



Catalytic dehydrogenation of propane over iron-silicate zeolites



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ABSTRACT

Isomorphously substituted iron-silicate zeolites were prepared and their catalytic properties for the monomolecular propane reaction were investigated. [Fe]ZSM-5 (MFI) samples with Si/Fe ratios of 26 and 48, and [Fe]beta zeolite (BEA*) with Si/Fe ratio of 15 were synthesized and characterized using X-ray powder diffraction (XRD), N₂ adsorption and ultraviolet–visible (UV/Visible) spectroscopy. Unit cell volumes, determined using XRD, were used to monitor the presence of Fe in the framework and the migration of Fe species from framework to extra-framework positions. Most of the Fe atoms remain in framework positions after mild calcination (753 K in air), but most of the Fe species migrate to extra-framework positions after steaming at 973 K. Migration of Fe species from framework to extra-framework positions can occur during the monomolecular propane reaction as well. Isolated framework Fe sites are the most important sites for hydrocarbon conversion even though Fe species in extra-framework positions also showed catalytic activity for dehydrogenation. The iron-silicate zeolites exhibited nearly 20 times higher dehydrogenation rates than cracking rates while H-[Al]ZSM-5 with similar Si/Al ratio (~26) showed low dehydrogenation selectivity (dehydrogenation-to-cracking ratio ~0.36). The activation energy for H-[Fe]ZSM-5 is also lower than the activation energy for H-[Al]ZSM-5. A redox catalytic cycle is suggested for the hydrocarbon reaction over isolated Fe framework sites in [Fe] zeolites via the formation of propane radical cations since a protolytic mechanism seems to be unable to explain the observed differences in activation energy and selectivity.

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1. Introduction

Zeolites are aluminosilicate materials that contain tetrahedral Si⁴⁺ and Al³⁺ as framework atoms. In the acid form of aluminosilicate zeolites, the negative charge of the alumina tetrahedra ([AlO₄][−]) is balanced by a proton (H⁺), forming a bridging hydroxyl group (Si–OH–Al) or Brønsted acid site (BAS). Other trivalent elements such as B³⁺, Fe³⁺, and Ga³⁺ can be used for isomorphous substitution of Al³⁺. Aluminosilicate zeolites are currently used for a number of industrially important Brønsted acid-catalyzed reactions [1–6], and their Fe-containing counterparts are of interest for performing various reactions such as olefin oligomerization and isomerization of m-xylene [7–13]. Previous reports regarding the dehydrogenation of para- and ortho-ethyltoluenes have claimed that the reaction occurs on Fe atoms in the zeolite framework [12–14]. Kresnawahjuesa et al. reported that H-[Fe]ZSM-5 could catalyze olefin oligomerization, with less hydride transfer and coke formation than H-[Al]ZSM-5 [8]. Propyl acetates were formed with high selectivity by acylation of propene over H-[Fe]ZSM-5 [7]. It was also reported

that isomerization of m-xylene is catalyzed by BAS in Fe-containing zeolites, and the conversion rates and selectivity are comparable to those exhibited by H-[Al] zeolites [10,11].

The strength of acid sites can be measured using heats of adsorption of bases such as ammonia, pyridine, and acetonitrile. The heats of adsorption for ammonia and pyridine are similar for both H-[Fe] and H-[Al]ZSM-5 (145 kJ mol^{−1} for ammonia and ~195–200 kJ mol^{−1} for pyridine), and the heat of adsorption of acetonitrile for H-[Fe]ZSM-5 (95 kJ mol^{−1}) is slightly less than that for H-[Al]ZSM-5 (110 kJ mol^{−1}) [9]. These heats of adsorption suggest that the deprotonation enthalpy of the H-[Al] zeolites and H-[Fe] zeolites is similar and the strength of acid sites is also similar. These reaction results over H-[Fe] zeolites with similar acidity than H-[Al] zeolites, lead to the question of whether typical protolytic chemistry, responsible for catalytic activity in the conversion of hydrocarbons over H-[Al] zeolites, is also the dominant reaction mechanism on H-[Fe] zeolites.

