 occurs with the formation of several products, with CO, methanol, and methane being the main ones (Scheme 1).

[†] The CuO–ZnO catalyst was a commercial SNM-U catalyst of methanol synthesis (Severodonetsk). The catalyst contained 62 wt% CuO, 36 wt% ZnO with the rest 2 wt% being alumina and trace amounts of carbon added as binders. The catalyst was activated in a flow of 10 vol% H_2 in N_2 in a temperature-programmed mode, the final temperature was 450 °C. The reaction of CO_2 with H_2 was studied under supercritical conditions in a plug-flow reactor. The $H_2 : CO_2$ ratio was 1 : 1 or 1 : 2. The catalyst loading in the reactor was 2 cm^3. The reaction temperature was ranged from 180 to 300 °C. Carbon dioxide was supplied with a syringe pump under the pressure of 80 atm at the rate of 4 cm^3 h^{-1} (1.54 g CO_2 per 1 g of the catalyst per hour), hydrogen was fed *via* a mass flow controller. The pressure in the reactor was maintained at 80 atm using a back pressure valve. Analysis of products was performed with a Crystallux-5000 gas chromatograph with a thermal conductivity detector and Porapack Q and zeolite CaA packed columns. The conversions of CO_2 and H_2 were



Scheme 1

The catalytic data on the conversion and selectivities to the main products on the CuO–ZnO–Al_2O_3 catalyst are given in Table 1 (the concentrations of the gas phase) and Table 2 (the yields and selectivities to the main reaction products). The dependences of the conversion and selectivities *vs.* reaction temperature in the experiments with H_2:CO_2 ratios of 1:1 and 1:2 are presented in Figures 1 and 2. Surprisingly, the yield of methanol, which is the main product of the reaction between CO_2 and H_2 on the same catalyst, is comparable to that of CO.

The dilution of the gas mixture with CO_2 results in a decrease of the activity, as well as the selectivity to methanol that is in the range of 10–30% (H_2 : CO_2 = 1 : 2). The increase in the reaction temperature also leads to the decrease of the methanol selectivity. The stability of the catalyst is quite good at least for the 8 h test.

Table 1 Performance of the CuO–ZnO–Al_2O_3 catalyst in hydrogenation of CO_2 (catalyst loading 2 cm^3).

H_2:CO_2 ratio	*T*/°C	Concentration in the gas mixture after the reaction (vol%)					
		H_2	CO	CH_4	CO_2	H_2O	CH_3OH
1:1	200	46.8	0.8	0	47.6	2.2	1.4
	220	45.7	1.2	0	47.8	3.0	1.8
	240	44.1	2.0	0	47.7	4.3	2.3
	260	42.5	3.6	0	47.8	6.7	3.2
	280	42.9	5.2	0	45.8	8.8	3.5
1:2	220	31.5	2.9	0	63.1	4.2	1.3
	240	28.7	3.6	0	64.1	5.3	1.8
	260	28.4	5.3	0	63.1	6.5	1.2
	280	30.0	7.2	0	59.5	8.4	1.3
	300	29.8	9.1	0	57.7	10.1	1.0
1:1	280, 1 h	47.0	5.1	0	43.4	7.4	2.3
	280, 2 h	43.7	5.0	0	45.7	7.1	2.1
	280, 8 h	46.5	4.6	0	44.9	6.5	1.9

Table 2 Performance of the CuO–ZnO–Al_2O_3 catalyst in hydrogenation of CO_2 (P = 80 atm).

