



Propane aromatization on hierarchical Ga/HZSM-5 catalysts

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ABSTRACT

Gallium containing ZSM-5 zeolites were prepared by ion exchange and mechanical mixture from the parent ZSM-5 and two desilicated zeolites to be tested in propane aromatization. The alkaline treatment was made by sodium hydroxide, with or without tetrabutylammonium hydroxide. The catalysts prepared from desilicated zeolites are less active in propane aromatization and cyclohexane transformation and less selective into aromatics than those prepared from the parent zeolite. The desilication did not affect the acid properties, especially the strength of acid sites as seen by CO adsorption at 77 K and *n*-hexane cracking.

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1. Introduction

The selective transformation of light alkanes into aromatics, that are more valuable and versatile feedstocks for the chemical industry, becomes again one of the major challenges of catalytic chemistry. ZSM-5 doped with gallium is a bifunctional and good proven catalyst for the aromatization of propane [1]. Ga can be incorporated into zeolite by different methods: ionic exchange [2–5], impregnation using Ga salts [6–8], mechanical mixing of Ga₂O₃ [9,10] with zeolite followed by thermal treatment. These different preparation methods of the bifunctional catalyst result in different possible initial locations of gallium: framework, extra-framework, exchange position or on external surface, as well as different oxidation states (0, +I, +III) [9,11–13]. At high temperature and under hydrogen atmosphere (T > 873 K), a reductive solid ionic exchange occurs through the diffusion of gallium suboxide in the zeolite micropores [7,9,14–22].

The creation of mesopores connected to the zeolite micropores appears as a simple method to improve both the diffusion of the mobile species and the level of connection between the two networks as well their diffusion efficiency. Through NaOH desilication [23], intracrystalline mesopores are created and the concentration of Brønsted acid sites are maintained, while the addition of a surfactant agent, such as tetrabutylammonium hydroxide (TBAOH), allows mesopores shaping [24].

The intracrystalline mesopores are like “highways” for mobile gallium species, the reactants and the products, improving both the accessibility of Ga₂O to protonic sites, the reactants to the active “bi-sites” (gallium cations and neighboring zeolite oxygen anions [25]) and products desorption.

The increase of the catalyst’s lifetime on the hierarchical zeolite is attributed to the enhancement of the mass transfer of products (coke precursors) to the external surface where they accumulate. Therefore, hierarchized materials appear to be more susceptible to coking; more coke is required to totally deactivate the catalyst [26,27].

Ogunronbi et al. [27] have shown, that the presence of intracrystalline mesopores is also beneficial for the aromatic compounds yield due to better penetration of gallium species within the zeolite crystal either during the cationic exchange or/and the reduction treatment. These combined effects result in the formation of a larger number of active species (gallium hydride) and a better distribution (Dispersion).

The aim of this study is to confirm that the presence of intracrystalline mesopores is beneficial to propane dehydrocyclization. Two series of bifunctional catalysts were prepared by mechanical mixture and ionic exchange from a ZSM-5 zeolite desilicated by NaOH with or without TBAOH; the gallium content ranging up to 6.8 wt%. The nature and acidic properties, concentration and strength of sites were characterized by using two probe molecules, pyridine for the nature and the number of acid sites and CO for their strength. The acidic, dehydrogenation and dehydrocyclisation properties were evaluated by using three model reactions:

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n-hexane cracking, transformation of cyclohexane and propane aromatization, respectively.

2. Experimental

2.1. Catalysts preparation

The generation of mesopores inside a commercial NH₄-ZSM-5 zeolite (CBV 8014) was carried out by using NaOH (0.2M, pH = 13.3 at 298 K) [23], or NaOH with TBAOH ([TBAOH + NaOH] = 0.2) [24], at 338 K for 30 min. The pH of solution after the alkaline treatment is around 12. The solution is cooled in ice in order to stop the zeolite modification. The desilicated zeolites, noted H_{NaOH} and H_{NaOH+TBAOH}, respectively, were calcined at 773 K for 12 h, then exchanged by a solution of NH₄NO₃ at 333 K for 1 h (three times), dried and calcined at 773 K for 12 h. H_{NaOH} and H_{NaOH+TBAOH} were washed with a solution of 0.1M HCl at 343 K for 6 h, then washed with distilled water, dried and calcined at 773 K.

The bifunctional catalysts with different gallium content were prepared by mechanical mixture (MM) (0.5–10 wt% Ga) or ionic exchange (IE) (0.5–6.8 wt% Ga). MM series (Ga+ zeolite), were simply obtained by mixing the zeolite (P, H_{NaOH} or H_{NaOH+TBAOH}) with β-Ga₂O₃ (purity 99.99%; Alfa Aesar); where P is the proton form obtained by calcination of the NH₄-ZSM-5 zeolite in a muffle furnace at 773 K (5 K min⁻¹) for 12 h.

The powders were mixed and milled several times in a mortar to ensure a homogeneous distribution of the catalysts. The bifunctional catalysts obtained by mechanical mixture will be named as follows: Ga + P, Ga + H_{NaOH} and Ga + H_{NaOH+TBAOH}. IE series (Ga/zeolite) was carried out at 373 K for 3 h with Ga(NO₃)₃ (purity 99.90%; Sigma Aldrich) by using a volume of the exchange solution per gram of zeolite of 100. Then, the material was calcined at 773 K for 12 h with a temperature increasing rate of 5 K min⁻¹. The bifunctional catalysts obtained by ionic exchange will be named as follows: Ga/P, Ga/H_{NaOH} and Ga/H_{NaOH+TBAOH}.