Conversion of small alkanes has been used frequently as a model reaction because the cleavage of C–C and C–H bonds in hydrocarbons is a problem of fundamental scientific interest. Product distributions tend to be simple and the results are easy to model and quantify. Alkane activation on acid sites in zeolites can proceed

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through bimolecular and monomolecular pathways. The bimolecular pathway involves hydride transfer between an alkane and an adsorbed carbenium ion when the concentration of surface species is high. On the contrary, the monomolecular pathway (protolytic mechanism), involving the formation of alkanium ions [4,15–19], is kinetically dominant at high temperatures (~ 773 K), low alkane partial pressure, and low conversion (<2%). The monomolecular alkane reaction proceeds through only two reaction channels: cracking and dehydrogenation. Through the protolytic mechanism, H-[Al]ZSM-5 samples exhibit higher selectivity for cracking of propane than for dehydrogenation by a factor of about three [20]. In contrast, dehydrogenation selectivity is enhanced (cracking-to-dehydrogenation ratio ~ 1) in H-[Al]ZSM-5 after thermal dehydroxylation [20]. Lower apparent activation energies for cracking (from 184 kJ mol^{-1} to 144 kJ mol^{-1}) and for dehydrogenation (from 187 kJ mol^{-1} to 127 kJ mol^{-1}) are also observed [20].

In this contribution, we investigate the catalytic activity and selectivity for the monomolecular propane reaction over H-[Fe]ZSM-5 with different Si/Fe ratios (26 and 48) and over H-[Fe]beta zeolite (Si/Fe ratio, 15). The migration of Fe species from framework to extra-framework positions was monitored using UV/Vis spectroscopy and using the volume of the unit cell determined using XRD patterns. Conversion of propane resulted in a high selectivity to propene on H-[Fe] zeolites with lower activation energies when compared to H-[Al] zeolites. The results suggest that a redox mechanism is a plausible explanation for the hydrocarbon conversion on [Fe] zeolites reported here, as had been hypothesized earlier for Al-containing zeolites [20,21]. The viability of [Fe] zeolite for dehydrogenation of propane was examined and compared to chromia catalysts.

2. Experimental section

2.1. Synthesis

[Fe]ZSM-5: [Fe]ZSM-5 zeolites were synthesized using a procedure reported by Brückner et al. [22] [Fe]ZSM-5 with different framework compositions were synthesized using the following molar batch compositions: (1) $30 \text{ Na}_2\text{O}:0.38 \text{ Fe}_2\text{O}_3:30 \text{ SiO}_2:5 \text{ TPABr}:1040 \text{ H}_2\text{O}:25 \text{ H}_2\text{SO}_4$ for Si/Fe ratio of 26, (2) $30 \text{ Na}_2\text{O}:0.19 \text{ Fe}_2\text{O}_3:30 \text{ SiO}_2:5 \text{ TPABr}:1040 \text{ H}_2\text{O}:25 \text{ H}_2\text{SO}_4$ for Si/Fe ratio of 48. Iron (III) sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$, reagent grade, Acros Organics) and sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, reagent grade, Sigma-Aldrich) were used for iron and silicon sources. The reactant solution was prepared in two containers. Iron sulfate (0.46 g for Si/Fe ratio of 26 and 0.23 g for Si/Fe ratio of 48), 5.5 g of concentrated sulfuric acid (H_2SO_4 , 95–98%, Sigma-Aldrich), and 25 g of DI water were mixed in container 1. In a second container, 21.32 g of sodium metasilicate was dissolved in 40.85 g of DI water. The solution in the second container was then added slowly to the first container while stirring. Next, 3.33 g of tetrapropylammonium bromide ($(\text{C}_3\text{H}_7)_4\text{NBr}$, TPABr, 98%, Sigma-Aldrich) was added to the mixture until a uniform solution was obtained. The pale yellow final mixture was heated to a temperature of 443 K for 3 days under rotation in a Teflon-lined Parr autoclave. The zeolite samples were recovered by vacuum filtration, washed with DI water, and dried at room temperature for 24 h. The samples were calcined in a horizontal quartz flow reactor (ID = 20 mm) with air (grade 0.1, Matheson) flow by increasing the temperature to 753 K at a rate of 2 K min^{-1} , and maintaining the final temperature for 4 h.

