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Comparison of zeolites LaX and LaY as catalysts for isobutane/2-butene alkylation

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Abstract

Lanthanum exchanged X and Y type zeolites were prepared by ion exchange and investigated as catalysts for isobutane/2-butene alkylation. With the reactions performed in a continuously operated stirred tank reactor under industrially relevant conditions ($T = 348$ K, $p = 20$ bar, paraffin/olefin molar ratio = 10, olefin weight hourly space velocity = $0.2\ h^{-1}$) the catalyst lifetime of LaX was nearly twice as long as that of LaY. Moreover, a much higher yield of octane isomers was observed with LaX. The product distributions showed that LaX had a high activity for hydride transfer and "self-alkylation" as well as a higher concentration of strong Brønsted acid sites. These differences are related to a higher residual concentration of sodium cations in LaY leading not only to less, but also weaker strong Brønsted acid sites in LaY than in LaX. The replacement of the residual sodium cations by lanthanum cations is less favorable in LaY due to the lower concentration of appropriate sites to accommodate multivalent cations.

Keywords: Acidity; Hydride transfer; MAS NMR; Lanthanum; Brønsted acid site; Alkylation; Ion exchange

1. Introduction

Isobutane/2-butene alkylation is an important petrochemical process for the production of a mixture of branched alkanes with high octane numbers. The concentration of sulfur and aromatic compounds in alkylate is very low, making it an ideal blending component for gasoline. The importance of alkylate is expected to increase further as the octane booster methyl-*tert*-butyl-ether is phased out in many industrial countries. Currently, industrial alkylation units use hydrofluoric or sulfuric acid as catalysts [1]. However, hydrofluoric acid is highly toxic and aerosols are easily formed. Therefore, its industrial application is progressively restricted. For the sulfuric acid based processes, acid consumption can reach 70–100 kg/t [2]. The spent catalyst must be regenerated in an expensive process removing water and tarry hydrocarbons. Consequently, considerable efforts have been made to replace hydrofluoric or sulfuric acid by solid acids, which are easier to handle and more environmentally benign [3,4]. Zeolites received the most attention among the solid acid catalysts tested for this reaction [5–20]. However, so far, rapid deactivation has prevented industrial application of solid acid catalysts [19–23].

The product distribution in isobutane/2-butene alkylation is determined by the relative rates of three main reaction steps: olefin addition, isomerization and hydride transfer [24]. In particular, a high ratio of hydride transfer to olefin addition is important to prevent the formation of oligomers, which strongly adsorb on the catalyst and, thus, lead to deactivation [19]. Part of this problem may be solved by application of frequent regeneration steps [11,17,22,25,26] and operation of the reaction at low olefin concentrations in a continuously operated stirred tank reactor [6]. However, optimization of the catalytic properties remains the most important task.

Only large pore zeolites are suitable for isobutane/2-butene alkylation, as diffusion limitations in medium and small pore zeolites lead to premature deactivation [27,28]. It was shown that zeolites with three dimensional pore networks allow more

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efficient diffusion of the products, which leads to an increase of the catalyst lifetime [29].

Although it is generally accepted that Brønsted acid sites are the active sites for isobutane/2-butene alkylation, there is an ongoing debate about the extent, to which the concentration and strength of Brønsted acid sites influence the catalytic activity and stability [2,16,30,31]. Feller et al. suggested that a high ratio of Brønsted to Lewis acid sites and a large fraction of strong Brønsted acid sites are key parameters for an extended catalytic stability [8]. Strong Brønsted acid sites are capable of stabilizing the charge separation in the transition state for reactions such as hydride transfer [24]. Strong Lewis acid sites promote the formation of unsaturated deposits, which lead to deactivation of the catalyst [13,19,31].

Several authors suggested that hydride transfer is favored for zeolites with a low Si/Al ratio [32,33]. In contrast, Yoo and Smirniotis found that the catalytic performance for isobutane/2-butene alkylation of zeolite beta hardly changed, when the Si/Al ratio was varied from 6 to 15 [5]. Only for a Si/Al ratio of 30, reduced activity was found.

