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Electric heating of the Mo–V–Fe–Nb–O_x catalyst bed in oxidative dehydrogenation of ethane

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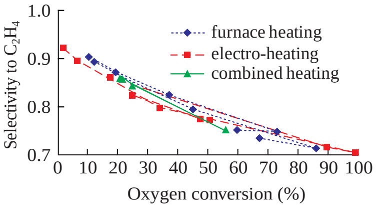
Oxidative dehydrogenation of ethane to ethylene over Mo–V–Fe–Nb–O_x conductive catalyst upon the passing of alternate current through the catalyst bed can be accounted for the electro-heating without additional electronic effects.



Keywords: oxidative dehydrogenation, ethane, ethene, Mo–V–Fe–Nb–O_x catalyst, electro-heating.

In search for improvement of thermal catalytic processes, microwave and plasma technologies as well as application of external electric field[1–4] are considered. This latter approach was studied in relation to different oxidation processes, a positive effect having been observed in some cases.[5–8] The catalysts studied were mainly semiconductors with a rather high conductivity at reaction temperatures (Pt/CeO_2, perovskites), however, catalyst supports could be insulators (ZSM-5 zeolite,[9,10] Al_2O_3). Results obtained are discussed mainly in terms of an electronic effect (non-Faradaic electrochemical modification of catalytic activity, the so-called NEMCA effect, an increase of lattice oxygen mobility with a decrease in the band gap, a change of the Fermi level due to external field, electrochemical oxidation[11]).

Specific quaternary oxide systems Mo–V–Te(Fe)–Nb–O_x are now widely investigated due to their unique ability to catalyze selective oxidative dehydrogenation of ethane.[12–20] From the physical viewpoint, these mixed oxides demonstrate semiconductor properties with a rather high conductivity at temperatures being typical for the active catalytic process (300–400 °C). So, these systems seem to be suitable for studying a possible role of additional electro-treatment. The catalytic bed consisting of small particles of the pure catalyst clipped between electrodes provides simultaneously multiple electrical contacts and good gas permeability. Therefore, the electric current supports additional heat release directly at the active surface. On the other hand, this approach can be modified to provide a conductivity current heating of the catalytic layer composed by the hybrid metal–catalyst material.[21] In the case of the sufficient content of the metallic component, the conductivity should be governed by the metal only with the catalyst particles intercalated in this porous structure and hence heated inside the catalyst bed from the metallic component. This approach seems to be much more energy-saving as compared with traditional outer heating.

The aim of this work was to monitor a possible role of *in-situ* electrical treatment of the Mo–V–Fe–Nb–O_x catalyst bed in oxidative dehydrogenation of ethane into ethene in search for a possible electronic effect and improvement of the process activity/selectivity. The four-component $MoV_{0.3}Fe_{0.17}Nb_{0.15}O_x$ sample was synthesized hydrothermally[13] with replacement of the Te component that is usually introduced in the known ethane oxidative dehydrogenation catalysts[14–18] by an appropriate amount of iron nitrate.[†] Iron-containing system was chosen due to its considerably higher thermal stability.[19] Industrial FeCrAl alloy was chosen due to its negligible catalytic activity under testing conditions. Considerable amount of FeCrAl component (75 vol%) was used to provide multiple contacts between metallic particles in the bed and, therefore, to support a good electro-conductivity of the catalytic layer governed by the metallic component only. Catalytic tests were performed with electro-treatment of the catalyst layer.

