Electronic supplementary materials *Mendeleev Commun.*, 2027, **37**, just accepted

Effect of hydrothermal treatment or thermal ageing on CrO_x/ZrO_2 catalysts for nonoxidative propane dehydrogenation

Igor Yu. Kaplin, Saveliy N. Urakhov, Ekaterina S. Lokteva, Oksana Ya. Isaikina, Konstantin I. Maslakov and Elena V. Golubina

S1. Experimental part

Catalytic tests

Nonoxidative propane dehydrogenation was carried out in a flow system using a tubular quartz fixed-bed reactor on a ULCat-1 catalytic setup ("UNISIT", Russia) equipped with a three-zone tubular furnace, a thermocouple, temperature controllers and gas flow controllers. The setup was controlled using the CatUnit software. A catalyst sample of 100 mg with a particle size fraction of 250–500 μm was loaded into the reactor between two layers of quartz wool.

The reaction was performed at 550°C under a total pressure of 1 bar. Before the reaction, the catalyst was heated to the required temperature in a nitrogen flow of 20 mL min^{-1}. Then, the reaction mixture containing 40 vol.% C_3H_8 and 60 vol.% N_2 was fed into the reactor at a total flow rate of F_0 = 30 mL min^{-1}. Gas samples were taken from the reactor outlet using a six-port valve connected to a gas chromatograph.

The reaction products were analysed using a Kristall-5000.2 gas chromatograph (Chromatec, Russia) equipped with an Al_2O_3 "S" HP-PLOT capillary column, 30 m × 0.53 mm i.d. (Agilent, USA), and a flame ionization detector. To ensure efficient, complete and reliable analysis of the reaction mixture, retention times and calibration factors for propane and the reaction products were determined in advance using standard gas mixtures of known composition.

Propane conversion, $X(C_3H_8)$, and propylene selectivity, $S(C_3H_6)$, were calculated using equations (1) and (2), respectively:

$$X(\mathrm{C_3H_8}), \% = \frac{\sum_{i(products)} f(i) \cdot A(i)}{\sum_{j(products)} f(j) \cdot A(j) + f(\mathrm{C_3H_8}) \cdot A(\mathrm{C_3H_8})} \times 100\% \quad (1)$$

$$S(\mathrm{C_3H_6}), \% = \frac{f(\mathrm{C_3H_6}) \cdot A(\mathrm{C_3H_6})}{\sum_{i,(products)} f(i) \cdot A(i)} \times 100\%, \quad (2)$$

where $A(i)$and $f(i)$ are the chromatographic peak area and the calibration factor for compound i, respectively, including propylene, methane, ethylene and other products. The uncertainty of the product analysis and propane conversion calculation did not exceed 1%.

The initial propylene formation rate was estimated using the equation for a differential fixed-bed flow reactor with a thin catalyst layer:

$$r_0(\mathrm{C_3H_6}) = F_0 \cdot \frac{x(\mathrm{C_3H_6})}{V_m \cdot m_{\text{кат}}}, \quad (3)$$

where $F_0$is the total volumetric flow rate, mL min–1; $x(C_3H_6)$ is the mole fraction of propylene in the outlet gas mixture; $V_m$is the molar gas volume, 22400 mL mol^{-1}; and $m_{\text{cat}}$is the catalyst weight, g.

Propylene was the main gaseous reaction product under the applied conditions. The deviation of propylene selectivity from 100% was caused by the formation of minor amounts of ethane and ethylene, as well as trace amounts of methane. At longer time on stream, the decrease in propane conversion was mainly attributed to catalyst deactivation due to coke formation.

Atomic adsorption spectroscopy (AAS)

Chromium content in the catalysts was measured by atomic absorption spectroscopy on an iCE 3000 series spectrometer (“Thermo Scientific”, USA) with the nitrous oxide-acetylene flame atomization. To prepare a sample for analysis, a weighed portion of catalyst was dissolved in aqua regia at reflux. The resulting solution was diluted to the concentration recommended by the instrument manufacturer. Calibration curves were plotted with a series of standard solutions of chromium nitrate.

X-ray diffraction analysis (XRD)

Diffraction patterns were recorded on a Rigaku Ultima IV powder diffractometer (“Rigaku”, Japan) (CuKα radiation, 1.5418 Å). The 2θ angle range was from 10° to 80° with a 0.02° increment. The JCPDS PDF-1 (ICDD) database was used for phase identification.

Raman Spectroscopy

The Raman spectra were recorded on a LabRAM HR 800 UV instrument (“Horiba JobinYvon”, Japan) using an argon laser with a wavelength of 514 nm.

