Supporting Information

New Zeolite Al-COE-4: Reaching highly shape-selective catalytic performance through interlayer expansion

Bilge Yilmaz [a, *], Ulrich Müller [b], Mathias Feyen [b], Haiyan Zhang [c], Feng-Shou Xiao [d], Trees De Baerdemaeker[e], Bart Tijsebaert [e], Pierre Jacobs [e], Dirk De Vos [e], Weiping Zhang [f], Xinhe Bao [g], Hiroyuki Imai [h], Takashi Tatsumi [h] and Hermann Gies [i]

[a] BASF Corporation, Chemicals Research and Engineering, Iselin, NJ 08830, USA; [b] BASF SE, Chemicals Research and Engineering, 67056, Ludwigshafen, Germany; [c] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, 130012, Changchun, China; [d] Department of Chemistry, Zhejiang University, 310028, Hangzhou, China; [e] Centre for Surface Chemistry and Catalysis, K.U. Leuven, 3001, Heverlee, Belgium; [f] State Key Laboratory of Fine Chemicals, Dalian University of Technology, 116024, Dalian, China; [g] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, 116023, Dalian, China; [h] Chemical Resources Laboratory, Tokyo Institute of Technology, 226-8503, Yokohama, Japan; [i] Institute of Geology, Mineralogy and Geophysics, Ruhr-University Bochum, 44780, Bochum, Germany

Experimental Procedures

1. Synthesis of layered silicate Al-RUB-36

Layered aluminosilicate Al-RUB-36 was crystallized from a synthesis mixture with a molar composition of SiO_2 : 0.005 Al_2O_3 : 0.5 SDA : 10 H_2O.

Diethyldimethylammonium hydroxide solution (DEDMAOH, 20% solution in water, Sachem Inc.) was used as the structure directing agent (SDA). Aerosil 200 was utilized as the silica source. Sodium aluminate was chosen as the alumina source. Seed crystals (RUB-36) were also used (3 wt. % based on silica amount in synthesis mixture). Crystallization was carried out at 140 °C in an autoclave without stirring for 9 days. The resulting product was filtered, washed and dried at 100 °C.

2. Interlayer expansion of Al-RUB-36 to form Al-COE-3 and Al-COE-4

Dichlorodimethylsilane (DCDMS) was used for interlayer expansion. In a typical preparation, 2.8 grams of Al-RUB-36 powder was mixed in to 120 grams of water, which was then mixed with 50 g of 1 molar HCl solution. After mixing for 5 minutes, 0.4 – 0.7 g of the interlayer silylation agent were introduced and the contents were stirred for 15 minutes. The resulting mixture was then transferred into a Teflon-lined autoclave (300-ml capacity, Berghoff) for thermal treatment at 170 °C for 24 hours, which gave the Al-COE-3 material. Calcination of Al-COE-3 at 500 °C (1°C/min ramp rate, hold for 15 hours) transformed the material into Al-COE-4.

3. Characterization of products

General powder XRD analyses for structural comparison among the set of samples were performed on a D4 Endeavor (Bruker/AXS) unit. High-resolution X-ray powder diffraction data on selected samples were collected at room temperature with a Siemens D5000 diffractometer operating in quasi Debye-Scherrer mode using Cu-Kα_1 radiation with the sample in a capillary sample holder.

4. Preparation of the bi-functional catalyst Pt-Al-COE-4

In an effort to eliminate any residual Na^+ and to improve platinum dispersion, samples were ion-exchanged three times in a solution of 0.5 M NH_4NO_3 at 80 °C for 24 h and washed with distilled water. After washing, the samples were dried at 70 °C. 0.5 wt.% Pt was introduced into Al-COE-4 via ion-exchange as $Pt(NH_3)_4^{2+}$. An aqueous solution of $Pt(NH_3)_4Cl_2$ was utilized for the ion-exchange.

5. Hydroconversion of decane on Pt-Al-COE-4

The decane hydroconversion experiments were performed at temperatures ranging from 160 °C to 260 °C, under 4.5 bar H_2 pressure, at a H_2/HC molar ratio of 375 using a contact time of 2522 kg/s.mol. Before reaction, the Pt-Al-COE-4 samples were first treated with an O_2-flow of 1.9 ml/min at 400 °C for the oxidation followed by a H_2-flow of 3.8 ml/min at 400 °C for the reduction of platinum. An intermediate cooling step was carried out under inert (helium) atmosphere. Samples from the reactor outlet were injected into a capillary GC equipped with a 25 m CPSil5 column, allowing separation of cracked products, n-decane and its monobranched isomers. The dibranched and tribranched decane isomers were combined. Conversion values were calculated from the intensity of the n-decane peak before and during reaction. Isomerization and cracking selectivities, as well as the product distributions, were determined from the respective chromatograms.