The catalysts were tested at an atmospheric pressure for the gas mixture of 75% C_2H_6 + 25% O_2. Ethane, ethene, water, oxygen, and CO_2 were detected as main components of the outgoing

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[†] Washed and dried powder (see ref. 13) was pressed, crushed and sieved to obtain the fraction of 0.3–0.5 mm. For test experiments, the sample (0.1 cm^3, 150 mg) was placed into the middle of a long quartz tube (inner diameter 4 mm) served as a microreactor. Hybrid sample containing metallic FeCrAl component (1 : 3, v/v) was prepared by mechanical mixing of the fractioned Mo–V–Fe–Nb–O_x catalyst (~130 mg) with FeCrAl microwires (0.×0.05 mm) and placed into the middle of the test reactor. The catalyst layer (~8 mm for the pure catalyst; ~20 mm for the hybrid sample) was fixed from both sides by FeCrAl grid discs and pressed slightly to reduce the free space and provide better electrical contacts in the layer. At the same time, the gas flow through the sample was not hindered. Stainless steel springs were used to maintain contacts with stainless steel connectors at two ends of the reactor. Steel capillaries of the gas line were substituted for TEFLON® (a registered trademark of DuPont de Nemours, Inc.) tubing for electrical isolation of the reactor from the chromatographic line. Electrical power supplied on the catalyst layer was regulated by variation of the electrical voltage (AC; 50 Hz) between two electrodes. The measuring thermocouple was fixed on the outer wall of the reactor close to the middle of the catalyst charge. The reactor was placed into the outer furnace in a horizontal position, and a regulating thermocouple was fixed on the wall of the furnace. Gas mixture (75% C_2H_6 + 25% O_2) was fed into the reactor at atmospheric pressure and at a flow rate of 6000 h^{-1}, the outgoing mixture was analyzed by gas chromatography.

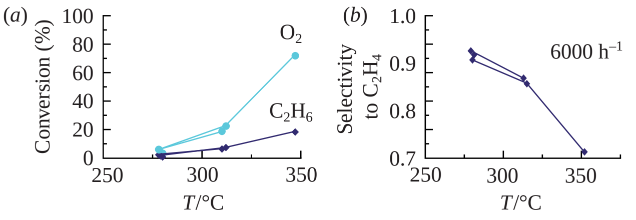

Figure 1 Oxidative dehydrogenation of ethane over the Mo–V–Fe–Nb–O_x catalyst without additional electric supply: (*a*) conversion of reactants; (*b*) selectivity to C_2H_4.

mixture, with trace admixture of acetic acid. The catalyst was tested first with outer heating only (280–360 °C), and then measurements were repeated at a fixed temperature of the furnace (310 °C) and additional, step by step, supply of the electrical power, with measurement of both voltage applied and current value. Starting resistance of the catalyst charge at 310 °C was ~29 kOhm. The hybrid sample was tested with electro-heating only, without additional external heating.

The results of catalytic testing with outer heating of the Mo–V–Fe–Nb–O_x sample in the reactor can be presented as temperature dependences (Figure 1). However, it is important to note that the reaction under study is highly exothermic, and additional heat release inside the bed of undiluted catalyst working in undiluted gas mixture causes additional heating of the layer, and the temperature gradient increases at higher conversions. So, in the case of testing the undiluted sample in our small reactor, even the precise measurement of the temperature by an outer thermocouple has some uncertainties.

Situation with temperature gradients becomes even more complicated in the case of combined treatment of the catalyst, namely, by outer heating and electric current passing. Electric current passed through the catalyst layer causes an additional heat recovery directly in the catalyst bed with dissipation from inside to outside. The thermocouple on the outer reactor wall would show values substantially lower than the temperature of working catalyst particles. Actually, the temperature difference between the reactor wall and the furnace wall rises measurably upon the increase of the voltage. So, the catalyst particles inside the bed are overheated with a non-uniform temperature field. In addition, flowing of the gas through the catalyst creates some additional gradient of the temperature. To take this effect into account, the results of catalytic testing with the combined treatment for Mo–V–Fe–Nb–O_x are presented as dependences on the applied electrical power (Figure 2). These results illustrate (at least qualitatively) that a quite weak electrical power provokes substantial additional rise of the catalyst activity. It looks, however, like no electronic effects take place in our system but rather additional electrical heating is completely responsible for the effect occurring. The additional heat release occurs just in the right place, namely, on the surface contacts between micro crystals of the active phase. Therefore, even low current is capable of providing a measurable surplus of the catalyst activity. On the other hand, the rise of the conversion is accompanied by a gradual loss of the selectivity [see Figure 2(*b*)], quite similar to that observed upon external-only heating. Consequently, an additional electro-heating of the pure active phase does not provide any substantial improvement of the process.