Temperature-programmed reduction (H_2-TPR)

The H_2-TPR profiles were recorded on a USGA-101 gas chemisorption analyzer (“UNISIT”, Russia) in a (5% H_2 + 95% Ar) flow in the temperature range from 30 to 400°C (heating rate of 10°C·min^{-1}). Approximately 0.05 g of the sample was studied. The sample was preliminary treated in argon (30 mL·min^{-1}) at 30°C for 30 min.

X-ray Photoelectron Spectroscopy (XPS)

The XPS spectra were acquired on an Axis Ultra DLD spectrometer (”Kratos Analytical”, UK) with a monochromatic AlKα radiation source (hν = 1486.7 eV, 150 W). The pass energies of the analyser were 160 eV for survey spectra and 40 eV for high resolution scans. The binding energy scale of the spectrometer was preliminarily calibrated using the positions of the peaks for the the Zr3*d* line at 182.3 eV.

S2. Powder XRD and Raman spectroscopy

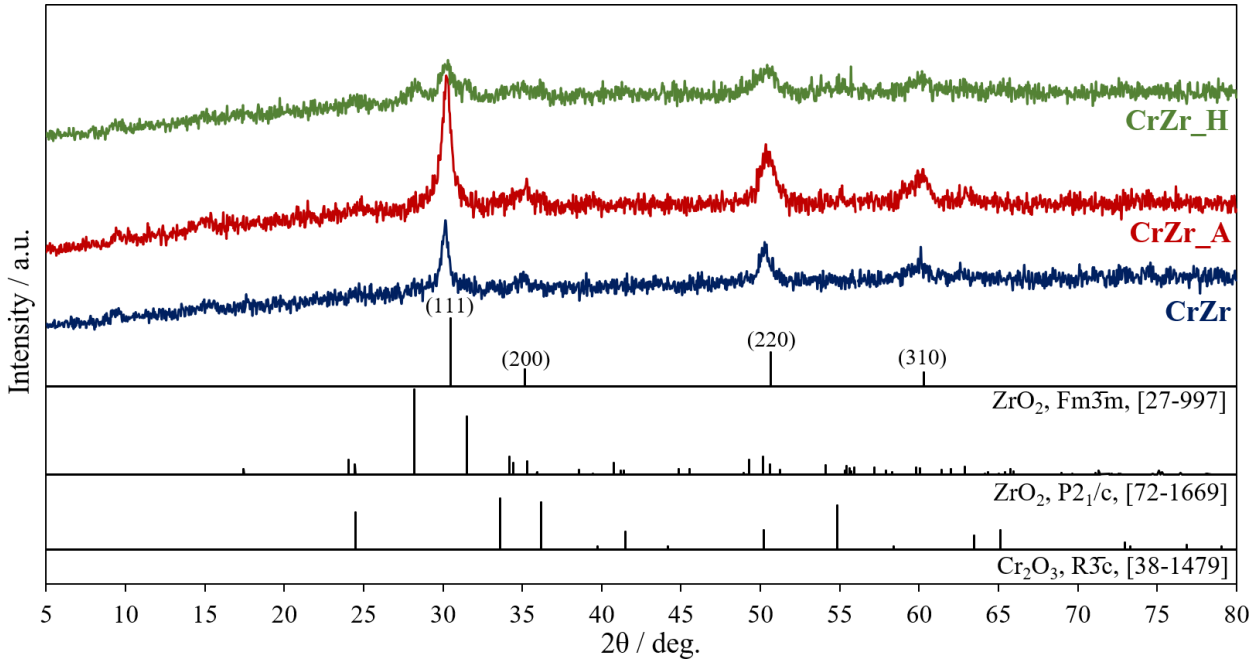


Figure S1. XRD patterns of the prepared samples

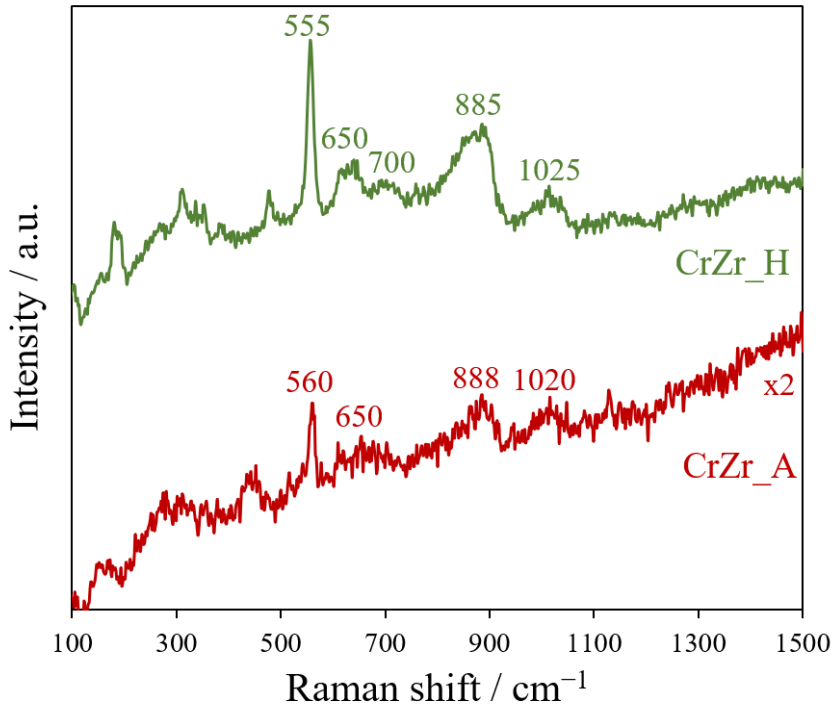


Figure S2. Raman spectra of CrZr_A and CrZr_H

S3. XPS results

Table S1. Surface elemental concentrations of the samples calculated from high-resolution XPS spectra, at.%.

Sample	Cr	O	C	Zr
CrZr	5.9	42.5	38.7	12.9
CrZr_A	15.1	47.7	28.4	8.8
CrZr_H	8.6	50.1	25.0	16.3

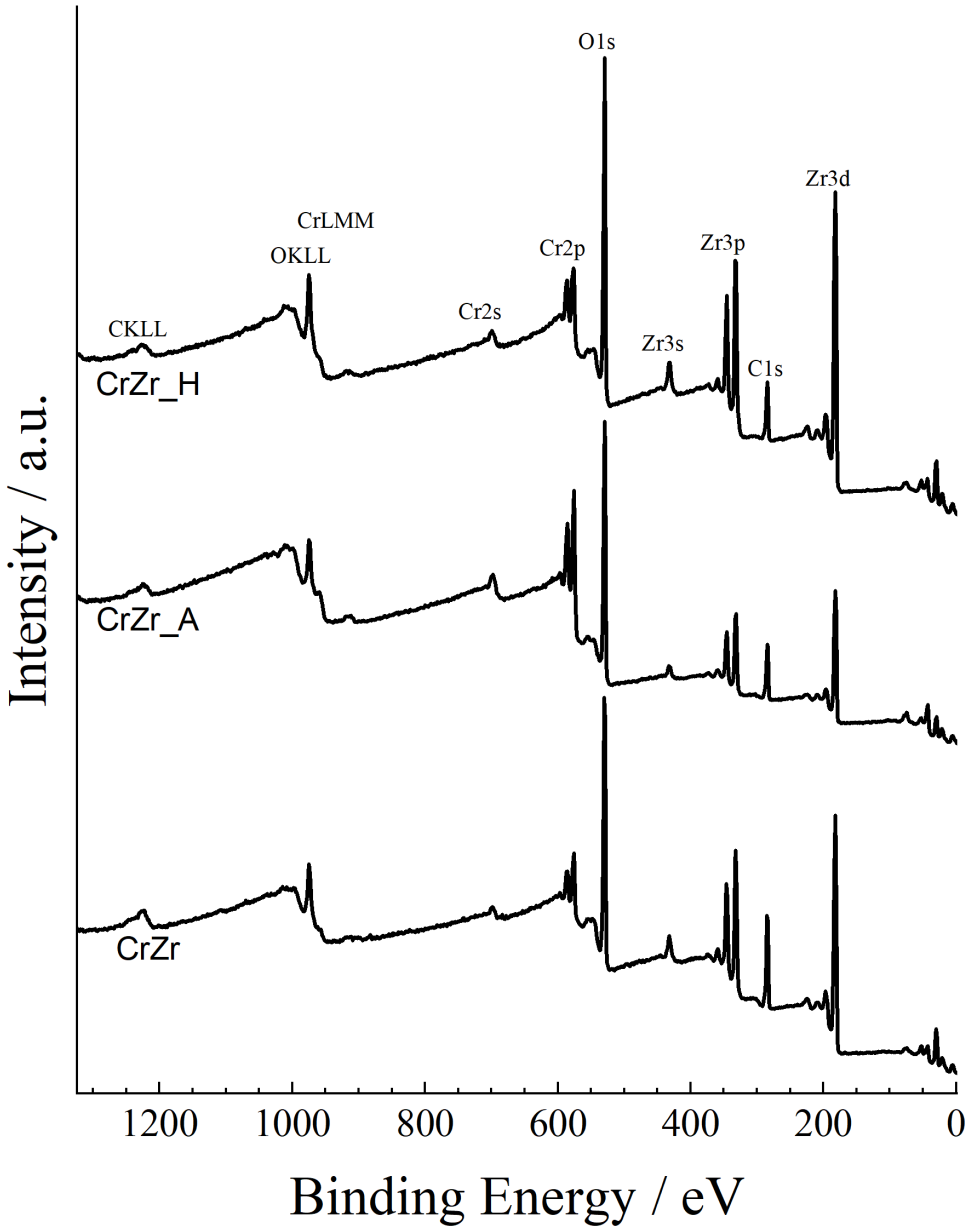


Figure S3. Survey XPS spectra.

