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Direct hydrogenation of CO_2 on deposited iron-containing catalysts under supercritical conditions

Nikolay D. Evdokimenko,[a,b] Alexander L. Kustov,*[a,b,c] Konstantin O. Kim,[c] Maria S. Igonina[c] and Leonid M. Kustov[a,b,c]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: kyst@list.ru, nikolayevdokimenko@bk.ru*
[b] *National University of Science and Technology 'MISIS', 119049 Moscow, Russian Federation*
[c] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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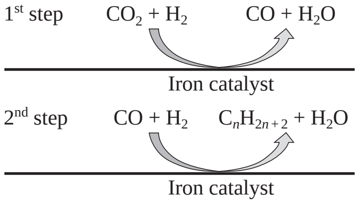
The hydrogenation of CO_2 in the supercritical state on supported Fe/TiO_2 catalysts (0.5–1% iron) at 350–550 °C affords carbon monoxide and methane, the conversion of CO_2 approaching 24%. The work demonstrates the possibility of significant increase in the productivity of CO_2 hydrogenation process and prolongation of the working time of the catalyst.



The constant significant growth of carbon dioxide in the Earth's atmosphere is a challenge to develop processes of utilization and conversion of CO_2. The main problem of CO_2 conversion is the inertness of its molecule.[1] One of the most promising methods of CO_2 conversion is its direct catalytic heterogeneous hydrogenation into valuable products such as hydrocarbons.[2] The possible routes for this process are presented by reactions (1)–(3).

$$CO_2 + H_2 \rightarrow CO + H_2O,\quad \Delta_R H_{573\,K} = 38\ \text{kJ mol}^{-1} \tag{1}$$

$$CO + 2H_2 \rightarrow C_nH_m + H_2O,\quad \Delta_R H_{573\,K} = -166\ \text{kJ mol}^{-1} \tag{2}$$

$$CO_2 + 3H_2 \rightarrow C_nH_m + 2H_2O,\quad \Delta_R H_{573\,K} = -128\ \text{kJ mol}^{-1} \tag{3}$$

In this way, CO_2 can be converted into the products directly or indirectly, for example, through the formation of CO or methanol. Nowadays the process of CO_2 methanation (the Sabatier reaction) is known. The target product can be selected based on economic reasoning. The most simple and economically profitable is the conversion of CO_2 into synthesis gas by reaction (1), defined as the reverse water shift reaction,[2] largely on using iron-based catalysts. In this case, the conversion of CO_2 is a two-stage reaction sequence proceeding through the step of CO formation.[3] The most probable mechanism for formation of hydrocarbons on these catalysts[4] involves CO formation followed by the Fischer–Tropsch reaction. It is also known that the metallic phase of iron does not emerge under the conditions of CO_2 conversion and iron remains in an oxidized form.[5,6] Obviously, the Fischer–Tropsch principles may be applied to the problem in question. For example, if the CO_2 conversion is aimed at producing hydrocarbons, the selectivity factor will be the ratio of the various phases of iron responsible for various stages of this process on the surface of catalyst. It can be speculated that iron carbides are responsible for chain growth, and iron oxides and metallic iron are responsible for hydrogenation processes.[7,8] When synthesis gas is the target reaction product, iron-containing catalysts also proved to be effective due to a high rate of CO_2 adsorption as compared with that of CO, in contrast to, for example, cobalt catalysts, where CO adsorption rate is higher than that of CO_2. The conversion of CO_2 on iron-containing catalysts reaches 40%.[9–12]

