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Hydrogenation of carbon dioxide: a comparison of different types of active catalysts

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Comparison of the activity and CO selectivity of four principally different types of catalysts in CO_2 hydrogenation, namely, $LaNi_5$, Rh/ZnO–CuO, fumed Fe_2O_3–K_2O–Al_2O_3 and Au/SO_4–ZrO_2, in the entire temperature range at an atmospheric pressure was performed. The use of the intermetallide $LaNi_5$ catalyst provides an enhanced activity in CO_2 hydrogenation with prevailing methane formation, while other catalysts demonstrated predominant formation of CO.

Catalytic carbon dioxide transformations are of prime importance in view of the potential industrial applications for organic syntheses.[1] Carbon dioxide is the major green house gas and its emissions should be reduced to the sustainable minimum. The challenge is not just the capture and storage of CO_2 emissions, but also finding attractive utilization for CO_2.[2,3] The existing approaches to solve this problem in chemical processes with the goal of producing value-added products are in their infancy: only a few feasible approaches are known, such as the production of polycarbonates from epoxides and CO_2. The inventive use of catalysts can help the enterprises producing vast amounts of CO_2 to diversify the product portfolio by designing the modern and green technologies for the synthesis of high-value added fine chemical products in responding to the needs of the market.

One of the solutions to the problem of CO_2 sequestration is CO_2 hydrogenation yielding either methane (methanation) or CO (the reverse water–gas shift reaction):[4,5]

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \tag{1}$$

$$CO_2 + H_2 = CO + H_2O. \tag{2}$$

Of particular interest is the conversion of CO_2 into a more reactive product, CO, which in turn can be further converted into methanol or diverse hydroformylation, carbonylation, alkoxycarbonylation products, in particular, to the marketable chemicals (linear aldehydes C_4–C_6, some esters).

The reactions of methane and carbon monoxide formation are reverse ones to the industrial process of methane water steam conversion ($CH_4 + 2H_2O = CO_2 + 4H_2$) and water–gas shift reaction ($CO + H_2O = CO_2 + H_2$). Therefore, one can anticipate that the catalysts that are active in the direct reactions are perspective for the application in the reverse reactions of hydrogenation of CO_2 with formation of methane and carbon monoxide.

Intermetallide $LaNi_5$ was reported[6–8] as a good catalyst for hydrogenation of carbon dioxide to produce methane at 250–350 °C and 5 MPa. The catalytic activity increased with the time on stream in the course of the reaction and X-ray diffraction analysis provided evidence for the decomposition of the intermetallide to $La(OH)_3$, $LaCO_3OH$, and metallic nickel.

The catalysis of the water–gas shift reaction by gold nanoparticles supported on metal oxides has recently been the subject of several studies.[9] Gold on zirconia and sulfated zirconia catalysts were tested in the water–gas shift reaction.[10] Sulfated catalysts showed higher activities than the samples prepared using unmodified zirconia, presumably, due to the stabilization of a higher specific surface area for the sulfated zirconia unlike the unsulfated carrier, which leads eventually to a better dispersion of gold nanoparticles on the surface.

The objective of this work was to examine and compare four principally different types of catalysts in hydrogenation of carbon dioxide at an atmospheric pressure.[†] Catalysts possessing high activity and selectivity in reactions with participation of CO, CO_2 and H_2, such as a Rh promoted ZnO–CuO catalyst for methanol synthesis from synthesis gas containing CO_2, an Au/SO_4–ZrO_2 catalyst for the water–gas shift reaction, a Fe_2O_3–K_2O catalyst for Fisher–Tropsh process and an intermetallide $LaNi_5$ catalyst for direct CO_2 methanization were chosen.

Figure 1 depicts the data on the performance of four catalysts in carbon dioxide hydrogenation. The data on the selectivity of catalysts studied towards CO formation are shown in Figure 2.

As it is seen in Figure 1, the catalytic activity of the $LaNi_5$ catalyst was significantly higher as compared with those of other

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[†] A conventional intermetallide $LaNi_5$ was prepared as described.[11] The specific surface area of the sample was 4 $m^2\,g^{-1}$.

5% Rh/ZnO–CuO is the Rhodium supported catalyst on the commercial 64% ZnO–36% CuO catalyst for methanol production from synthesis gas (CHM-1, Russia). The ZnO–CuO support (5 g) was loaded with 5 wt% Rh by incipient–wetness impregnation with a water solution of $RhCl_3$ (7 ml). The sample was dried overnight at room temperature in air. The resulting material was calcined at 500 °C (2 h) in flowing air (~300 ml min^{-1}). The specific surface area of the catalyst was 155 $m^2\,g^{-1}$.