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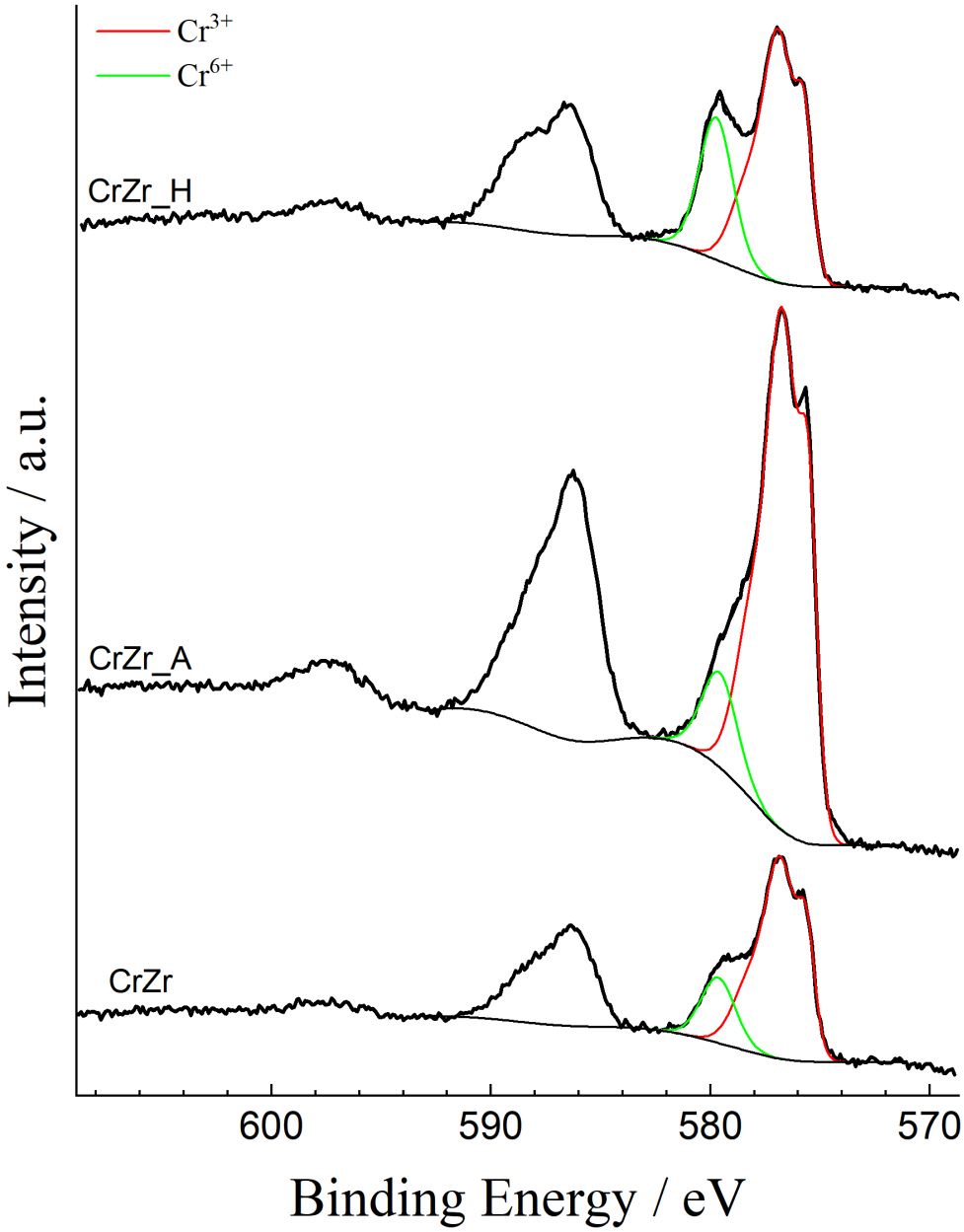


Figure S4. High-resolution Cr2*p* XPS spectra.

In the Cr2*p* spectra of the samples (Figure S4), two components of the Cr2$p_{3/2}$ line can be distinguished at binding energies of ca. 576.9 and 579.6 eV, which correspond to chromium in the +3 and +6 oxidation states, respectively. No noticeable degradation of the Cr2*p* spectra was observed during signal acquisition.