Microporous and Mesoporous Materials 164 (2012) 222–231

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Hydroisomerization of *n*-alkanes over Pt-modified micro/mesoporous materials obtained by mordenite recrystallization

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ARTICLE INFO

Article history:
Available online 23 August 2012

Keywords:
Mordenite recrystallization
Micro/mesoporous materials
Hydroizomerization of *n*-hexane, *n*-octane and *n*-hexadecane

ABSTRACT

Hydroisomerization of *n*-hexane, *n*-octane and *n*-hexadecane has been studied over Pt-containing micro/mesoporous materials obtained by mordenite (MOR) recrystallization in alkaline solution in the presence of cethyltrimethylammonium bromide. The degree of recrystallization was controlled by varying the concentration of NaOH. Micro/mesoporous nanocomposites MOR/MCM-41 with intermediate degree of recrystallization showed remarkably high activity and selectivity in hydroisomerization of *n*-octane and high selectivity in hydroisomerization of *n*-hexadecane. The effect is due to high accessibility of the active sites, improved transport of bulky molecules provided by mesopores and optimal size of Pt particles located in mesopores.

1. Introduction

Hydroisomerization of linear alkanes nowadays is among the most demanded technologies for paraffins transformation into high octane gasoline. However, while the processes for hydroisomerization of C_4 and C_5–C_6 cuts are well established (PENEX, ISOTEX, TIP, HYSOMER, ISOFIN, SKIP, PAR-ISOM [1,2]), there is still no suitable technology for the conversion of longer-chain alkanes (C_7–C_8 cuts and higher).

The major difficulty in the isomerization of *n*-alkanes with more than six carbon atoms is their pronounced tendency to cleave. Professor Jens Weitkamp has made a tremendous contribution to the understanding of the influence of an alkane chain length on its hydroisomerization/hydrocracking conversion over bifunctional catalysts [3–11]. He was among the first to show that high selectivity for hydroisomerization of *n*-alkanes with 7–15 carbon atoms can be achieved over Pt-containing zeolite catalysts, such as Pt/CaY and Pt/USY [3–8]. Basing on these early studies he has introduced the term of "ideal" bifunctional hydroconversion of *n*-alkanes, which is characterized by low reaction temperature, high isomerization selectivity and high possibility of pure primary cracking [4]. This "ideal" hydroconversion can be achieved over bifunctional catalysts in which metal phase performs only hydrogenation–dehydrogenation reactions, while isomerization and cracking reactions are catalyzed exclusively by acid sites; the main requirement for such catalysts being careful balance between acidic and hydrogenation functions. The detailed investigations of Weitkamp et al. [3–11] on the distribution of the products from long-chain alkane hydroisomerization and hydrocracking over Pt/zeolites led to the important information on the mechanism of these reactions.

Further studies allowed to quantify the ratio of acid and hydrogenation sites required for the "ideal" hydroisomerization catalyst. This ratio was found to be $n_A/n_{Pt} < 10$ (i.e. 0.5–1 wt.% Pt per zeolite with Si/Al ratio of 7–45) [12,13]. Besides that it was demonstrated that high metal dispersion is required for high isomerization activity [14,15].

Numerous studies were devoted to the investigation of the influence of zeolite structure, pore geometry and acidity on the hydroisomerization activity [16–22]. Among the large number of the catalysts studied zeolites Y [3–8,16], BEA [17–19], ZSM-22, -23 [20] and zeotypes SAPO-11, -31, -41 [20–22] were found to be the most active and selective in hydroisomerization of *n*-heptane and *n*-octane. These results pointed that zeolites modified with nobel metals are among the most perspective catalysts for hydroisomerization *n*-alkanes with more than six carbon atoms. The main drawbacks related to these catalysts are rather low efficiency and limited selectivity at high conversion levels [23,24].

The kinetic studies performed for hydroisomerization of various alkanes and their mixtures over Pt/MOR catalyst pointed that for C_5–C_6 alkanes in low pressure range (<4 bar) the rate-limiting step is the isomerization reaction on acid sites, while at higher pressures of n-C_6 and for *n*-alkanes with more than six carbon atoms the reaction is limited by diffusion [25]. The effectiveness factor for transformation of *n*-hexane over Pt/mordenite calculated

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http://dx.doi.org/10.1016/j.micromeso.2012.08.017

basing on Thiele model pointed that only 30–40% of zeolitic pore system is involved in the catalytic reaction [23,24]. Hydroisomerization of *n*-octane over Pt-Pd containing SAPO-11 and SAPO-41 catalysts was shown to occur at the pore mouths, at a short distance from the external surface of the crystal [21,22].

It has been demonstrated that the diffusion limitations can be reduced or even cancelled by the creation of mesopores in zeolitic crystals [23,24,26–30]. Thus, the creation of mesopores by dealumination procedure was shown to alleviate intracrystalline diffusion limitations for *n*-hexane in mordenite pore system and therefore resulted in fourfold increase of its hydroisomerisation activity [23,24]. Besides that, selectivity to monobranched isomers was increased due to easier desorption of products.

Since 1992, when mesoporous molecular sieves have been discovered, numerous studies have been devoted to the investigation of *n*-alkane isomerization over mesoporous and composite micro/mesoporous materials [31–34]. It has been observed that although zeolites Pt/ZSM-5, Pt/ZSM-22, Pt/H-β [34] with strong acid sites show relatively higher activity than mesoporous Pt/Al-MCM-41 catalysts, they give mainly hydrocracking products. At the same time, mesoporous Pt/Al-MCM-41 catalysts show considerably high selectivity to isoalkanes and the highest yield of multibranched isoalkanes due to their weaker acidity and transport properties [34].