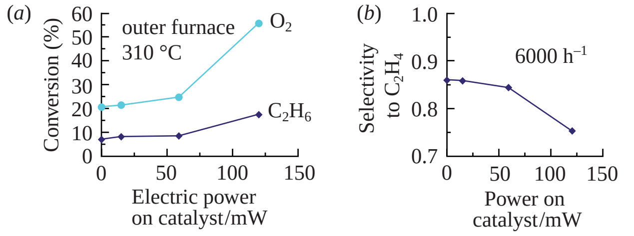

Figure 2 Oxidative dehydrogenation of ethane over the Mo–V–Fe–Nb–O_x catalyst with additional electrical supply at T = 310 °C for the outer furnace: (*a*) conversion of reactants, (*b*) selectivity to C_2H_4.

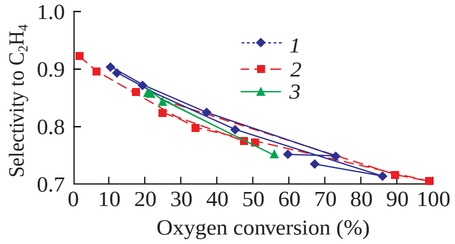

Figure 3 Oxidative dehydrogenation of ethane over the Mo–V–Fe–Nb–O_x catalyst under different heating conditions: (*1*) heating by outer furnace, (*2*) direct electro-heating of the catalyst mixed with FeCrAl (1:3), (*3*) combined heating of pure Mo–V–Fe–Nb–O_x catalyst.

An important problem restricts the use of direct electric heating of pure Mo–V–Fe–Nb–O_x catalyst which is a semiconductor, and the rise of the temperature causes a decrease in resistance of the catalyst (a positive feedback). If the dissipation of the additional heat is not effective enough, the current can rise like a snowball resulting in overheating and electrical breakdown (reached experimentally). Therefore, an alternative approach was tested with the use of the hybrid system containing large fraction of metallic component providing the metallic type of conductivity of the active layer with a negative feedback.

The results of catalytic testing of the hybrid sample in the reactor employed cannot be presented *a priori* as temperature dependence. Heat is recovered directly on metallic micro-wires interweaving in the catalyst bed, and its dissipation is going from hot inside to cold outside. So, the thermocouple on the outer reactor wall shows values being far lower than the temperature of the working catalyst particles. In addition, no preheating of the gas flow takes place in this case and flowing of the cold gas through the hot catalyst creates some additional gradient of the temperature.

However, properties of the samples working under different heating conditions can be compared qualitatively by plotting the results as a dependence of the selectivity *vs.* oxygen conversion (Figure 3). The measurable deviation of curves, with a difference in the selectivity, could point out to existence of an electronic effect for the pure semiconductor catalyst. However, the data superimposed coincide quite well (see Figure 3) thereby demonstrating that the variation of the heating mode does not provide any improvement of the process selectivity.

On the other hand, the direct electrical heating method with application of the metallic matrix in the hybrid catalyst seems to be energy-saving. Other reactions that need additional heat either due to the nature of the reaction or because of heat losses from the equipment can be explored in this manner as well.

In conclusion, oxidative dehydrogenation of ethane over Mo–V–Fe–Nb–O_x catalyst upon the passing of electric current through the catalyst layer can be rationalized in terms of simple electric heating without additional electronic effects. Direct electro-heating of composites (catalyst/metal grains) can be proposed as an energy-saving way of realization of not only oxidative dehydrogenation of ethane but also other reactions including endothermic ones.

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