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BEA zeolite nanocrystals dispersed over alumina for *n*-hexadecane hydroisomerization

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ABSTRACT

The direct synthesis of BEA nanocrystals was performed on an α-Al_2O_3 surface, in order to avoid the typical aggregation of the zeolite, which causes diffusion limitations. Two different composite samples, with different zeolite loadings were synthesized and compared with a pure BEA nanocrystals sample (similar synthesis gel composition). The characterizations showed that both the BEA zeolite sample and the zeolite nanocrystals on the composite samples had similar textural and acidic properties. However, through TEM and SEM characterizations it was possible to confirm not only the smaller occurrence of zeolite aggregates on the composite samples, but also the existence of completely isolated BEA nanocrystals, indicating the success of the synthesis procedure.

The catalytic test results of *n*-hexadecane hydroisomerization, at 220 °C and 30 bar, showed a positive effect of the decrease in nanocrystal agglomeration on both activity and isomers selectivity. The composite catalysts were 3.5 times more active than the pure zeolite sample and the maximum isomers yield increased from 35 to 80 wt.%.

1. Introduction

The Fischer–Tropsch waxes composed, mainly, of linear paraffins must be upgraded for liquid fuel or lubricant base oil applications [1,2]. The catalytic dewaxing process, through skeletal isomerization of the paraffins, reduces the pour points, enhancing the low temperature properties of diesel and lubricating oils [3]. The skeletal branching of *n*-alkanes is achieved using bifunctional catalysts containing both metallic sites, for the dehydrogenation and hydrogenation reactions, and acidic sites for the isomerization (and cracking) reactions [3]. Zeolites loaded with platinum or palladium have been widely used for this purpose [4,5]. The olefins formed from the paraffins through dehydrogenation on the metallic sites are protonated on the acidic sites into an alkylcarbenium ion. This ion undergoes skeletal rearrangement and eventually, cracking through β-scission [6,7]. The later is favored as the branching degree of the carbon chain increases. Consequently, high isomers selectivity is directly linked to low cracking rates.

When the hydrogenating function is highly active, the activity and selectivity will depend on the number, the strength and the location of the acidic function [8–10]. Therefore, a decrease in acidity will lessen not only cracking but also the global activity, since the acid step is rate limiting. The zeolite pore structure can also modify the activity and the selectivity of the bifunctional catalyst [1,5,11–14]. If the geometry and the dimensions of the zeolites pores are such that cracking is suppressed by molecular shape-selectivity, the yield in isomerization is improved substantially [1,5,15]. For instance, PtHZSM-22 (10 MR zeolite, TON framework structure) is very selective for the production of monobranched isomers [15–17]. Indeed, since the reaction intermediates are too bulky to be formed within the ZSM-22 channels the reaction only takes place at the pore entrance ("*pore mouth catalysis*") limiting the formation of monobranched isomers [15–17]. Nonetheless, the consequence of this small penetration is a rather low activity of the catalyst [18]. The molecular shape-selectivity obtained with the ZSM-22 zeolite is lost on similar pore size zeolites with two- or three-dimensional pore systems, *i.e.* ZSM-5 and MCM-22. On these supports the reaction occurs inside the zeolite channels resulting in high cracking yields. Indeed, the reaction intermediates are blocked inside the channels where they crack after multi-isomerization steps [19]. In order to avoid this phenomenon, Christensen et al. introduced, through disilication, a complementary mesoporous system in ZSM-5 zeolites reducing the isomers residence time inside the zeolite framework and, consequently, limiting cracking [20]. As a result, better acid site accessibility and rapid isomers desorption outside the zeolite crystal improved both hydroisomerization activity and selectivity.

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Soualah et al. have shown that PtHBEA (12MR, BEA framework structure) was more active and more selective for the hydroisomerization of long *n*-alkanes (n-C_{14}, n-C_{16}) than catalysts based on MCM-22 or ZSM-5 zeolites [19]. This was explained by a rapid diffusion of the reactant and reaction intermediates inside the large channels of the BEA zeolite. Yet, the PtHBEA catalyst yielded significant amounts of cracked products due to rather strong protonic acidity. Thus, decreasing the zeolite acidity would decrease the cracking reactions rate. This was confirmed by Merabti et al., using partially sodium exchanged BEA zeolites, which showed an isomerization selectivity similar to that of ZSM-22 [18]. Nonetheless, this was achieved with a 75% loss of the BEA zeolite activity, even if the PtNaHBEA ($0.7\ g_{n\text{-}C_{16}}\ g_{cat}^{-1}\ g^{-1}$) catalyst remained two times more active than PtHZSM-22 ($0.3\ g_{n\text{-}C_{16}}\ g_{cat}^{-1}\ g^{-1}$).

Like for the ZSM-5 zeolite, the reduction of the isomers residence time inside the BEA zeolite crystal would positively enhance the selectivity towards isomerization. Moreover, this approach would not cause an activity loss. Zeolite nanocrystals are often used for this purpose [21–24]. However, the BEA nanocrystallites aggregate into micrometric clusters, more than 1 μm, creating an intercrystalline disordered porous system, which alters the molecular diffusion [25,26]. Lima et al. showed that the diffusivity values of *n*-alkanes obtained from zeolite BEA nanocrystals were extremely low when compared to those of zeolites with similar pore aperture, *e.g.* FAU [26]. The authors suggested a possible influence of extracrystallite diffusion. Thus, in order to improve the catalytic properties, it is essential to avoid the BEA crystallite agglomeration in order to minimize the isomers residence time inside the zeolite catalyst. This can be obtained by the direct BEA zeolite germination on a support, such as alumina [27]. Lovallo et al. have shown that in the case of nanocrystal zeolites (<100 nm), the matrix impedes growth and aggregation [28].

