Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

High-performance Cr-Zr-O and Cr-Zr-K-O catalysts prepared by nanocasting for dehydrogenation of propane to propene

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1. Experimental

1.1. Preparation of hard templates and catalysts

SBA-15 was synthesized under acidic conditions using Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$, supplied by Aldrich) and tetraethyl orthosilicate (TEOS) as a silica source. In a polypropylene bottle, 8 g of Pluronic P123 was dissolved in a solution containing 60 g of distilled water and 120 g of 2 M HCl at 308 K. The mixture was vigorously stirred until complete dissolution of polymeric surfactant. Subsequently, 17 g of TEOS (98 %, Aldrich) was added dropwise to the solution under vigorous stirring (400 rpm) at 308 K. Finally, the mixture was stirred (400 rpm) for another 20 h at 308 K and then hydrothermally treated under static conditions for 24 h at 363 K. The obtained white precipitate was filtered off without washing, dried overnight at 333 K and calcined in air by rising temperature from ambient to 823 K over 9 h period and an isothermal step at 823 K for another 12 h.

The prepared SBA-15 material was used as a hard template to the synthesis of CMK-3 replica. Mesoporous silica (1 g) was impregnated with a solution containing 5 g of water, 1.25 g of sucrose and 0.14 g of sulfuric acid. The sample was dried in two steps: at 373 K for 6 h and then at 433 K for another 6 h. The sample of SBA-15 containing partially polymerized and carbonized sucrose was impregnated again. In the second impregnation, a solution with 0.8 g of sucrose and 0.09 g of sulfuric acid dissolved in 3 g of water was used. The drying procedure was repeated. Carbonization was completed by rising temperature (1 K/min) up to 1073 K in flowing N_2 and an isothermal step at 1073 K for another 12 h. The carbon-silica composite obtained after pyrolysis was washed two times in 10% hydrofluoric solution at room temperature to remove the silica template.

1.2. Catalytic characterization

Activity, specific activity, conversion of propane (X_p), yield of propene (Y_p) and selectivity to products (S_i) were calculated based carbon balance in inlet and outlet of the reactor based of the equations reported elsewhere.

$$Activity\left(mol_{C_3H_8}\, s^{-1} g^{-1}\right) = F_p \times C_p;$$

$$X_p = \frac{n_{C_3H_8,inlet} - n_{C_3H_8,outlet}}{n_{C_3H_8,inlet}} \cdot 100\%;$$

$$Y_p = \frac{n_{C_3H_6,outlet}}{n_{C_3H_8,inlet}} \cdot 100\%;$$

$$S_i = \frac{a_i}{3} \cdot n_i \cdot \frac{100\%}{n_{C_3H_8,inlet} - n_{C_3H_8,outlet}}$$

where: F_p is a number of propane moles fed per second, C_p is conversion of propane per gram of a catalyst, n_{Cr} is a number of chromium moles per gram of a catalyst, $n_{C_3H_8,inlet}$ and $n_{C_3H_8,outlet}$ are numbers of propane moles in the reactor inlet and outlet, respectively, $n_{C_3H_6,outlet}$ is a number of propene moles in the reactor outlet, a_i is a number of carbon atoms in a product, and n_i is a number of moles of "i" product.