Lanthanum exchanged faujasites are among the most promising candidates for zeolite catalyzed isobutane/2-butene alkylation [8,9,13,21,22,34,35]. Particularly interesting is LaX, in which a high concentration of strong Brønsted acid sites can be achieved [8,9,21,35]. However, the presence of La^{3+} influences the properties of zeolites in a complex way. After calcination, most La^{3+} cations are located in the sodalite cages [36]. For zeolite Y, La^{3+} cations stabilize the lattice better than mild steaming leading to H-USY [37]. However, the La^{3+} cations may generate also strong Brønsted acid sites by hydrolysis of water [35,38,39]. In this context, it has been suggested that incorporation of La^{3+} cations leads to an increase in the strength of Brønsted acid sites *via* polarization of the zeolite framework [37]. It should also be noted that extraordinarily strong polarization of sorbed alkanes on LaX has been reported [40].

It is therefore of interest, to what extent the concentration of aluminum influences acid strength, hydride transfer and alkylation. Here, lanthanum exchanged zeolites X and Y, which both have a faujasite structure but different Si/Al ratios, were compared as catalysts for isobutane/2-butene alkylation. The differences in the catalytic performance are related to the physicochemical properties of the catalysts, in particular, Brønsted acidity.

2. Experimental

2.1. Catalyst preparation

La-exchanged zeolite X (LaX) was prepared from NaX (Si/Al = 1.1) provided by Chemische Werke Bad Köstritz. NaY from Akzo Nobel (Si/Al = 2.4) was used for the preparation of lanthanum exchanged zeolite Y (LaY). Both catalysts were prepared following the same ion exchange procedure, which was shown previously to provide almost quantitative ion exchange for LaX [35]. The parent material was ion exchanged twice in 0.2 M $La(NO_3)_3$ for 2 h at 353 K using a ratio of solution to zeolite of 11 ml g^{-1}. The zeolite was thoroughly washed with bi-distilled water and dried at room temperature. Then, the sample was calcined in a flow of air with a heating rate of 0.5 K min^{-1} up to 723 K. After rehydration on air, three additional ion exchange steps followed by washing, drying, calcination and rehydration were applied.

2.2. Alkylation reaction

The alkylation reactions were performed in a continuously operated stirred tank reactor with a volume of 50 ml. Prior to reaction, the catalyst was activated *in situ* at 453 K for 14 h in H_2. Then, the reactor was cooled to 348 K, pressurized with H_2 to 20 bar and filled with pure isobutane (AIR LIQUIDE, 99.95%). The reaction was started by feeding a mixture of isobutane and 2-butene (Messer, 99.4%) with a molar ratio of 10/1. The olefin space velocity was 0.2 $g_{butene}g_{catalyst}^{-1}h^{-1}$ and the stirring rate 1600 rpm. Samples from the product stream were taken periodically and analyzed with a HP 6830 gas chromatograph equipped with an FID-detector and a 50 m DB-1 column.

2.3. Physicochemical characterization

For atomic absorption spectroscopy (AAS), 20–40 mg of the sample was dissolved in 0.5 ml of hydrofluoric acid (48%) and heated to 343 K until the entire liquid was evaporated. The residue was dissolved in water and the concentrations of silicon, aluminum, and sodium were determined with a UNICAM 939 atomic absorption spectrometer.

The lanthanum content was measured by neutron activation analysis (NAA). Aliquots of 40 mg of each sample were closed in PE-bags and co-irradiated with a Al–Au monitor for 5 min in position Strang-6 at the FRM-II reactor in Garching, Germany. Five days after irradiation, the samples and Al–Au monitor were counted at positions of 15 cm from calibrated detectors. The k_0-method [41] implemented in the program MULTINAA [42] was applied to calculate all the elements in the samples. In this work, the nuclide ^{198}Au of the co-irradiated Al–Au monitor was used as the comparator in the k_0-method.

The BET surface area and micropore volume were determined by nitrogen physisorption on a PMI Automated BET Sorptometer. Prior to the measurements, the samples were heated to 393 K for 2 h in vacuum.

The unit cell size of the samples was determined by XRD. The position of the signals was referenced against silicon powder. A Philips X'Pert Pro System (Cu Kα1-radiation, 0.154056 nm) was used at 40 kV/40 mA. The measurements were performed with a step scan of 0.0047° min^{-1} from 50° to 60° 2θ.

Acid site concentrations were obtained from IR spectra of adsorbed pyridine. The samples were pressed into self-supporting wafers, dried in vacuum at 393 K for 4 h and activated at 453 K for 8 h to remove most of the physisorbed water. The heating rates were 5 K min^{-1}. Pyridine was adsorbed at 423 K with a pressure of 0.1 mbar until no changes were observed in the spectrum. The samples were outgassed for 1 h to remove weakly physisorbed pyridine and a spectrum was