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In situ CO_2 reactivation of $FeCrO_x$/C catalyst in the oxidative dehydrogenation of ethane to ethylene

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Catalyst $FeCrO_x$/C in the course of oxidative dehydrogenation of ethane with carbon dioxide to ethylene at temperatures of 600–700 °C was found to undergo *in situ* regeneration with CO_2 to give a stoichiometric amount of CO by the Boudoir–Bell reaction with the surface carbonized material.

$$C_2H_6 + CO_2 \xrightarrow[650\ °C,\ 1\ atm]{FeCrO_x/C} C_2H_4 + CO + H_2O$$

Keywords: oxidative dehydrogenation, ethane, carbon supports, Fe–Cr oxide catalysts, ethylene, 'Sibunit' support.

The heterogeneous catalytic oxidative dehydrogenation of light hydrocarbons is a highly efficient and energy-saving process that is an alternative to the industrial production of olefins by pyrolysis of liquid petroleum distillates and homogeneous dehydrogenation of light hydrocarbons at temperatures above 800 °C. Typically, the low-temperature oxidative dehydrogenation is performed at 400 °C using oxygen as the oxidizing agent. However, the explosiveness of oxygen mixtures with hydrocarbons in a wide concentration range is a significant drawback. The use of carbon dioxide as a reagent in the oxidative dehydrogenation of hydrocarbons solves the process safety issues and, in part, the CO_2 utilization problem. However, dehydrogenation involving CO_2 occurs at temperatures above 600 °C where complete dehydrogenation results in coking and deactivation of the catalyst surface.

To date, the oxidative dehydrogenation of ethane (ODE) with CO_2 is well documented.[1–18] Chromium oxide-based systems were used as catalysts for the ODE with carbon dioxide.[1,2] Nanosized Cr_2O_3/ZrO_2 catalysts modified with Ni, Fe, Co and Mn were obtained by coprecipitation.[3] Addition of Fe, Co and Mn oxides markedly improved the selectivity for ethylene in the ODE process, while the $Fe_2O_3/Cr_2O_3/ZrO_2$ sample was the most efficient catalyst.

In this work, we obtained data on the ODE with carbon dioxide on supported Ga, Fe and Cr oxide systems prepared according to reported techniques (see Online Supplementary Materials) and tested under identical reaction conditions (650 °C, 1 atm, $CO_2 : C_2H_6 = 1:1$).[4] However, all the samples that we tested were irreversibly deactivated in time. A colour change of the catalysts was observed due to surface carbonization (see Online Supplementary Materials, Figure S1). The $Fe_2O_3/Cr_2O_3/ZrO_2$ catalyst was the best of those tested in terms of the conversion/stability ratio. However, even in this case, the selectivity for ethylene did not exceed 40%.[4]

Due to the rapid deactivation of all the catalytic systems studied, we tested alternative supports for the ODE process. After a series of preliminary catalytic experiments, we chose 'Sibunit' being a microcrystalline graphite-like form of carbon as the support.[19,20] Unlike the other samples, 'Sibunit' is a good reducing agent thus facilitating the $Fe_2O_3 \leftrightarrow Fe_3O_4 \leftrightarrow FeO \leftrightarrow Fe^0$ transitions. Catalyst reoxidation becomes possible due to the involvement of CO_2 active at high temperature in the Boudoir–Bell reaction.

A supported $FeCrO_x$/C oxide catalyst containing 5 wt% iron and 5 wt% chromium was synthesized by incipient wetness impregnation. The ODE process was performed on a flow-through set-up at a pressure of 1 atm, a temperature of 650°C and a $C_2H_6 : CO_2$ ratio of 1:1 (see Online Supplementary Materials).

In the diffraction pattern of the original $FeCrO_x$/C catalyst sample (Figure S2), reflexes at angles of 25.6 and 43.7° belong to the support, while the maxima at 30.4, 35.9, 53.7, 57.6 and 63.3° indicate the presence of the Fe_3O_4 phase.[21] Analysis of the diffraction pattern of the $Fe_2O_3/Cr_2O_3/ZrO_2$ catalyst which provided the best results among the samples prepared by reported methods, showed only the presence of a modified tetragonal ZrO_2 phase.[4] The absence of maxima corresponding to phases based on Cr and Fe oxides is most likely due to a high dispersity of these oxides.

The presence of magnetite in the $FeCrO_x$/C catalyst is also confirmed by temperature-programmed reduction (TPR) and magnetic methods (Figure 1; for the procedure, see Online Supplementary Materials). One can see from these plots that

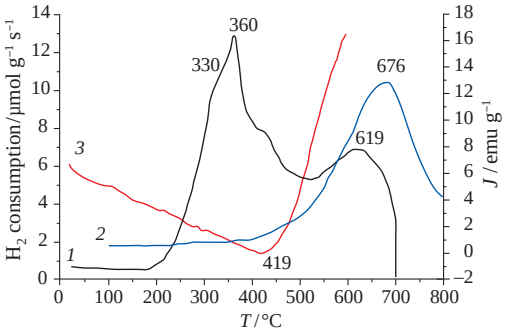

Figure 1 TPR curve of (*1*) the $FeCrO_x$/C catalyst and (*2*) 'Sibunit' support, and (*3*) the temperature dependence of magnetization (*J*) of $FeCrO_x$/C.

Table 1 Oxidative dehydrogenation of ethane on a $FeCrO_x$/C catalyst.

T/°C	Conversion (mol%)		Molar content of products (%)[a]				Selectivity (%)		Carbon balance (%)
	C_2H_6	CO_2	CO	CH_4	C_2H_4	H_2	C_2H_4	CO	
650	12	19	52	7	18	23	80	20	96
700	18	30	45	8	22	25	82	18	95
750	43	40	40	10	16	34	52	48	92

[a] Excluding water; $v(C_2H_6) = v(CO_2) = 21$ ml min^{-1}.