The common drawbacks of the most processes described are their low productivity, as well as the short lifetime of the catalyst. In the course of the reaction, the solid products are deposited on the surface of the catalyst and block its active centers, followed by formation of inactive carbide phases of iron such as Fe_3C.[4] In the gas phase, the productivity is limited by slow diffusion of reactants to the surface of the active sites and the diffusion of products from these centers. In liquid solvents, the productivity is limited by the small concentration of dissolved components in the reaction medium. To change the situation, the process can be conducted under supercritical conditions for CO_2 known as the safe and environmentally friendly solvent, which corresponds to the concept of 'green' chemistry.[13–16] Any quantities of nonpolar substances, such as hydrogen, can be dissolved in the supercritical CO_2. Under these conditions, the life of the catalyst is prolonged due to improvement of the diffusion of solid reaction products from active sites of the catalyst, and the productivity of the process is significantly increased by higher density of the reaction medium.[17–19]

Therefore, to investigate direct hydrogenation of CO_2 under supercritical conditions on iron-containing catalysts with different iron contents is a good challenge.

The samples of catalysts were prepared by incipient wetness impregnation of the support[†] with an iron nitrate solution in distilled water of the appropriate concentration. The wet impregnated samples were left to dry at room temperature for 48 h and then

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[†] For the catalyst support, granular titanium(IV) oxide was prepared by the modification of the anatase (Degussa AG). The support was ground in a ceramic mortar and the fraction of 0.25–0.5 mm was selected, ideally suitable for carrying out the catalytic experiment. Then, the support was dried at 120 °C for 2 h. The surface of the resulting fraction, measured in air, was 71 $m^2\ g^{-1}$, and the water capacity was 1.3 ml per gram of the support.

they were calcined in a quartz reactor in air flow of 50 ml min^{-1} at a temperature of 500 °C for 4 h. The activation of the catalysts was carried out *in situ* in the catalytic unit in a hydrogen flow of 60 ml min^{-1} at 500 °C and the pressure of 40 atm for 4 h. Using this method, a series of iron-containing catalysts with the different mass concentrations of iron atoms (0.1, 0.25, 0.5, 1, 2.5 and 5%) was prepared.

It was established that catalytic activity of the samples was not affected by the activation of the catalyst carried out before the start of the experiment.[‡] Both activated and non-activated samples differed only in the initial time of reaching the equilibrium. For the activated samples, the equilibrium was reached in 3–4 h from the beginning at 300 °C, while for the non-activated ones this parameter was 6–8 h. This allowed us to assume that the iron phase on the catalyst was not metallic it and changed on movement to the point of equilibrium state between the reactants and the products. The fact that iron remains oxidized and does not transform to metal finds analogies in the literature.[6,7]

The main gaseous products formed on all samples in the entire temperature range were CO and methane. The selectivity of the conversion of CO_2 to CO on each sample was similar under the same contact time (~55 s) and amounted to 67% calculated on the gaseous products at 350 °C, and decreased slightly to 60% when the temperature was raised to 550 °C (Figure 1). The other gaseous products of the reaction contain mainly methane. At the temperatures above 400 °C, ethane and propane were detected in low quantities ($\leqslant$ 3%). Since the hydrogenation of CO_2 on iron-containing catalysts is described as a two-stage process involving the step of CO formation, it may be assumed that, with increasing temperature, the formed CO is converted to hydrocarbons, which explains the decrease in the selectivity of CO formation and the appearance of low amounts of C_2–C_3 hydrocarbons.[3] However, there is little information on the reaction mechanism under supercritical conditions on iron-containing catalysts of this type, that is why this question requires further study. It may only be concluded that the selectivity of CO formation does not depend on the concentration of the deposited phase.

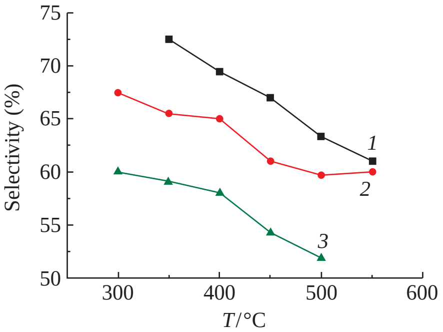

Figure 1 Selectivity of CO formation at different contact times on Fe/TiO_2 catalysts with an iron content of 0.1% to 5% and contact time of (*1*) 40, (*2*) 55 and (*3*) 70 s.

