Mitigating coking during methylcyclohexane transformation on HZSM-5 zeolites with additional porosity

F. Ngoye [a], L. Lakiss [b], Z. Qin [b], S. Laforge [a], C. Canaff [a], M. Tarighi [a], V. Valtchev [b], K. Thomas [b], A. Vicente [b], J.P. Gilson [b], Y. Pouilloux [a], C. Fernandez [b,*], L. Pinard [a,*]

[a] IC2MP, Université de Poitiers, CNRS, 4 Rue Michel Brunet, 86073 Poitiers, TSA 51106, France
[b] Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Boulevard Maréchal Juin, 14050 Caen, France

ABSTRACT

The effects of two different hierarchization procedures (alkaline and fluoride leaching) on the performances of ZSM-5 catalysts in the transformation of methylcyclohexane at 723 K are highlighted and discussed in relation to their porosities. The hierarchical catalysts exhibit different porosities; namely, the fluoride treatment leads to a zeolite combining micropores and macropores, while alkaline leaching adds mesopores interconnected with the native micropores. While the initial activities and selectivities of catalysts derived from the three zeolites are very similar in the conversion of methylcyclohexane, the presence of mesopores (alkaline leaching), close to the active sites, greatly improves the stability of such a hierarchical catalyst by favoring the desorption of products. This behavior is similar to a reduction in zeolite crystal size. This increased stability is not due to a decrease of the coke toxicity, but rather to an inhibition of the growth of coke precursors, in turn related to the shorter diffusion paths of reactants and products. Two types of coke are present on the meso-/micro-porous zeolite: (i) a "light coke" composed of alkylbenzenes strongly adsorbed on Lewis acid sites and silanols, (ii) a "heavy coke" (alkylphenanthrenes and alkylpyrenes) trapped at the intersection of the zeolite channels. While the light coke has no impact on the catalyst stability, the heavy coke poisons active sites, most probably remote from the mesopores.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Zeolites are among the most successful solid catalysts in oil refining, petrochemicals, and chemicals manufacturing [1,2]. They are crystalline microporous molecular sieves with pore diameters commensurate with many reactants, products, and transition-states [3]. The presence of regular pores of molecular dimensions can have multiple effects on the catalyst lifetime. In favorable cases, the microporous shape selectivity can prevent the formation of the bulkier molecules that block the pores and thus dramatically slow down the catalyst deactivation. In many cases, however, depending on pore shapes and dimensionality, bulky molecules, usually called "coke", can accumulate inside the porous network and impede the diffusion of reactants/products to/from the active sites by pore blocking or poisoning, leading to a rapid deactivation [3–8].

At low temperature, coke consists of non-aromatic compounds while alkylpolyaromatics appear at higher temperature [9]. Coke formation requires condensation and rearrangement steps followed by hydrogen transfer, dehydrocyclization and dehydrogenative coupling [10,11]. At low temperature, the retention of these bulky molecules inside the porous system is mainly due to their low volatility, while at higher temperature, steric blockage plays an important role. As a consequence, the morphology of the coke molecules is mainly determined by the geometry and topology of the zeolite pore system. The size and shape of the micropores, the channel intersections, the external surface apertures determine the shape and the maximum size of the trapped coke molecules [10].

The pore architecture of zeolites is one key feature of coke formation, affecting both the rate and catalytic consequences (toxicity) of deactivation [12,13]. The size and shape of the zeolite crystals also plays a decisive role in coke formation, because diffusion constraints on its precursors in the zeolite micropores increase with crystal size, leading to a faster coking rate [4–6,9,14,15]. Indeed, with small crystals, coke precursors formed near the outer surface can be easily desorbed while with large

crystals, an increased residence time in the micropores favors successive secondary reactions leading to highly polyaromatic molecules. The difference in coke composition with the crystal size is clearly highlighted during methylcyclohexane transformation at 723 K on HBEA zeolites, i.e. in this particular case, (polyaromatic) coke insoluble in methylene chloride appears only on large crystals [9]. Moreover, it was reported that zeolites with hierarchical porosity are more resistant to coke formation: Ryoo et al. showed recently that in the MTH (methanol to hydrocarbons) reaction, catalyst lifetime increases by a factor of three when mesopores are added [16]. The creation of mesopores by post-synthesis treatment of zeolites shortens the diffusion path length in the micropores, reducing condensation reactions and thus coke formation, thereby improving catalyst stability [17–19]. The beneficial effect of hierarchization on the coking of zeolites is thus similar in nature to a reduction in crystal size.

The aim of this work was to establish a relation between the textural properties of different HZSM-5 zeolites (crystallite size and the presence of mesopores and macropores) and the toxicity of coke formed during the methylcyclohexane transformation (MCH). MCH can undergo many reaction pathways e.g. isomerization, cracking, and hydrogen transfer, each giving important information on the state of the working catalyst. Such a model reaction is therefore a good proxy to investigate the coking of zeolites [20,21].

2. Experimental

2.1. Catalysts preparation

The starting material, NH_4-ZSM-5 (Si/Al = 19), is a commercial micro-sized zeolite provided by Clariant (formerly Süd Chemie). The hydrogen form of the zeolite, the parent (P), was obtained by calcination under air flow (150 ml min^{-1}) at 773 K.