'Sibunit' is not neutral to hydrogen at temperatures above 400 °C and undergoes hydrogenation that corresponds to a broad peak in the temperature range of 370–850 °C with a maximum at 676 °C. Two peaks are observed on the TPR profile of the $FeCrO_x$/C catalyst. The gradual decrease in magnetization in the temperature range of 20–420 °C indicates the transition of magnetite Fe_3O_4 (ferromagnetic) to wustite FeO. The series of shoulders at the first peak in the TPR curve is probably due to the presence of yet another phase (Fe_2O_3) in the catalyst that has no magnetic properties but is also reduced in the temperature range of 200–500 °C. The subsequent increase in magnetization reflects the formation of metallic iron. The second peak with a maximum at 619 °C apparently corresponds to the hydrogenation of the carbon support with a shift towards lower temperatures compared to the pure support (*T* = 676 °C). This is due to the catalytic effect of Fe-containing active sites on the hydrogenation of 'Sibunit'.

Therefore, based on the difference in the phase composition of the catalysts studied and the reducing properties of the carbon support, one should expect to observe changes in the ODE process on the $FeCrO_x$/C catalyst in comparison with the other catalytic systems. This is confirmed by the results of catalytic experiments (Table 1).

Along with reaction (1) of direct dehydrogenation of ethane to ethylene, ODE reaction (2) also occurs due to CO_2 activation by the catalyst, where CO_2 acts as the oxidizing agent. The hydrogen/ethylene ratio obtained exceeds 1, indicating that a fraction of ethane undergoes deep dehydrogenation by reaction (3) to give amorphous deposits of carbon. In turn, carbon reacts with water to produce synthesis gas (4) and carbon dioxide by the Boudoir–Bell reaction (5). Wherein, the loss in the catalyst weight after the reaction (12 h) did not exceed 5%.

$$C_2H_6 \rightarrow C_2H_4 + H_2 \quad (1)$$

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + H_2O + CO \quad (2)$$

$$C_2H_6 \rightarrow 2C + 3H_2 \quad (3)$$

$$C + H_2O \rightarrow H_2 + CO \quad (4)$$

$$C + CO_2 \rightarrow 2CO \quad (5)$$

Calculation of the equilibrium concentrations of hydrogen for the mixture CO_2/C_2H_6 = 1:1 at 750 °C (in the software package HSC 4.0) confirms the experimental fact that the amount of hydrogen evolved exceeds the amount of ethylene formed more than twofold. The high content of carbon monoxide in the products is explained by an increase in its concentration by reactions (2), (4), (5), (6), (7), (8).

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (6)$$

$$C_2H_6 + 2CO_2 \rightarrow 4CO + 3H_2 \quad (7)$$

$$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2 \quad (8)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (9)$$

It is also worth noting that methane is found in significant amounts in the products due to occurrence of the Sabatier reaction (9). This fact was established in catalytic experiments on the hydrogenation of CO_2/H_2 = 1:1 on a $FeCrO_x$/C catalyst under atmospheric pressure (Table S1). At 500 °C, CO_2 conversion is 30% with CO selectivity equal to 94% and CH_4 selectivity of 6%. At 600 °C, CO_2 conversion reaches 54% with CH_4 selectivity of 57% and CO selectivity of 43%. Thus, a high hydrogen content in the gas mixture favours the Sabatier reaction (see Table 1).

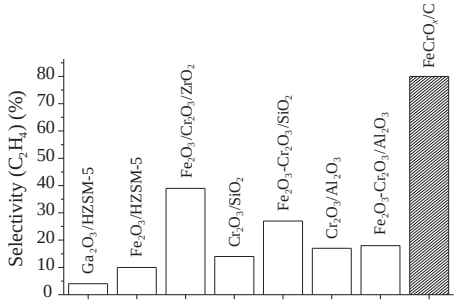

Figure 2 Comparison of the selectivity of catalysts for ethylene in ODE with carbon dioxide (*T* = 650 °C).

Figure 2 presents data on the selectivity of ethane conversion to ethylene on Fe–Cr catalysts supported on various supports.

Despite the higher initial activity of Fe–Cr catalytic systems on oxide supports (see Figure S1), all these samples were deactivated irreversibly in several hours and the selectivity for ethylene did not exceed 40%, while on the $FeCrO_x$/C catalyst it was possible to reach 80% selectivity for the olefin with a possibility of *in situ* regeneration in a stream of CO_2. The data on the catalyst reactivation are presented in Figure S3. First, the C_2H_6/CO_2 = 1:1 mixture was passed through the activated catalyst for 80 min at 650 °C, then pure CO_2 was supplied for 10 min. After that, the cycle was repeated. In the very beginning, ethane conversion had a maximum and amounted to 20% but then decreased abruptly to 12%. This type of behavior of the catalytic system may be due to the reduction of $Fe^{II,III}$ to Fe^0 and fast carbonization of the active centers. When the supply of ethane is stopped, CO_2 would react with carbon to give a stoichiometric amount of CO by the Boudoir–Bell reaction [reaction (5)]. The catalyst surface is reactivated and, upon subsequent supply of ethane, the conversion again reaches 20%.

In summary, the ODE process with carbon dioxide carried out on a $FeCrO_x$/C catalyst allows one not only to achieve up to 80% selectivity for ethylene but also reactivate the catalyst *in situ* in a CO_2 stream at the reaction temperature. After reactivation, the catalyst shows stable selectivity and activity values for more than one hour.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.033.

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