Fused Fe_2O_3–K_2O is a commercial catalyst (Sasol) for the Fischer–Tropsch process prepared by fusion of iron at 1600–2000 °C with the subsequent oxidation of the fusion while supplying oxygen and introducing K_2CO_3 and Al_2O_3 promoters. The specific surface area of the catalyst was 95 $m^2\,g^{-1}$.

2% Au/SO_4–ZrO_2, the sample for the water–gas shift reaction, was prepared as described.[12] The sulfated zirconia support and the catalyst sample prepared after calcination contain 2 wt% of sulfates. The specific surface area of the catalyst was 140 $m^2\,g^{-1}$.

The catalytic activity of the samples was tested using a conventional flow-type fixed-bed reactor made of a quartz tube with an inner diameter of 7 mm under an atmospheric pressure. In a typical experiment, 1.0 g of a catalyst was packed in the reactor tube and was pretreated in a hydrogen stream at VHSV = 1800 h^{-1} at 250 °C for 3 h. Then a reactant gas mixture (33% carbon dioxide in hydrogen) was introduced at VHSV = 1800 h^{-1} and the temperature was raised to 500 °C with a step of 50 °C. The effluent gas was analyzed by an on-line gas chromatograph with packed columns (Porapak-Q for carbon dioxide and molecular sieves 5A for methane and carbon monoxide).

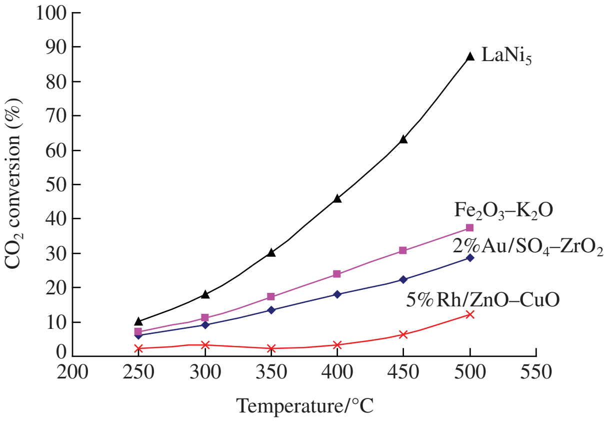

Figure 1 Dependence of the conversion of CO_2 in the reaction with hydrogen on the reaction temperature.

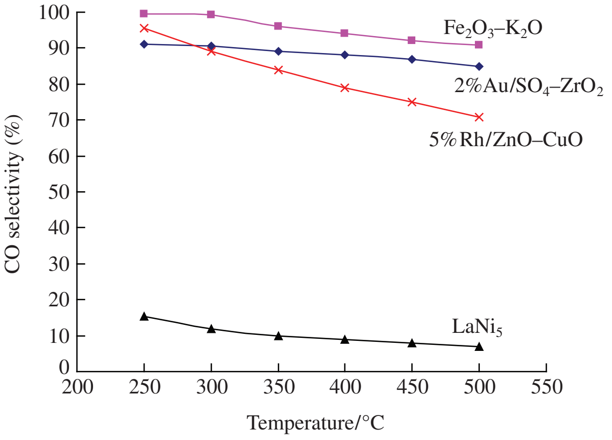

Figure 2 Dependence of the CO selectivity on the reaction temperature.

three catalysts. The conversion of CO_2 at 500 °C is near 90%. The main products of the hydrogenation of carbon dioxide over the $LaNi_5$ catalyst were methane and water. Small amounts of carbon monoxide were also formed with the selectivity below 15% in total. No coke formation occurs on this catalyst up to 500 °C.

The other studied catalysts perform the hydrogenation process mainly with CO formation, and the best catalyst both in terms of the activity and selectivity is the fused Fe_2O_3–K_2O (see Figures 1 and 2). The conversion of CO_2 on this sample at 500 °C is close to 40% and the selectivity towards CO in the entire temperature range does not fall below 90%. Note that the conversion of 40% is close to the thermodynamic equilibrium of the reaction (2).

In conclusion, the obtained results provide a rationale in choosing the best catalysts for the reduction of CO_2 into CO. This reaction is considered nowadays to be the most economically vaiable method of CO_2 utilization with downstream conversion of CO into other valuable chemicals *via* carbonylation, hydroformylation and other reactions.

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