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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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The supported 6% Ga_2O_3/HZSM-5 catalyst containing 6 wt.% gallium oxide was synthesized *via* incipient wetness impregnation of HZSM-5 zeolite (Si/Al = 15) with an aqueous solution of $Ga(NO_3)_3$ (Aldrich, 99.9%) [Z. Shen, J. Liu, H. Xu, Y. Yue, *Appl. Catal. A: Gen.*, 2009, **356**, 148]. HZSM-5 zeolite in the form of a powder was preliminarily calcinated for 2 h at 500 °C. The $Ga(NO_3)_3$ salt solution was applied dropwise with thorough stirring. After the impregnation, the sample was kept at room temperature for 12 h, then left in an oven at 100 °C until complete dryness. After that, the catalyst was calcined in a stream of dry air at 650 °C for 6 h in order to decompose $Ga(NO_3)_3$ to the oxide.

A two-component catalyst 15% Fe_2O_3/5% Cr_2O_3/SiO_2 was synthesized by a reported procedure [M.M.B. Noureldin, N.O. Elbashir, K.J. Gabriel, M.M. El-Halwagi, *ACS Sustain. Chem. Eng.*, 2015, **3**, 625]. Silica was pre-fractionated (particle size 0.25-0.5 mm), then calcined for 2 h at 500 °C. Based on the known moisture capacity of the support, the amounts of the $Cr(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ salts and solvent required to prepare the solution were calculated. A solution of the $Cr(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ salts was added dropwise with thorough stirring. After that, a wet sample was kept for 24 h at room temperature with recurrent stirring. The catalyst sample was calcined in a quartz reactor in a stream of dry air at 600 °C for 2 h. The sample of 5% Cr_2O_3/Al_2O_3 was prepared using a similar procedure.

The 5% Fe_2O_3/10% Cr_2O_3/ZrO_2 oxide catalyst was obtained by co-precipitation by a reported procedure [S. Deng, H. Li, S. Li and Y. Zhang, *J. Mol. Catal. A: Chem.*, 2007, **268**, 169]. The salts $Cr(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich, 99%), $Fe(NO_3)_3{\cdot}9H_2O$ (Acros Organics, 99%) and $ZrO(NO_3)_2$ (Sigma-Aldrich, 99%) were used as the precursors. The solution of the $Cr(NO_3)_3$, $Fe(NO_3)_3$ and $ZrO(NO_3)_2$ salts was added dropwise with continuous stirring at 40 °C to a solution of NaOH (pH~11). The resulting precipitate was filtered off and washed with distilled water until a weakly alkaline medium was reached (pH~8). Subsequently, the sample was dried in air at 80 °C for 8 h and calcined in a stream of dry air at 600 °C for 3 h to decompose the metal hydroxides to oxides.

Precursors for the synthesis: $Cr(NO_3)_3{\cdot}9H_2O$ (Sigma-Aldrich, 99%) and $Fe(NO_3)_3{\cdot}9H_2O$ (Acros Organics, 99%). 'Sibunit' (manufacturer: Institute of Hydrocarbon Processing Problems,

SB of the RAS) in the form of granules was preliminarily calcined for 2 h at 500 °C. The precursor solution was applied dropwise with thorough stirring on 'Sibunit'. After that, the wet sample was dried in an oven at 100 °C for 12 h until it was completely dry. The catalyst sample was then calcinated in a stream of nitrogen at 600 °C for 4 h.

Catalytic experiments. The catalyst (1 g, sieve fraction: 1-2 mm) was loaded into a quartz reactor (inner diameter 0.9 cm; total reactor length 50 cm) with a fixed catalyst layer (2.5 cm) located in the center, while the rest of the reactor was filled with quartz sand. The reactor was heated in a stream of CO_2. On reaching the desired temperature, the flow of ethane was turned on. The supply of CO_2 and C_2H_6 was controlled by Bronkhorst mass flow controllers. The total flow rate of the initial reaction mixture was 42 ml min^{-1}. Analysis of the reaction products was carried out by gas chromatography on an LKhM–80 chromatograph with a thermal conductivity detector and two packed columns: Porapack Q (1.5 m) for the analysis of hydrocarbons and CO_2 and Zeolite A for the analysis of O_2 and CO. The resulting catalysts were studied using X-ray powder diffraction analysis on DRON-2 diffractometer with Cu K-alpha radiation (the sample weight was 80 mg; 2 ρ from 10 to 70^o).