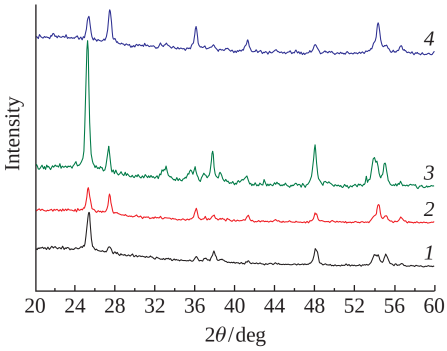

Figure 2 XRD catalyst diagram 10% Fe/TiO_2: (*1*) TiO_2 anatase, (*2*) catalyst before reaction, (*3*) catalyst after reaction, (*4*) catalyst after reaction and DTA.

Figure 2 shows the typical XRD pattern of the 10% Fe/TiO_2 samples and the support. Initially, anatase lines predominate on the pattern ($2\theta = 25.23°$).[§] After preparing the catalysts and their air calcination at 500 °C, the intensity of anatase peaks decreases in respect to that of rutile peaks ($2\theta = 27.45°$). One can expect increase in intensities of iron(III) oxide modification hematite ($2\theta = 33.20°$ and 35.68°) which can form at high calcination temperatures. However, these characteristic peaks are absent and start to appear only after several hours of the reactor work, with negligible intensities. DTA study of air calcined spent catalyst does not reveal significant changes of these peaks. Unfortunately, characteristic peaks of other iron oxides (magnetite $2\theta = 35.58°$ and 43.25°, maghemite $2\theta = 45.211°$ and 41.715°) overlap with those of titanium oxides. Thus, it can be assumed than during preparation of the catalysts, amorphous iron oxides are formed which are responsible for the reverse water shift reaction and the formation of CO. In the course of catalysis process, a crystalline phase of iron oxide-hematite starts to form.

The contact time influenced significantly the dependence of the gaseous product pattern on the catalyst composition. Thus, on the sample of 2.5%, three regimes of the reaction were investigated at different contact times maintaining the amount and composition of the initial flow. The contact time was controlled by the amount of the catalyst loading. Three points with the contact times of 40, 55 and 70 s were thus examined. The experiments showed that the conversion did not change when the contact time was varied, but the composition of the catalytic gases changed significantly. The selectivity of CO formation calculated on the gaseous products of the reaction decreased from 72 to 60% with raising the contact time from 40 to 70 s. Thus, the selectivity of hydrocarbon formation increased. This observation was expected, since it is known that the adsorption and, accordingly, the activation of CO_2 molecule on iron-containing catalysts proceeds faster than those of CO molecule.[7] It can be assumed that during the formation of hydrocarbons, the limiting step is the adsorption and the activation of CO molecule produced in the first stage of the hydrogenation of CO_2.

The conversion of CO_2 (which was close to the total yield of the products) depended on the concentration of the deposited phase only in the concentration range from 0.1 to 0.5% of iron and then remained approximately constant in the examined range of concentrations (Figure 3). On the samples containing 0.5, 1, 2.5 and 5% of iron, the maximum of CO_2 conversion reached 22–23%, while on the sample containing 0.25 and 0.1% of iron the maximum conversion was 20 and 17%, respectively. This is

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[‡] The reaction of CO_2 with H_2 was carried out in a flow catalytic unit with the fixed-bed catalyst. The H_2 : CO_2 ratio was 1:1. The catalyst loading was 1 g. The reaction was investigated in the temperature range of 300 to 600 °C. Carbon dioxide in the liquid state was supplied by the liquid syringe pump at the pressure of 90 atm, hydrogen was supplied at the pressure of the experiment by a mass flow controller (Bronhorst). The pressure in the reactor (90 atm) was controlled by the valve manufactured in N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences. Gas products were analyzed online on a Crystal-5000 chromatograph using thermal conductivity detectors and packed columns Heysep Q and Zeolite CaA. The analysis of liquid products was performed on a chromatograph with the mass detector and on a chromatograph with the flame ionization detector and capillary column OV-101.