2. Catalysts characterization

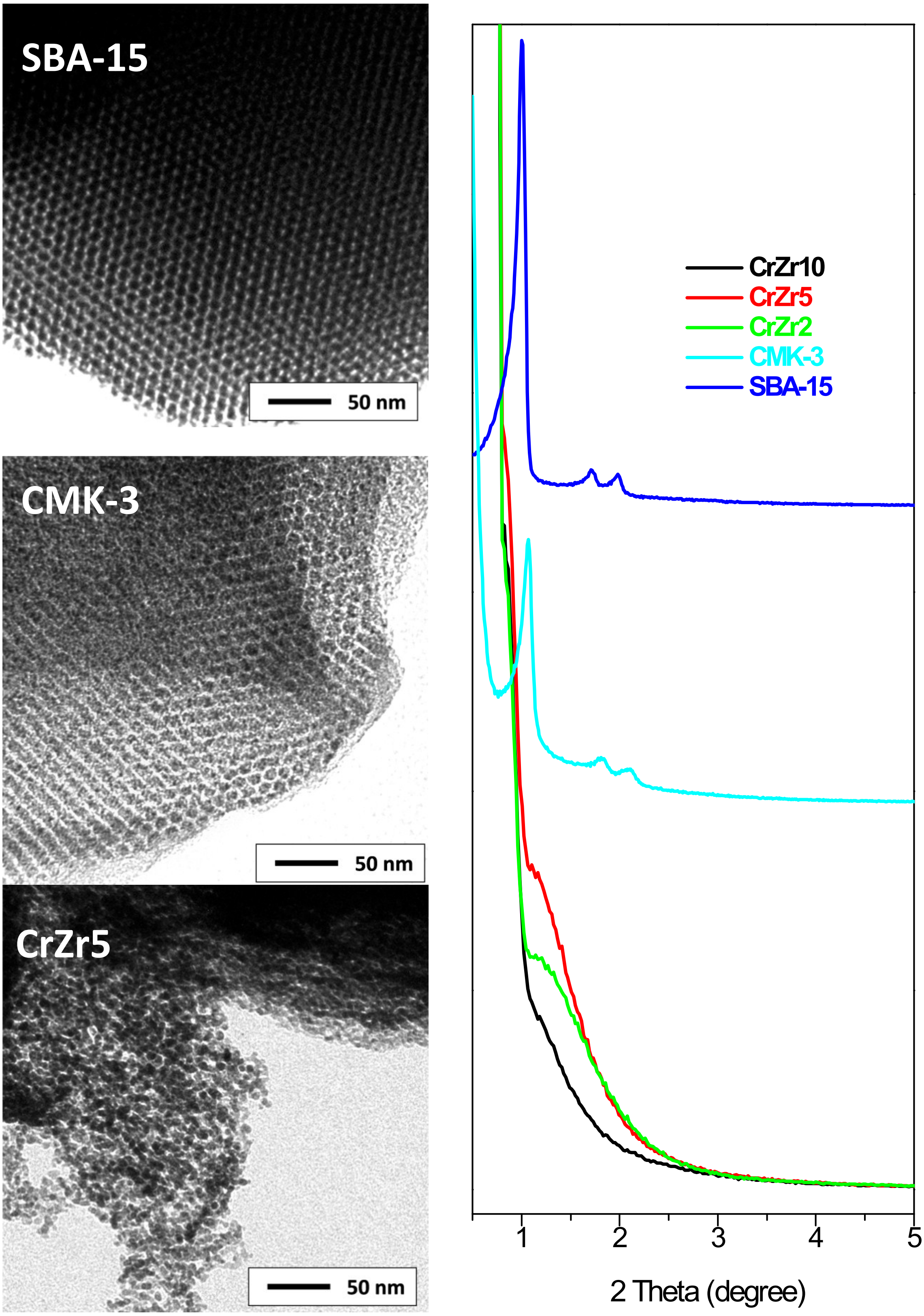

Fig.S1. TEM images (left panel) and XRD (right panel) of hard templates and nanoreplicas.

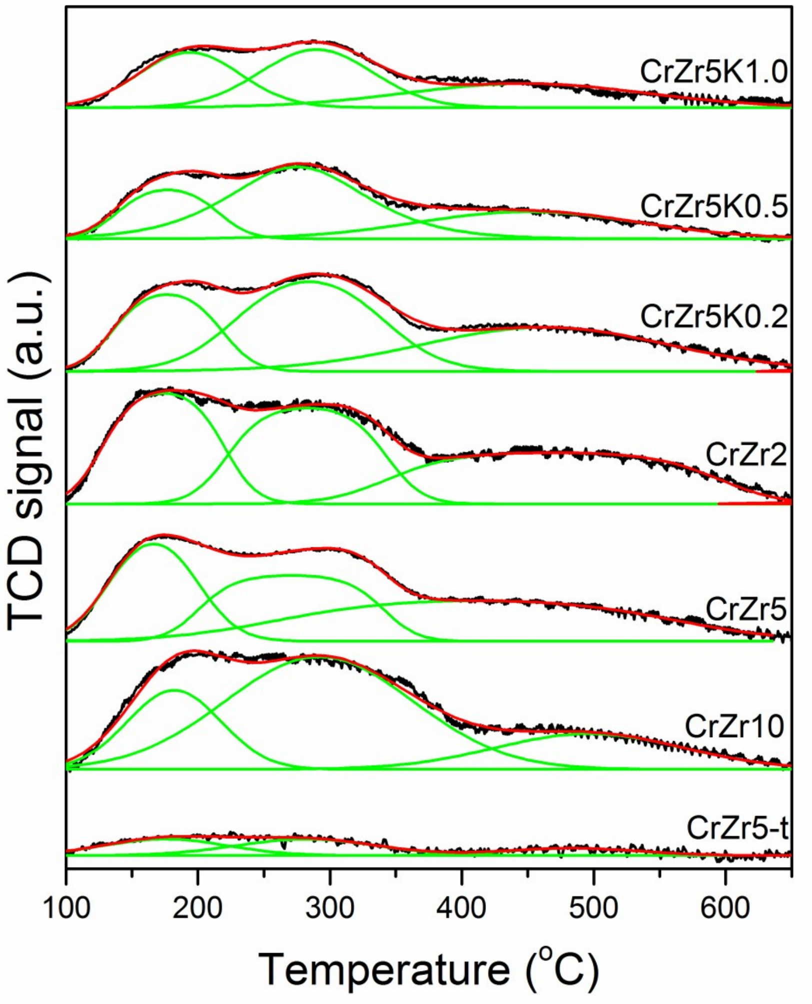

Fig.S2. NH_3-TPD profiles with deconvolution of samples.

