

Catalytic Activation of OKO Zeolite with Intersecting Pores of 10- and 12-Membered Rings using Atomic Layer Deposition of Aluminium

Supplementary Information

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Catalysts preparation

-COK-14 was synthesized by slurring freshly calcined IM-12 zeolite in a 12 M HCl solution at 90 °C for two days followed by extensive washing with distilled water until pH 6 was reached. The weight ratio of zeolite to HCl solution was 1:50. The zeolite powder was recovered by filtration, and dried overnight at 60 °C.

Aluminosilicate -COK-14 was obtained by applying Atomic Layer Deposition (ALD) in a home-built deposition chamber with a base pressure of 10^{-4} Pa.¹ 200 mg of -COK-14 powder was highly dispersed onto the ca. 25 cm² bottom of an aluminium tray and placed on top of a resistive heater. Prior to ALD deposition, the powder was kept in vacuum at 200 °C for 90 minutes. The sample temperature was sustained at 200 °C during the ALD process comprising sequential exposures to trimethylaluminium (TMA) and water vapour. The chamber walls were heated to 100 °C and the TMA and H₂O delivery lines to 50 °C to prevent vapour condensation. An ALD cycle consisted of 60 s TMA exposure at 0.3 Pa, 120 s evacuation, 40 s H₂O exposure at 0.3 Pa, and another 120 s evacuation. This cycle was repeated 5 times.

The ALD treated aluminosilicate -COK-14 powder was ammonium exchanged using 20 mL 0.5 M NH₄Cl solution under reflux conditions for 90 minutes, filtered, washed and dried. To obtain the proton form, the ammonium-exchanged aluminosilicate -COK-14 was heated under air at 400 °C.

The all-silica -COK-14 and ammonium-exchanged aluminosilicate -COK-14 samples were loaded with 0.5 wt.% Pt via incipient wetness impregnation with Pt(NH₃)₄Cl₂, washed and dried overnight at 60 °C.

Zeolite characterisation

X-ray Diffraction

X-ray powder diffraction data were recorded on a STOE Stadi MP diffractometer with focusing Ge(111) monochromator (CuK α 1 radiation, $\lambda = 1.54056$ Å) in Debye-Scherrer geometry with a linear position sensitive detector (PSD) (6 °2 θ window) from 6 to 30 °2 θ , a step width of 0.5 degree, internal PSD resolution of 0.01 degree and a step time of 400 s. The samples were continuously rotated in a 0.5 mm glass capillary (Hilgenberg) to improve statistics. Measurements were done at room temperature.

²⁷Al MAS NMR

The ²⁷Al MAS NMR spectrum was recorded on a Bruker Avance400 spectrometer with a magnetic field of 9.4 T. 36000 scans were accumulated with a recycle delay of 100 ms. The sample was packed in a 2.5 mm rotor. The spinning frequency of the rotor was 20 kHz. A 0.1 M aqueous solution of Al(NO₃)₃·9H₂O was used as chemical shift reference.

EDX

EDX analysis of -COK-14 was performed on a FEI Quanta 200F instrument linked to an EDAX Genesis 4000 system for elemental analysis.

FTIR

Infrared spectra were recorded using a Nicolet Nexus FTIR spectrometer. All-silica -COK-14 and aluminosilicate COK-14 were placed in the FTIR cell and outgassed in vacuum at 200 °C and 400 °C,

respectively. All samples were saturated with pyridine vapour at 120 °C. After equilibration, the samples were outgassed at 150 °C and 200 °C and the IR spectra recorded. The Brønsted acidity was evaluated using 1.02 cm μmol^{-1} as extinction coefficient value.

Nitrogen adsorption

The porosity of the samples was determined using nitrogen adsorption at -196 °C (Autosorb-1, Quantachrome). Prior to nitrogen adsorption, the aluminosilicate -COK-14 and aluminosilicate COK-14 were evacuated for 12 h at 120 °C and 350 °C, respectively. The specific surface area, external surface area and micropore volume, and the micropore size distribution were analysed using the BET method, the t-plot method and the SF method, respectively.

SEM

HR SEM images were obtained with a Nova NanoSEM450 (FEI). The powder samples were mounted on aluminium stubs and were imaged without any further modification.

n-Decane hydroisomerisation and hydrocracking

Amounts of 35 mg of zeolite catalyst in ammonium form and with 0.5 wt.% Pt were loaded in quartz reactor tubes with internal diameter of 2 mm. The *n*-decane hydroconversion was performed in a high-throughput reactor with on-line automated reaction product analysis.² The samples were heated in the reactor to 400 °C with a rate of 5 °C/min and pretreated for 1 hour under oxygen flow. After purging with nitrogen for 10 min, a hydrogen flow was supplied to reduce the formed Pt²⁺ to Pt. The H₂/*n*-decane molar ratio in the catalytic experiments was 214, the space time, W/Fo, 980 kg.s/mol and the pressure 0.45 MPa. The reaction temperature was increased stepwise at constant space time. Reaction products were sampled for on-line gas chromatographic (GC) analysis after reaching the reaction temperature set point. The absence of deactivation was verified by returning to initial reaction conditions and verifying conversion a second time 4 months later.

References

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2. W. Huybrechts, J. Mijoin, P.A. Jacobs and J.A. Martens, *Appl. Catal. A-Gen.*, 2003, **24**, 31.