The development of composite micro/mesoporous materials [26–30] opens new perspectives for the improvement of hydroisomerization activity of zeolitic catalysts. These materials combine the advantages of both zeolites and mesoporous molecular sieves, in particular, strong acidity, high thermal and hydrothermal stability and improved diffusivity of bulky molecules. It can be expected that the creation of secondary mesoporous structure, on the one hand, will result in the improvement of the catalytic activity in hydroisomerization process and, on the other hand, will lead to the decrease of the residence time of products and minimization of secondary reactions, such as cracking.

In this paper we present the results on the effect of mesoposity on hydroisomerization of *n*-hexane, *n*-octane and *n*-hexadecane over Pt-containing micro/mesoporous materials obtained from commercially dealuminated mordenite. The composite micro/mesoporous materials with different degree of mesoporosity were prepared by mordenite recrystallization, the procedure, which has been successfully used for the synthesis of hierarchically structured porous materials from various zeolites [35–40].

2. Experimental

Dealuminated mordenite (MOR) with Si/Al = 45 supplied by Zeolyst was used as a starting material. Composite micro/mesoporous materials were obtained by two-step procedure including partial destruction of zeolite in NaOH aqueous solution, followed by its hydrothermal treatment in the presence of cethyltrimethylammonium bromide (CTMABr) at 373 K [32]. The degree of recrystallization was adjusted by variation of NaOH concentration (0.5, 0.8, 1.6 M). The materials obtained were denoted as RM-1, RM-2 and RM-3.

Products were recovered by filtration, washed thoroughly with distilled water and dried overnight. The organic template was removed by calcination in a dry air flow at 823 K for 24 h. Afterwards the samples were subjected to threefold ion-exchange with aqueous solution of 0.1 M ammonium nitrate. After ion-exchange the materials were washed, dried overnight and calcined in a dry air flow at 823 K.

Platinum was deposited by incipient wetness impregnation with $Pt(NH_3)_4Cl_2$ aqueous solution. The content of Pt was 0.7 wt.%.

The chemical composition of the samples was determined by atomic emission spectroscopy (AES). X-ray diffraction (XRD) data in the region of $5 < 2\theta < 80$ were obtained on a DRON-3M powder diffractometer using CuKa radiation. The diffraction data in the range $0 < 2\theta < 5$ were recorded at the station DICSY in Kurchatov Institute. Transmission electron microscopy images (TEM) were obtained using JEOL JEM 2010 electron microscope, operating at 200 kV.

Sorption/desorption isotherms of nitrogen were measured at 77 K using an automated porosimeter (Micromeritics ASAP 2000). Micropore volumes (V_{micro}) were determined using *t*-plot method. The total sorbed volumes (V_{tot}), including adsorption in the micropores and mesopores and on the external surface, were calculated from the amount of nitrogen adsorbed at relative pressure p/p_0 of 0.95, before the onset of interparticle condensation.

The acidic properties were studied by temperature programmed desorption of ammonia (TPD-NH_3) and FTIR spectroscopy of adsorbed probe molecules. TPD experiments were carried out on chemisorption analyzer USGA-101 (UNISIT) in the temperature range of 293–1053 K in a flow of dry He (30 ml/min). The rate of heating was 8°/min IR spectra were recorded with a Nicolet Protégé 460 FT-IR spectrometer at 2 cm^{-1} optical resolution. Prior to the measurements, the catalysts were pressed in self-supporting discs and activated in the IR cell attached to a vacuum line at 723 K for 4 h. Adsorption of pyridine (Py) and 2,4,6-treemethylpyridine (TMPy) was performed at 423 K for 30 min. The excess of probe molecules was further evacuated at 423 K for 1 h. The adsorption – evacuation was repeated several times until no changes in the spectra were observed.

Hydroisomerization of *n*-alkanes was performed in a fixed bed flow reactor under 2 MPa and in the temperature range of 430–600 K. Weight hourly space velocity of *n*-alkane was 2.0 g/(g h) and the molar ratio of *n*-alkane: H_2 = 1:5. The analysis of the products was performed on GC using 50 m capillary column SE-30.

3. Results and discussion

3.1. Characterization of micro/mesoporous catalysts

3.1.1. Structure and texture

The typical procedure for the preparation of micro/mesoporous materials by zeolites recrystallization involves treatment of parent zeolite in NaOH aqueous solution followed by hydrothermal treatment in the presence of CTMABr [35–40]. The alkaline treatment induces partial dissolution and extraction of highly siliceous fragments of the structure from the zeolite resulting in perforation of zeolite crystals by mesopores. The following hydrothermal step in the presence of CTMABr leads to the assembling of these dissolved species into mesoporous phase, which, depending on the degree of zeolite dissolution, either just covers zeolite surface, or forms Zeolite/MCM-41 composites, or completely immerses the residual zeolite.

Variation of dissolution level is the most important parameter for tuning the textural characteristics of recrystallized materials. It can be controlled by the variation of the time of alkaline treatment, temperature or alkalinity of the solution, the latter being the most important factor [36]. In the present work, by varying the NaOH concentration in the range of 0.5–1.6 M, a series of recrystallized mordenites with low, intermediate and deep degrees of recrystallization are synthesized. The characteristics of the parent and recrystallized materials are given in Table 1.

The comparison of the chemical composition of the parent and recrystallized mordenites (Table 1) shows that the recrystallization does not affect significantly the overall Si/Al ratio, as it is observed in the case of alkaline-mediated mesoporous mordenites [41,42]. This effect is due to the involvement of dissolved siliceous species in the formation of mesoporous phase during recrystallization