The purpose of this work was to study the structural and the morphological properties of a zeolite–alumina composite obtained by mixing a zeolite synthesis gel with alumina particles. *n*-Hexadecane hydroisomerization was chosen as the model reaction to check if a self-organized zeolite nanocrystal allowed to obtain a high activity together with a high selectivity into isomers. For this purpose, the catalytic performance of a BEA nanocrystalline zeolite was compared with those of composite materials with different zeolite loadings.

2. Experimental

2.1. BEA coated alumina synthesis

Particles of α-Al_2O_3 were used as support for the BEA nanocrystals germination, due to their high stability. They were obtained from extrudates supplied by PREMICAT (University of Poitiers), which were crushed and sieved to 0.2–0.4 mm particles (particle size required for the catalytic testing).

The supported zeolite synthesis was carried out using the following precursor gel molar composition: $23.6SiO_2{:}1.0Al_2O_3{:}1.9NaO_2{:}1.9TEA_2O{:}235H_2O$. The alumina particles were then mixed with the gel in a PTFE lined autoclave and the synthesis was performed under hydrothermal conditions at 155 °C during 7 days without stirring. Two samples were synthesized with a weight ratio between the synthesis gel and alumina of 5/1 and 5/3. Consequently, the two resulting samples were called HL (ratio 5/1) and LL (ratio 5/3), respectively, for high loading and low loading of BEA zeolite over the alumina support.

In addition, a synthesis without alumina particles was also done, in order to be used as reference (noted BEA). After crystallization, the samples were filtered and rinsed several times with distillated water. The resulting solids were subsequently dried at 90 °C overnight. Then, the organic template was removed through calcination at 550 °C for 12 h under air flow. The zeolites ammonium forms were prepared by ion exchange of the raw materials with a 2 M ammonium nitrate solution, 50 mL g^{-1} of catalyst, under reflux during 1 h at 80 °C. This procedure was performed twice. The protonic form of the materials was obtained by calcination in a muffle furnace at 450 °C. The alumina particles coated with zeolite were recovered by sieving. In order to remove the weakly anchored zeolite particles, the materials were sonicated in distillated water during 10 min. Then these wet materials were dried at 90 °C and re-sieved to obtain 0.2–0.4 mm particles.

Platinum was introduced into the samples (BEA, LL and HL) through ion exchange by $[Pt(NH_3)_4]^{2+}$ in competition with NH_4^+ ($NH_4^+/Pt = 100$), followed by calcination under a dry air flow at 450 °C for 4 h. The amount of platinum in solution was calculated to reach 1 wt.% on the bifunctional catalyst.

2.2. Physicochemical characterization

The structural characterization of the zeolite and composite samples was carried out by X-ray powder diffraction (XRD). The XRD patterns were obtained on a D5005 BRUKER AXS diffractometer using a Cu-Kα radiation ($\lambda = 1.5406$ Å) as incident beam. The zeolite crystal sizes were calculated through the Scherrer equation.

Nitrogen adsorption and desorption measurements were carried out at −196 °C over a Micromeritics ASAP 2010 apparatus. Prior to analysis, the samples were pretreated at 350 °C under vacuum for 8 h. The specific surface area was determined by the BET method [29] and the micropore volume (pore diameter < 2 nm) was estimated through the *t*-plot method applied to a layer thickness between 5 to 7 Å [30,31] and the Dubinin–Raduskevitch method [32], which enabled to distinguish between ultra-micropores (pore diameter < 0.8 nm) and super-micropores (pore diameter between 0.8 and 2 nm). Consequently, the mesopore volume was determined by the difference between the total pore volume, determined at 0.97 of relative pressure, and the micropore volume.

The zeolite framework aluminum (Al_{Fram}) content was determined by infrared spectroscopy measurements on a FT-IR Magna 550 Nicolet spectrometer. The position of the zeolite structure bands (450–1250 cm^{-1}) and especially that of the asymmetric stretching vibration (νTOT) at 1080–1200 cm^{-1} allowed to calculate the Al_{Fram} from the correlation given in literature [33]. The TOT bands were determined using KBr wafers containing 2 wt.% of sample. The acidity of the samples was measured by infrared spectroscopy of adsorbed pyridine. The concentration of the Brønsted and the Lewis acid sites were calculated from the integrated area, after pyridine adsorption at 150 °C, of the PyH^+ and PyL bands at 1545 and 1450 cm^{-1}, respectively. The experimental methods were described in details in a previous paper [34].

The catalyst morphology was observed through scanning electron microscopy (SEM) performed on a FEG-SEMJEOL microscope (JSM 5600-LV model). The mapping of the silicium element on the coated catalysts was performed on an energy dispersive X-ray (EDX) scanning Brucker apparatus.

The bifunctional catalysts were characterized by transmission electronic microscopy (TEM) using a Philips CM 120 microscope equipped with a LaB_6 filament. To prepare the sample, a small drop of a zeolite suspension in ethanol was put on an Au grid and the solvent was evaporated. TEM observations allowed determining the zeolite crystallite size and the platinum particles average size, as well as the metal location on the zeolite and on the α-Al_2O_3. The platinum size determination was done on the average of 500 particles, assuming that metallic particles were sphere-like.

2.3. Hydroisomerization reaction

The transformation of n-C_{16} (Aldrich, >99.9% purity) was carried out in a fixed-bed stainless steel reactor under the following