Two hierarchical ZSM-5 zeolites, **A** and **B**, were derived from **P** using acidic and basic post-synthesis treatments, respectively. For sample **A**, the fluoride treatment was performed as described by Qin et al. [22]. First, 2.5 g NH_4F was dissolved in 15 ml of 0.3 M HF and 0.2 M of HCl (37 wt.%). 0.5 g of ZSM-5 was then added to the aqueous solution and kept under stirring at room temperature for 6 min. The solid was filtered and subsequently thoroughly washed with distilled water and dried overnight at 373 K. For sample **B**, the alkaline treatment was performed as described by Groen et al. [18]. The parent **P** was first treated in an aqueous solution (0.2 M NaOH, 333 K, 30 min). The H-form of both samples **A** and **B** was obtained by ion exchange with 0.1 M NH_4Cl followed by air calcination at 773 K.

A nano-sized commercial zeolite NH_4-ZSM-5 (noted N) with Si/Al = 41, from Clarian, was also used in this work.

2.2. Characterization techniques

X-ray diffraction (XRD) data were acquired on a PANanalytical (X'Pert Pro MPD) diffractometer over a 5° to 50° 2θ range with a scan rate of 1 K min^{-1} using the Cu Kα radiation (λ = 154.05 pm). Scanning electron microscope (SEM) pictures were recorded on a Tescan (MIRA/LMH) microscope equipped with a field emission gun. Zeolite **N** was characterized by transmission electronic microscopy (TEM) using a Philips CM 120 microscope equipped with a LaB_6 filament.

Elemental analyses were performed using inductively coupled plasma–atomic emission spectroscopy (ICP-AES) on an Optima 4300 DV (Perkin-Elmer).

^{27}Al and ^{29}Si NMR spectra were recorded on a Bruker Avance-400 (magnetic field of 9.4 T) spectrometer using 4 mm rotors spinning at 12 kHz. The ^{29}Si MAS NMR spectra were recorded at 79.4 MHz, using a pulse length of 4 μs (30° flip angle) and a repetition time of 20 s. The ^{27}Al MAS NMR spectra were recorded at 104.3 MHz with a pulse length of 2.2 μs (π/12 flip angle) and a recycle delay of 1 s.

Infrared spectra (FTIR) of pyridine were recorded on a Nicolet Magna 550-FT-IR spectrometer with a 2 cm^{-1} optical resolution. The zeolites are first pressed into self-supporting wafers (diameter: 1.6 cm, 18 mg) and pretreated from room temperature to 723 K (heating rate of 1.5 K/min for 5 h under a pressure of 10^{-6} Torr) in an IR cell connected to a vacuum line. Pyridine adsorption takes place at 423 K. After establishing a pressure of 1 Torr at equilibrium, the cell is evacuated at 523 K to remove all physisorbed species. The amount of pyridine adsorbed on the Brønsted and Lewis sites is determined by integrating the band areas at respectively 1545 cm^{-1} and 1454 cm^{-1} and using the following extinction coefficients: ε_{1545} = 1.13 and ε_{1454} = 1.28 cm mol^{-1}.

A Micromeritics 2020 ASAP gas adsorption analyzer is used for nitrogen sorption measurements. Prior to measurement, the samples are outgassed at 373 K for 1 h and 623 K for 10 h. Specific surfaces areas are determined from the BET equation. The total pore volume corresponds to the nitrogen volume adsorbed at P/P_0 = 0.99, and the t-plot method is used to distinguish micropores from mesopores.

The temperature-programmed desorption of ammonia (NH_3-TPD) profiles was measured using a flow-through micro-reactor system connected to a thermal conductivity detector (TCD). Samples (0.1 g) were activated in air at 773 K for 1 h and then cooled down to 373 K, before adsorption of ammonia for 0.5 h. The physisorbed ammonia was removed by purging with helium at 373 K for 1h30. Ammonia desorption was achieved in the temperature range of 373–823 K with a ramping rate of 10 K min^{-1}.

2.3. Methylcyclohexane transformation

The conversion of methylcyclohexane (MCH, Aldrich, 99% pure) was performed at atmospheric pressure in a downflow fixed bed reactor at 723 K, with a N_2/reactant molar ratio of 6.8 at a contact time (1/WHSV) of 13 min. Before testing, the catalysts were compacted, crushed, and sieved to obtained homogeneous particles (0.2–0.4 mm). The samples were first activated in situ at 723 K under a flow of air (60 mL min^{-1}). The reaction products were analyzed online by gas chromatography using a VARIAN 450 gas chromatograph equipped with a FID detector and a capillary column (CP-Al$_2$O$_3$/Na$_2$O$_4$, 50 m, d_i = 320 μm).

2.4. Spent catalyst characterization

The carbon content was measured using a full burning at 1293 K with a mixture of helium and oxygen in a Thermoquest NA2100 analyzer.

Prior to measuring their residual acidity and porosity, the spent catalysts were outgassed first at 363 K for 1 h and then at 423 K for another hour, whereas the fresh catalysts were outgassed at 523 K overnight.

The chemical composition of coke was determined using the method developed in Poitiers [23,24]. The zeolite was dissolved at room temperature with a 51 wt.% hydrofluoric acid (HF) solution to release, without modification, the molecules trapped in the pores. Then, the coke molecules soluble in methylene chloride were analyzed by GC–MS ("Thermo Electron DSQ" equipped with a DB5 ms column).