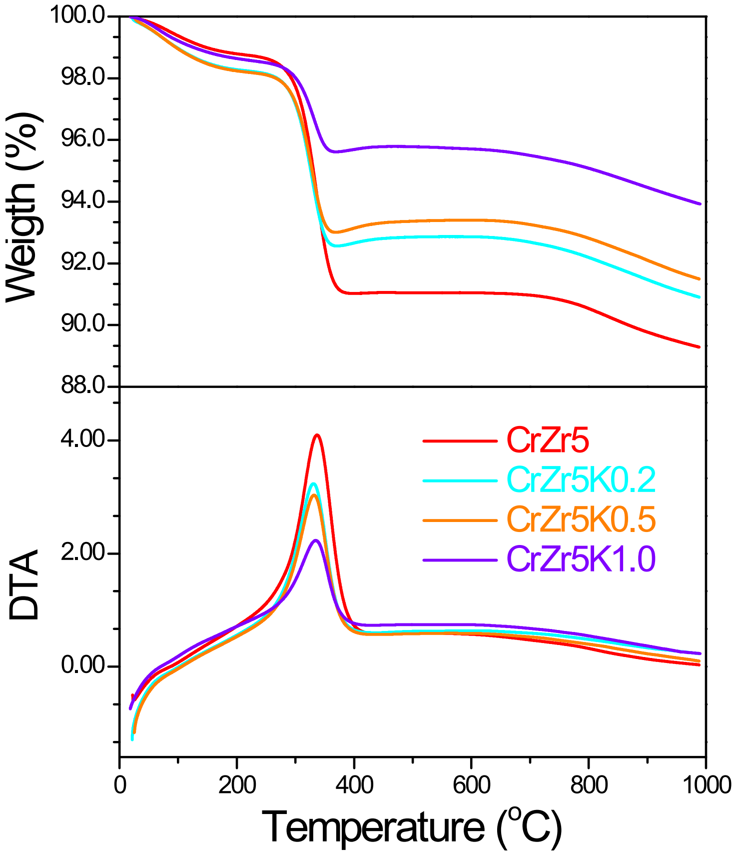

Fig.S3. TG-DT analysis of nanoreplicas used after PDH process carried out at 550 °C for 220 min on stream.

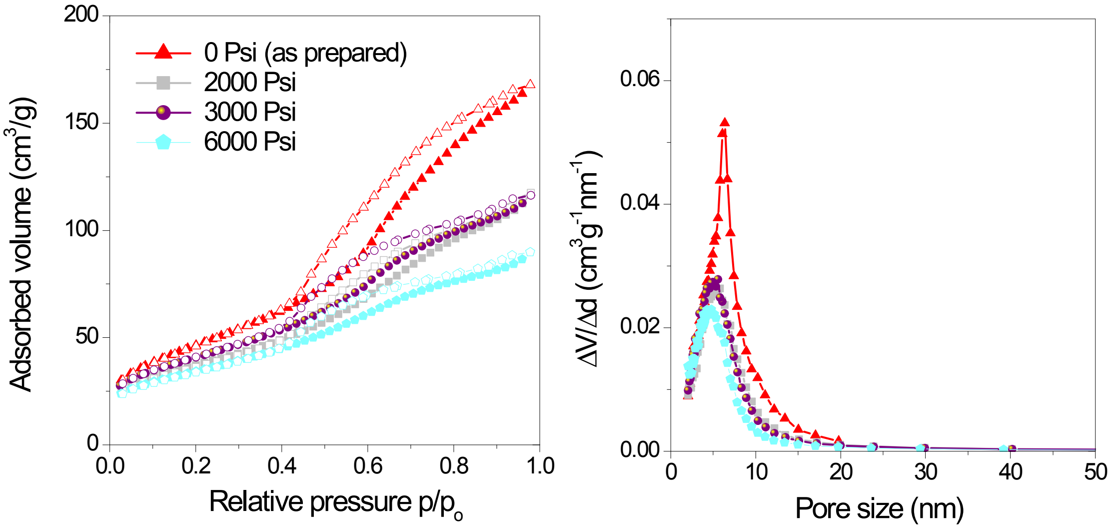

Fig.S4. N_2 adsorption-desorption isotherms and BJH pore size distributions for CrZr5K0.5 nanoreplica pelletizing at different pressures.