Thermally programmed reduction procedure. The dependence of the rate of hydrogen absorption in the TPR mode of the catalysts was recorded on a KL-1 laboratory setup (Russia). The reduction was performed with a 5% H_2/Ar gas mixture, flow rate 20 ml min^{-1}, to a temperature of 800 °C. The rate of linear heating of the reactor was 10 K min^{-1}. The chemical transformations in the catalysts during the reduction process were studied *in situ* by the magnetometric method. A sample of a catalyst (50 mg) was placed between two gas-permeable porous quartz membranes into a flow-through quartz microreactor that served as the measuring cell of a vibration magnetometer. The reduction was carried out in a 50 ml min^{-1} stream of hydrogen with heating to 600 °C at a rate of K min^{-1} and the system was kept for 30 min at this temperature. After that, the reactor was cooled to room temperature while recording the changes in magnetization at a frequency of 1 Hz and with an external field of 3 kOe. In this manner, the temperature plots of magnetization, which are thermomagnetic curves, were obtained for reduced catalysts.

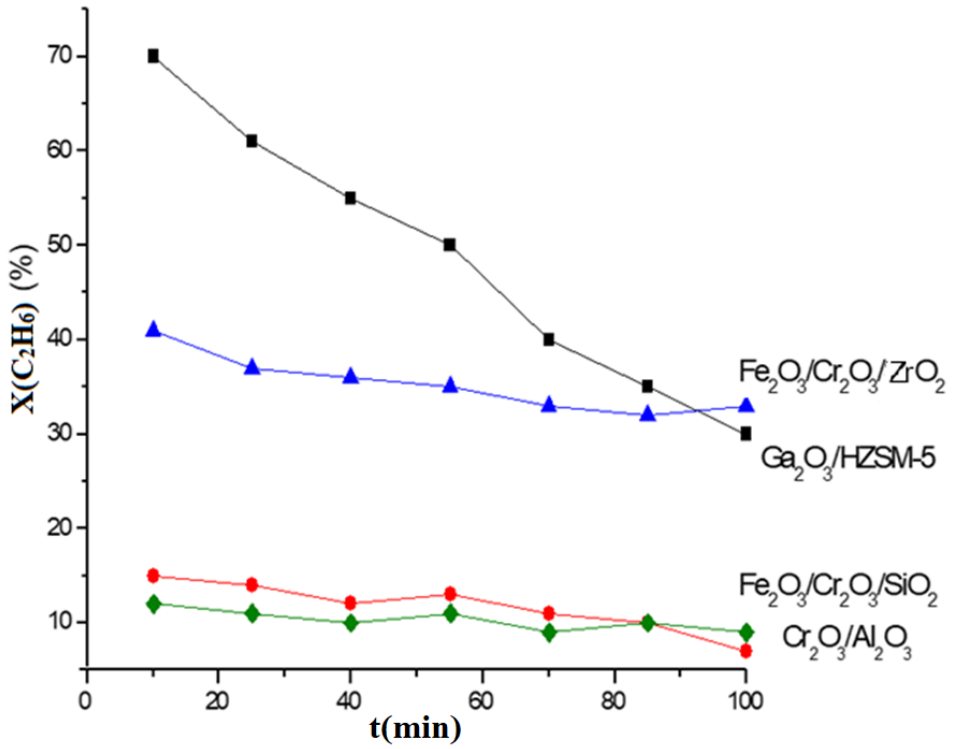

Figure S1 Stability of operation of Fe-Cr oxide catalysts in ODE (650 °C, 1 atm, CO_2:C_2H_6 = 1:1 , X - conversion).