H_2:CO_2 ratio	*T*/°C	CO_2 conversion (%)	Selectivity (vol%)	
			CO	CH_3OH
1:1	200	4	37	63
	220	6	41	59
	240	8	47	53
	260	12	53	47
	280	16	60	40
1:2	220	6	70	30
	240	8	67	33
	260	9	81	19
	280	12	85	15
	300	15	90	10
1:1	280, 1 h	15	69	31
	280, 2 h	13	71	29
	280, 8 h	13	71	29

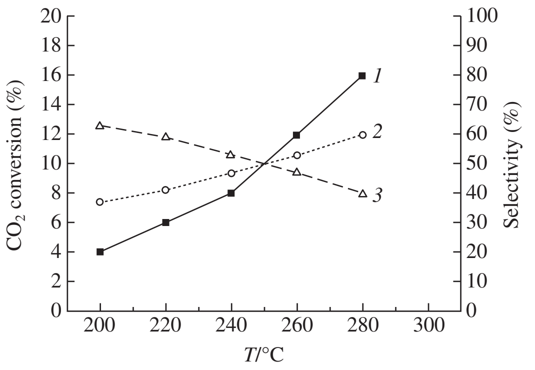


Figure 1 (*1*) CO_2 conversion and selectivities to (*2*) CO and (*3*) CH_3OH *vs.* reaction temperature for the $CO_2 + H_2$ reaction on the CuO–ZnO–Al_2O_3 catalyst (H_2 : CO_2 = 1 : 1, catalyst loading 2 cm^3).

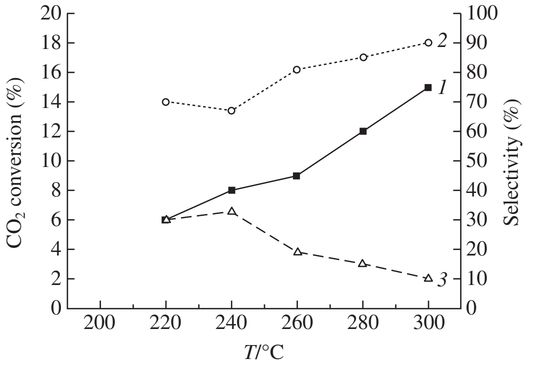


Figure 2 (*1*) CO_2 conversion and selectivities to (*2*) CO and (*3*) CH_3OH *vs.* reaction temperature for the $CO_2 + H_2$ reaction on the CuO–ZnO–Al_2O_3 catalyst (H_2 : CO_2 = 1 : 2, catalyst loading 2 cm^3).

The advantage of the catalytic experiments under supercritical conditions is the high throughput, *i.e.* the productivity of the catalyst expressed in terms of grams of CO_2 passed or converted per gram of the catalyst per hour. Most gas-phase experiments were performed in diluted gas mixtures, with H_2 or N_2 serving as diluents, including one of the best result obtained by Martin *et al.* who tested the Ni- and Ru-containing catalysts (5 wt%) in CO_2 reduction with H_2 at 350–400 °C, 1–20 bar, molar ratio H_2 : CO_2 of 4 : 1, with a gas hourly space velocity 6000 h^{-1}.[10] Also, the productivity was quite limited (about 0.2 g g^{-1} h^{-1}). In our tests, the productivity reached 1.54 g g^{-1} h^{-1}, which is about 7–8 times higher compared to the literature data.

Only one publication was devoted to the study of Cu/ZnO and Cu–Zn/Al_2O_3 catalysts of methanol synthesis from CO and H_2 that were also used for CO_2 reduction.[15] But the tests were carried out under gas-phase conditions.

In conclusion, the use of $scCO_2$ in the CO_2 hydrogenation reaction is quite a new approach. Only the synthesis of formamide was the focus of recent publications on supercritical tests starting, for instance, from CO_2, H_2, and dimethylamine[19–22] using homogeneous catalysts that very often demonstrate poor recyclability.

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determined by the formula $C = [(n_{\text{in}} - n_{\text{out}})/n_{\text{in}}]\times 100$, n_{in} and n_{out} are the quantities of CO_2 or H_2 at the inlet and outlet of the reactor, respectively; $n = cV$, where c is the concentration and V is the gas flow rate. The carbon balance was closed at 99–100%. The hydrogen conversion was calculated on the basis of the CO_2 conversion and selectivities to all the products: $C_{\text{calc}}(H_2) = C(CO_2)\,[S(CO) + 4S(CH_4) + 3S(CH_3OH) + 7S(C_2H_6)]/100$.

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