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Effect of thermal treatment on surface and bulk properties of Fe/ZSM-5 zeolites prepared by different methods

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Abstract

Fe/ZSM-5 samples (5 wt.% Fe) prepared by in situ incorporation using TPABr template under hydrothermal conditions (Fe–ZSM-5_{in}), chemical liquid deposition (Fe–ZSM-5_{imp}) and solid–solid (Fe–ZSM-5_{ss}) interaction were characterized by N_2 physisorption, TG/DSC, X-ray diffraction, FTIR spectroscopy, UV–Vis diffuse reflectance spectroscopy and ^{57}Fe Mössbauer spectroscopy techniques. Calcination at 550 °C leads to almost complete removal of template that was associated with dislodgment of significant fraction of Fe to external positions as recognized for the in situ prepared sample (Fe–ZSM-5_{in}). This sample showed an increase in lattice volume suggesting the presence of the majority of Fe ions in tetrahedral positions inside zeolite channels and offered as well the lowest crystallites size (75 nm) and maximum S_{BET} (453 m^2/g) between all samples. On the other hand, Fe–ZSM-5_{ssbef}, resulting from solid–solid interaction and subjected to heat treatment in vacuum at 200 °C, measured the lowest mean pore radius (r^-; 23 Å), and pore volume (V_p; 0.3887 cm^3/g), giving a hint about the probability of finding neutral iron oxide nanoparticles (α-Fe_2O_3) as a separate phase that has been validated by Mössbauer (IS = 0.3 mm/s, QS = −0.2 mm/s, H_{eff} = 520 kOe) and UV–Vis (400 nm) investigations. This sample also demonstrated that the majority of Fe occupied framework positions beside a fraction identified as small oligonuclear oxo-iron ions (Fe_x^{3+}–O; 290 nm). Interestingly, Fe–ZSM-5_{ssaft}, resulting from solid–solid interaction and subjected to air calcination at 550 °C, measured maximum V_p (0.6380 cm^3/g) and r^- (39 Å) values, reflecting the enforced location of Fe in this sample leading to an effective pore widening and thus a pronounced mesoporosity is attained. IR bands due to v_{as}T–O in ZSM-5 (1105 cm^{-1}) showed a shift to lower wave numbers (1059 cm^{-1}) following Fe incorporation reflecting the extent of exchanging Fe in this sample (Fe–ZSM-5_{ssaft}), unlike the rest of the samples which showed splitting, which accounted for the presence of residual Al^{3+} beside Fe^{3+} ions in the same site. Mössbauer data of this sample confirmed the latter result and indicated the maximum lattice imperfection and showed as well the lowest degree of crystallinity. The Fe–ZSM-5_{impaft} sample, subjected to heat treatment at 550 °C, showed α-Fe_2O_3 species where that heated at 110 °C presented the lowest S_{BET} (361 m^2/g). More correlations were evaluated and discussed on the effect of thermal treatment on the existence of various Fe species (either framework or non-framework), their electronic states and local structures.

Keywords: Fe–ZSM-5; In situ preparation; Impregnation; Solid–solid interactions; Characterization; Fe species; Mössbauer spectroscopy

1. Introduction

Zeolites with 10-membered oxygen rings normally possess a high siliceous framework structure. The 10-membered oxygen ring zeolites also possess other important characteristic properties including high

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activity, high tolerance to coking and high hydrothermal stability. Among the family of 10-membered oxygen ring zeolites, the MFI type (ZSM-5) zeolite is probably the most useful one.