[§] Powder X-ray diffraction data were obtained on a DRON3 diffractometer using CuKα radiation. The samples were scanned in the region of $2\theta = 35$–65° with a scanning rate 1 deg min^{-1}. The crystallite size was calculated based on the broadening of the diffraction maxima.

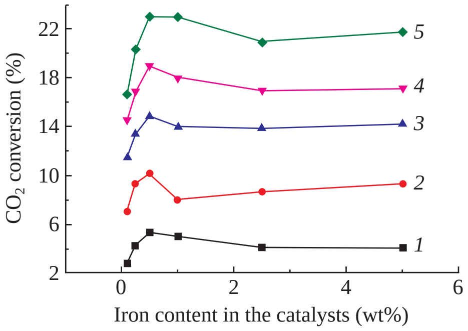

Figure 3 Conversion of CO_2 into gaseous products on Fe/TiO$_2$ catalysts with an iron content of 0.1% to 5% at different temperatures: (*1*) 350, (*2*) 400, (*3*) 450, (*4*) 500 and (*5*) 550 °C.

probably caused by the morphology and the number of the active catalyst centers. One may also assume that at lower iron concentration in the catalyst (below 0.5%), the conversion is lower mainly due to the decrease in the number of the active centers of CO_2 hydrogenation. At the same time, the variation of the contact time does not affect the conversion of CO_2 but changes the product distribution.

The investigated catalysts showed high productivity towards CO, namely, 0.66 g per pram of the catalyst per hour (for the catalysts with the iron concentration of 0.5 to 5% at 500 °C). This value is higher nearly an order of the productivity of CO formation as compared with the experiments without supercritical CO_2.^{3,13} For the catalysts with the iron concentration less than 0.5%, the conversion is lower. The productivity on CO significantly depends on the temperature. The amount of produced CO is extremely low at 300 °C, and grows as the temperature approaches 500 °C. With further raising the temperature, there is a tendency to reduce CO productivity and to increase the yield of hydrocarbons. Therefore, performing the hydrogenation of CO_2 under supercritical conditions significantly increases the productivity of the process, whilst the catalyst activity remains practically unchanged. After the completion of the experiment, there was practically no coking of the catalyst surface.

The sample discharged after several hours of work was examined by TG-DTA method.[¶] Figure 4 shows the TG-DTG-DTA plots of 10% Fe/TiO$_2$. The total weight loss of 1.1% is small enough, however it is possible to distinguish two peaks on DTG curve at 80 and 290 °C. These weight losses may be assigned to the removal of adsorbed water and probably to combustion of residual deposited carbon. On account of insignificant effects DTA curve is not informative. Thus we do not observe coking of the catalyst under the reaction conditions.

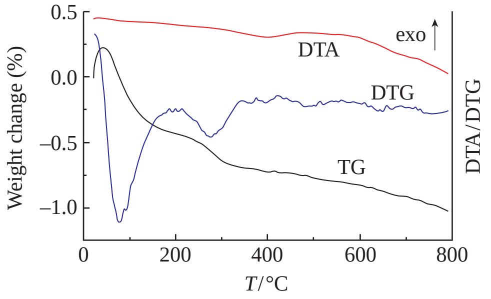

Figure 4 TG-DTG-DTA curves of sample 10% Fe/TiO$_2$ after operation.

Another advantage of carrying out the process under supercritical conditions of CO_2 is prolongation of operation time of the catalyst through the prevention of the coke formation on the catalyst surface by increasing the diffusion of solid products of the reaction from the active centers of the catalyst.

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[¶] Thermogravimetric differential thermal analysis (TG-DTA) of dried samples was performed using a thermoanalytical Derivatograph-C instrument (MOM). The sample (15 mg of the bulk or 20 mg of the supported sample) was placed in an alund crucible and heated in air from 20 to 500 °C at a heating rate 10 K min^{-1}.