2.2. Characterization

The elemental composition of the bifunctional catalysts (Si, Al, Ga) was measured by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on an Optima 2000 DV (Perkin-Elmer). The crystals size and morphology were determined by scanning electronic microscopy (SEM) on a FEG-SEMJEOL microscope (JSM 5600—LV model) and by transmission electronic microscopy (TEM) on a Philips CM 120 microscope equipped with a LaB₆ filament. The crystallinity of the zeolite was obtained by using a PAN analytical (X'Pert Pro MPD) diffractometer over a 5–50° 2θ range using the CuKα radiation (α = 154.05 pm). The textural properties were determined by nitrogen sorption measurements at 77 K, on a Micromeritics ASAP 2000 gas adsorption analyser. Prior to measurement, the samples were outgassed at 623 K for 4 h after a plateau at 363 K for 1 h. The acidity of the samples and the strength of the OH groups were measured by adsorption of two probe molecules followed by infrared spectroscopy: pyridine at 423 K and carbon monoxide at 77 K, respectively. CO is injected stepwise in the IR Cell through a calibrated volume (0.9837 cm³) pressurized between 50 and 500 mbar. The FT-IR measurements were carried out on a Nicolet 750 Magma FTIR 550 spectrometer (resolution 2 cm⁻¹). Samples were pressed into thin wafers (≈20 mg) and activated in situ in the IR cell under secondary vacuum (10⁻⁶ mbar) at 623 K. Prior to measurement, the samples were treated for 12 h either under air (100 mL min⁻¹) at 723 K (2 K min⁻¹) or under hydrogen (100 mL min⁻¹) at 873 K. Adsorption of pyridine at 423 K probed the Brønsted and Lewis acid sites and their concentrations were calculated by integrating the band

areas at 1545 and 1451 cm⁻¹ by using extinction coefficients 1.13 and 1.28 cm·μmol⁻¹, respectively [28]. The temperature-programmed reduction (TPR) measurements were carried out using a Quantachrome Autosorb 1-C analyser. The catalyst (200 mg) was pre-treated in situ at 373 K (5 K min⁻¹) for 1 h under helium (He) flow (30 mL min⁻¹). After cooling to room temperature under He (30 mL min⁻¹), the reduction was carried out up to 1273 K under H₂ (1 vol%) diluted in argon (Ar) with a flow rate of 30 mL min⁻¹ and a heating rate of 5 K min⁻¹.

2.3. Catalytic tests

Cyclohexane transformation at 803 K: the bifunctional catalysts (100 mg) were reduced under hydrogen (90 mL min⁻¹) at 873 K for 10 h. The cyclohexane transformation was carried out in a down-flow fixed-bed reactor at 803 K, at atmospheric pressure with a H₂/cyclohexane molar ratio of 16 and a contact time (1/WHSV) of 0.08 s. The products were analysed on-line with a gas chromatograph (Varian 3400 X) equipped with a flame ionization detector connected to a capillary column (PLOT/Al₂O₃, 50 m, d_i = 530 μm).

***n*-Hexane cracking at 803 K:** the bifunctional catalysts (60 mg) were reduced under hydrogen flow (50 mL min⁻¹) at 873 K for 10 h. The *n*-hexane cracking was carried out in a top-flow fixed-bed reactor at 803 K under atmospheric pressure with N₂/*n*-C₆ molar ratio of 34 and a contact time of 0.04 s. The products were analysed on-line with a gas chromatography (VARIAN 450) equipped with a flame ionized detector connected to a capillary column (Al₂O₃/KCl: 50 m, d_i = 320 μm).

Propane aromatization at 803 K: the bifunctional catalysts (300 mg) were reduced under hydrogen (60 mL min⁻¹) at 873 K for 10 h. The propane dehydrocyclisation was carried out in a top flow fixed bed reactor at 803 K under 0.1 MPa of propane (purity: 100%, Air Liquid) and a contact time of 0.18 s. The products were analysed on-line using a gas chromatography (7890A Agilent) equipped with a TCD connected to a mole sieve column (13 X, 1.5 m, d_i = 0.2 mm) and a FID linked to a capillary column (CP-Sil PONA CB, 100 m, d_i = 250 μm).

3. Results and discussion

The textural and acidic properties of the parent zeolite (P) and the two hierarchical zeolites (H_{NaOH} and H_{NaOH+TBAOH}) are summarized in Table 1. Fig. 1 compares the nitrogen adsorption isotherm of the parent (P) and the two desilicated zeolites (H_{NaOH} and H_{NaOH+TBAOH}). The parent zeolite exhibits a type I isotherm with a small increase at high relative pressure (P/P₀ > 0.9) due to the formation of few mesopores by the agglomeration of zeolite crystals (V_{meso}^{inter} = 0.04 cm³ g⁻¹). Upon alkaline treatment, the shape of the isotherm changes significantly and can be described as a combination of type I and type IV isotherms, with a hysteresis loop indicating the presence of mesopores (V_{meso} = 0.38 cm³ g⁻¹) for the H_{NaOH}

Table 1
Textural and acidic properties of parent zeolite (P) and two desilicated zeolites, (H_{NaOH} and H_{NaOH+TBAOH}).

Zeolite	V _{micro} ^a cm ³ ·g ⁻¹	V _{meso} ^b	S _{BET} ^c m ² ·g ⁻¹	S _{ext} ^a	[PyH ⁺] ^d μmol·g ⁻¹	[PyL] ^d
P	0.17	0.07	480	149	304	44
H _{NaOH}	0.15	0.38	390	160	231	63
H _{NaOH+TBAOH}	0.17	0.30	507	225	224	55

^a Estimated by t-plot method.

^b V_{tot} - V_{micro}.

^c Specific surface area measured by BET.

^d Measured by pyridine adsorption on Brønsted [PyH⁺] and Lewis [PyL].

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