It has been acknowledged that the tetrahedral surrounding could be stable for cations with $0.414 > \rho > 0.225$ ($\rho = r_M/r_O$, where r_M and r_O are the radii of the cation and the oxygen ion, respectively). Cations that do not fulfill this criterion such as Fe^{3+} may also be introduced into the framework under specific synthesis conditions. The introduction into the framework of ZSM-5 atoms other than Si and Al can modify significantly the acid–base and catalytic properties of the zeolites. Some modification studies have been made with framework iron insertion substituting aluminium in the synthesis process [1–4]. Such isomorphous substitution of Fe either for Al or Si of zeolites has been reported to exhibit improved catalytic properties in a variety of chemical reactions. Among them are ethanol conversion to hydrocarbons, polymerization, isomerization, dehydrogenation, reduction of NO either by NH_3 or hydrocarbons and selective oxidations [5–11]. For most of these reactions, the catalytic activity is thought to be related to extra-framework iron species (iron oxides, dinuclear iron sites and oxohydroxides aggregates) formed during ion exchange and solid–solid treatments [12,13]; those acting either independently or in synergy with protonic-Fe(OH)Si sites (Brönsted acid). Fe exchanged ZSM-5 zeolite exhibited a high and stable catalytic activity in several selective redox reactions of great importance: NO [14], N_2O [15] decomposition as well as selective catalytic reduction of NO by hydrocarbons in an excess of O_2 [16]. On the other hand, CuZSM-5 showed lower catalytic activity and less stability towards NO reduction due to the alteration of the copper ionic state on the catalyst surface and to dealumination consequences. Accordingly, Fe–ZSM-5 is subjected to numerous studies principally for correlating the structure of the active site(s) in various applications. Thus, an intense attention still attracting many researchers to study structure–activity relationship for each active Fe site can be revealed.

From the analysis of the literature data briefly discussed above, it is however evident that the formation of framework and non-framework Fe–ZSM-5 is primarily connected with the conditions applied during preparation and to the applied thermal treatment that is far from being completely understood. In this essence, the coordination and oxidation changes of Fe^{3+} species when incorporated with ZSM-5 were followed before and after calcination for samples prepared by different methods, including in situ incorporation during synthesis, impregnation and solid–solid interactions in conjunction with their electronic states, surface properties and local structures.

2. Experimental

2.1. Materials

The materials used were: silicic acid powder, sodium hydroxide pellets (A.R. 98%), aluminum sulfate ($Al_2(SO_4)_3 \cdot 16H_2O$ Merck), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$ Merck), tetrapropylammonium bromide (TPABr, Fluka), *n*-propyl amine (Merck) and concentrated sulfuric acid.

2.1.1. Preparation of ZSM-5

The hydrogels of the following oxide molar compositions were prepared for the synthesis of ZSM-5 zeolite:

$$3.12Na_2O : 0.162Al_2O_3 : 6.185SiO_2 : 0.185Q : 100H_2O$$

where Q is the tetrapropylammonium bromide template.

A specific amount of NaOH was added to silicic acid in a small amount of H_2O (40 ml) while stirring, followed by heating at 80 °C until a clear solution was reached. The TPABr was dissolved in a little amount of H_2O (10 ml) with heating at 50 °C for 20 min. The solution of TPABr was added to that of sodium silicate solution whilst stirring for 15 min. In addition, 1 ml of *n*-propyl amine was added as a mobilizing agent to that mixture. The aluminum sulfate, on the other hand, was dissolved in a small amount of H_2O (10 ml) while adding 0.05-ml concentrated H_2SO_4 with stirring until reaching a clear solution. To the latter solution, the combined solution of sodium silicate and TPABr was added followed by stirring for 30 min. The pH of the mixture was adjusted at 11 by using NaOH (0.1 M) and H_2SO_4 (0.1 M) solutions. Finally, the mixture was hydrothermally treated at 160 °C in an oil bath, using stainless steel autoclaves, for 6 days. The autoclaves were removed at the specified time from the oil bath and quenched immediately with cold water. The solid product was filtered and washed with distilled water until the pH of the filtrate dropped to 8. The products were dried at 110 °C for 10 h, then calcined at 550 °C for 6 h in an air oven.

2.1.2. Preparation of Fe–ZSM-5

2.1.2.1. Inclusion of Fe–ZSM-5 zeolite (built-in). The synthesis procedure is described in molar compositions as follows:

$$3.12Na_2O : 0.138Al_2O_3 : 6.185SiO_2 : 0.0103Fe_2O_3 : 0.185Q : 100H_2O$$

where Q is the tetrapropylammonium bromide.

Aluminum sulfate was dissolved in a small amount of water (5 ml) followed by addition of 0.05-ml H_2SO_4. On the other hand, the soluble complex of sodium silicate was formed onto which the template tetrapropylammonium bromide (TPABr) was added with *n*-propyl amine