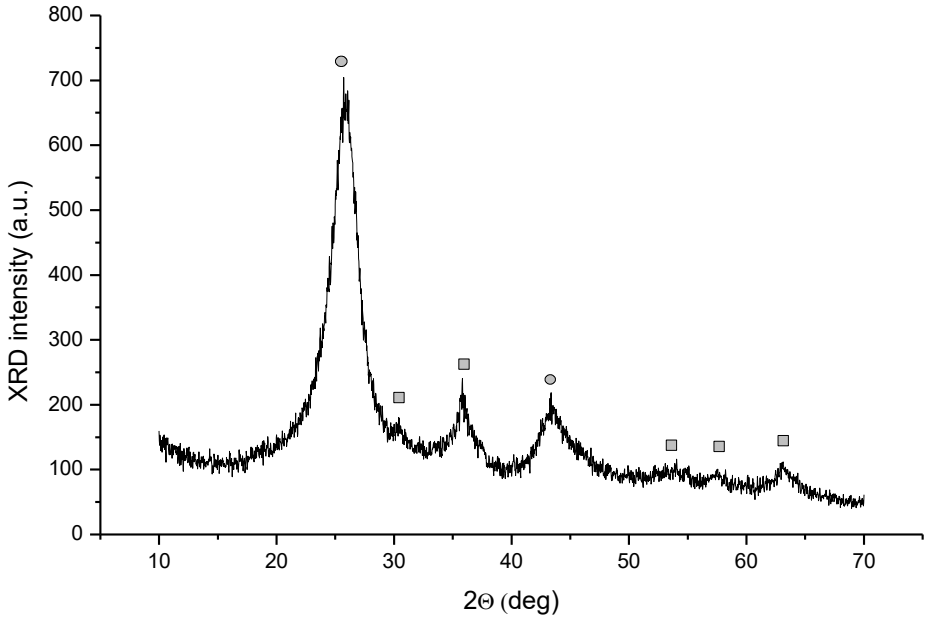

Figure S2 X-Ray diffraction pattern of a freshly prepared $FeCrO_x/C$ catalyst sample (the maxima correspond to: ○–Sibunit; □ - Fe_3O_4).

Table S1 Hydrogenation of CO_2 on a $FeCrO_x$/C catalyst.

T, °C	X(CO_2), %	S(CO), %	S(CH_4), %
500	30	94	6
600	54	43	57

v(H_2) = v(CO_2)=20 ml•min^{-1}; quartz reactor (Ø=0.9 cm, 50 cm, 1 g of the catalyst)

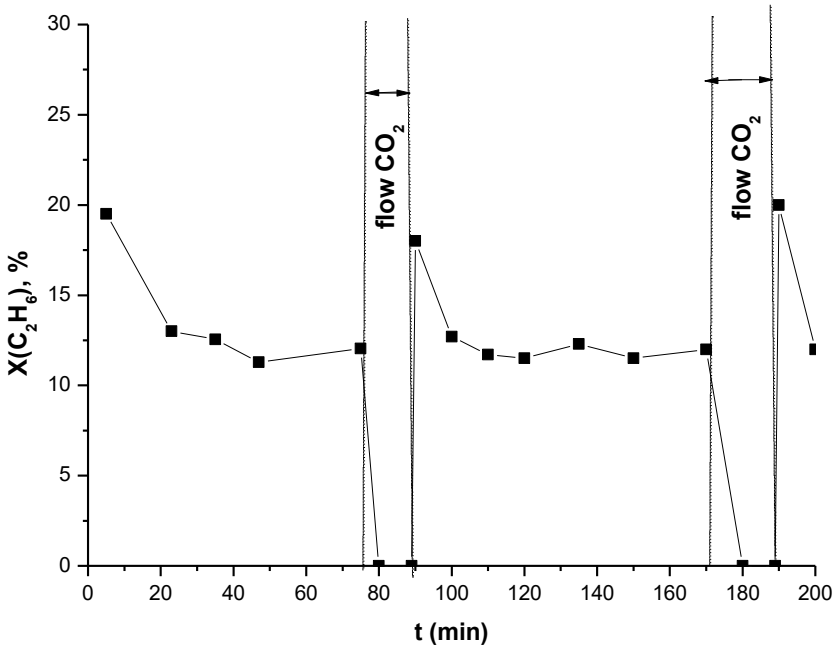

Figure S3 Reactivation of the catalyst in a stream of CO_2 (V_{cat} = 1 cm^3; *P* = 1 atm; *T* = 650 °C).