[Fe]beta zeolite: [Fe]beta zeolite was synthesized using a procedure reported by Raj and Sivasanker [23]. The gel composition was $2.3 (\text{Na} + \text{K})_2\text{O}:40 \text{ SiO}_2:0.5 \text{ Fe}_2\text{O}_3:1 (\text{TEA})_2\text{O}:800 \text{ H}_2\text{O}$. Specifically, 0.62 g of sodium hydroxide (NaOH, Fisher Scientific), 0.46 g of potassium hydroxide (KOH, Fisher Scientific), and 74 g of

tetraethylammonium hydroxide ($(\text{C}_2\text{H}_5)_4\text{NOH}$, TEAOH, 40 wt% solution, Sigma-Aldrich) were mixed, and the resulting solution was added to 24 g of fumed silica (CAB-O-SIL M-5, Cabot). The mixture was stirred until an optically clear solution was obtained. The silica solution was slowly added to a solution containing 2.45 g of iron sulfate dissolved in 40 g of DI water. The final solution was transferred into a Teflon-lined autoclave and heated in a convection oven at 413 K for 15 days. The sample was collected, washed, and dried in the same way as the [Fe]ZSM-5 samples. The sample was calcined in a horizontal quartz flow reactor (ID = 20 mm). The temperature was first increased with a ramp of 2 K min^{-1} up to 753 K under N_2 (ultra high purity grade, Matheson) flow. When the temperature reached 753 K, the N_2 flow was changed to an air flow, and the final temperature was kept for 8 h with the air flow.

[Al]ZSM-5: An aluminosilicate zeolite ([Al]ZSM-5) sample with Si/Al ratio of 26 was synthesized with gel composition $16 \text{ Na}_2\text{O}:1.9 \text{ Al}_2\text{O}_3:100 \text{ SiO}_2:3000 \text{ H}_2\text{O}$ using a procedure reported by Kim et al. [21,24] Colloidal silica (Ludox AS-40, 40 wt% suspension, Sigma-Aldrich) and sodium aluminate (NaAlO_2 , EM Science) were used as the silica and alumina sources. First, 11.13 g of colloidal silica was dissolved with 2.9 g of a 5 M NaOH solution and 19.88 g of DI water. Concurrently, 0.22 g of sodium aluminate was mixed with 1.46 g of 5 M NaOH solution and 10 g of DI water in a different container. After mixing for 1 h separately, the solutions were combined. After one additional hour of continuous stirring, the final solution was loaded into a Teflon-lined Parr autoclave and heated in a convection oven at 463 K for 40 h under rotation. The product was vacuum-filtered, washed with DI water, and dried in air.

[Si]ZSM-5 (silicalite-1): All silica zeolite ([Si]ZSM-5 or silicalite-1) samples were prepared using the molar composition, $40 \text{ SiO}_2:9 \text{ TPAOH}:1500 \text{ H}_2\text{O}$ [25]. A solution of 13.2 g of 1 M tetrapropylammonium hydroxide (TPAOH, aqueous solution, Alfa Aesar) and 28.34 g of DI water was stirred for 0.5 h. Then, 12 g of tetraethyl orthosilicate ($\text{SiC}_8\text{H}_{20}\text{O}_4$, TEOS, 98%, Sigma-Aldrich) was added to the solution and stirred until the solution appeared transparent. The final solution was transferred into a Teflon-lined autoclave and heated at 383 K for 3 days in a convection oven. The zeolite was separated from the solution by vacuum filtration, washing, and drying. The sample was calcined in a furnace under an air atmosphere by increasing the temperature up to 823 K with a ramp of 2 K min^{-1} , holding this temperature for 10 h. In addition, a chemical vapor deposition method (by subliming FeCl_3) was used to obtain iron clusters and/or iron oxide particles incorporated in the structure of the [Si]ZSM-5 samples [26,27].

For the ion exchange with NH_4 cations, 1 g of the sample was mixed with 500 ml of aqueous solutions of NH_4NO_3 (0.1 M) and stirred at room temperature overnight. The samples were then filtered and washed with DI water three times. For sodium exchange, the protocol was the same except that ~ 0.1 g of the zeolite (recovered from the reactor) was used for the ion exchange.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Phillips X'Pert X-ray diffractometer using a $\text{Cu K}\alpha$ radiation. The samples were mixed with silicon standard (10–20 wt%) to correct the peak positions, and the UnitCellWin program was used to calculate unit cell volumes of the samples from the corrected XRD data as reported by Holland [28,29]. Energy-dispersive X-ray (EDX) analysis was obtained on JEOL JSM 7400F scanning electron microscope (SEM) to measure the elemental composition of the zeolites. The elemental composition was also measured with inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis (Galbraith Laboratories, TN). The micropore volumes of samples were determined from N_2 adsorption isotherms measured using a Micromeritics ASAP 2020 instrument. Before adsorption of N_2 , the samples

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