



# Determination of acid sites in porous aluminosilicate solid catalysts for aqueous phase reactions using potentiometric titration method



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## ABSTRACT

A potentiometric acid–base titration method was developed to characterize the acid–base properties of H-Beta-25, H-Beta-300, H-Ferrierite-20 and Si-MCM-48 zeolites in aqueous solutions. The method is based on linearization of the titration curve. The zeolite powders were dispersed in a sodium nitrate solution which was then titrated with a standard solution of sodium hydroxide. Various acid sites were found in the studied zeolites, and both the protonation constants and the concentrations of these acid sites were determined. The chemical composition (aluminum and silicon), distribution of the aluminum sites, crystallinity as well as the acidic properties of the titrated zeolites were compared with those of the pristine zeolites by using Inductively Coupled Plasma Optical Emission Spectrometer (ICP–OES), X-ray Diffraction (XRD), <sup>27</sup>Al NMR spectroscopy and the commonly used gas phase Fourier Transform Infrared spectroscopy (FTIR) of pyridine adsorption method.

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## 1. Introduction

Zeolites are commonly composed by a three dimensional network of SiO<sub>4</sub><sup>4-</sup> tetrahedral structure [1]. When a heteroatom with lower valency than Si, such as Al, B, Ga and Fe, is introduced to the framework, the formal charge on that tetrahedron changes from neutral to negative. This negative charge is then balanced either with a hydroxyl proton to form a strong Brønsted acid site (BAS) or with a metal cation to form a weak Lewis acid site (LAS) [2]. Due to the presence of the acid sites in the framework structure, the solid acid and metal modified zeolites are used as catalytic materials in several petro-chemicals and oil refinery processes, as well as in synthesis of fine and specialty chemicals [3,4]. Acidic and metal modified zeolite catalysts are also used in environmental applications such as exhaust gas purification from mobile and stationary sources, pretreatment of industrial and municipal waste water stream, agricultural soil contamination and nuclear waste treatment [5–8]. Since these acid sites play an important role in the catalytic and sorption properties of zeolites [9], better knowledge of them is important for successful industrial applications of zeolites as solid catalysts.

Numerous gas phase methods and techniques have been published to quantify and characterize the acidity of zeolites. One of the methods uses Fourier Transform Infrared spectroscopy (FTIR) of various probe molecules (ammonia, pyridine) adsorption to study the fundamental stretching vibrations of hydroxyl groups at varying temperatures to determine the Brønsted and Lewis acid sites [10,11]. Another commonly used method is the temperature-programmed desorption (TPD) technique to measure the reacted amount of a gaseous base (ammonia) with zeolites for characterizing the density and strength of the acid sites [12]. Both FTIR–pyridine and TPD–ammonia methods are performed in the gas phase at high temperature (100–450 °C). However, many catalytic reactions especially related to valorization of biomass are carried out in aqueous solutions at ambient or somewhat elevated temperature [13,14] and therefore the catalytic properties based on the acidity of the zeolites determined with FTIR–pyridine and TPD may not be relevant. Therefore a technique, which can be used to characterize the acidic properties of the zeolites in the aqueous phase, is necessary.

Acid–base titration of zeolites in non-aqueous solvents has been used earlier to study the acidity of zeolites. The method was introduced by Benesi in 1950s [15] and then modified by other researchers [16]. In that method the surface of zeolite was titrated with amine, i.e., *n*-butylamine, in a non-aqueous solvent and a series of Hammett indicators with various acidity constant values or *pK<sub>a</sub>* values, i.e., benzeneazodiphenylamine (*pK<sub>a</sub>* = 1.5) and

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phenylazonaphthylamine ( $pK_a = 3.3$ ), were used to characterize the acid sites [17]. However, it was demonstrated later that the additional indicators in the non-aqueous solvent could disturb the equilibrium state of the zeolite system during the titration [18,19]. Another drawback of using the Hammett indicators is their molecule size, which is too large for the indicator molecules to enter the channels and cages of some zeolites [20]. Due to these fundamental limitations and the long time of the experiments, the titration using indicators did not become a popular technique in studying zeolites.

In the current study, a specific potentiometric acid–base titration method developed from the traditional titration method will be used to characterize the acid sites in zeolites. This method has a high resolution in determining the various acid groups present in the samples. Moreover, it is not necessary to use any indicators to monitor the acid–base reaction. During the titration, pH of the solution is measured as a function of the volume of a strong base added and the obtained titration curve is used to analyze the titrated samples. In addition, the small  $\text{OH}^-$  ions can penetrate deep inside the zeolite channels and the acid sites in those channels can therefore also be determined.

The studied zeolites are the proton forms of H-Beta type with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 25 and 300, H-Ferrierite type with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 20 and Si-MCM-48 which belongs to a pristine silica mesoporous material without any aluminum in the framework. The frameworks of Beta, Ferrierite and Si-MCM-48 are shown in Fig. 1 [21,22]. The three dimensional structure of the Beta zeolite has two tetragonal crystal systems: one channel consists of 12-membered rings with dimensions of  $5.6 \times 5.6 \text{ \AA}$  and the other consists of 12-membered ring with dimensions of  $6.6 \times 6.7 \text{ \AA}$ . The two dimensional structure of the Ferrierite zeolite contains two type channel systems: one channel consists of 8-membered rings with dimensions of  $3.5 \times 4.8 \text{ \AA}$  and the other consists of 10-membered rings with dimensions of  $4.2 \times 5.4 \text{ \AA}$ . The three dimensional cubic structure of Si-MCM-48 is composed by unconnected pore system with dimensions of 20–80  $\text{\AA}$  [22–24].

## 2. Experimental work

### 2.1. Chemicals

Two Beta type zeolites with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 25 and 300 and one Ferrierite type zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 20 were obtained in  $\text{NH}_4$ -form from Zeolyst International.  $\text{NH}_4$ -Beta-25,  $\text{NH}_4$ -Beta-300 and  $\text{NH}_4$ -Ferrierite-20 were calcined in a muffle oven at  $450 \text{ }^\circ\text{C}$  for 4 h to generate H-Beta-25, H-Beta-300 and H-Ferrierite-20. A pristine silica mesoporous material Si-MCM-48 was prepared in our laboratory by using a modified templating hydro-thermal synthesis method described by Kaldstrom et al. [25].

The titrant, 0.1 M NaOH + 0.1 M  $\text{NaNO}_3$ , was made from reagent-grade chemicals obtained from Merck and its accurate concentration was determined using the conventional acid–base standardization titration method. The titrant was stored in argon environment with carbon dioxide adsorbent to avoid  $\text{CO}_2$  contamination. A stock solution of 0.1 M  $\text{NaNO}_3$  was also prepared as the titration medium for the zeolites. The distilled water from system PureLAB Ultra (ELGA) was boiled to expel  $\text{CO}_2$  before using it as the solvent for the NaOH and  $\text{NaNO}_3$  solutions.

### 2.2. Potentiometric titration

Potentiometric titrations were performed with an automatic titration system Mettler Toledo DL 50 Graphix Titrator (Mettler Toledo GmbH Analytical). The pH was measured with a combined glass electrode DG111-SC from Mettler Toledo and the system was calibrated in standard buffer solutions of pH 4.00, 7.00 and 10.00 prior to use. A total of 10 ml titrant (NaOH) was consumed in the end of the titration. Titration of the zeolite suspension was performed only to pH 10 in order to avoid possible dissolution of the zeolites at higher pH values.

The Gran method, which is based on the Sørensen's [26] earlier work and described by Gran in 1952 [27], was selected for the data

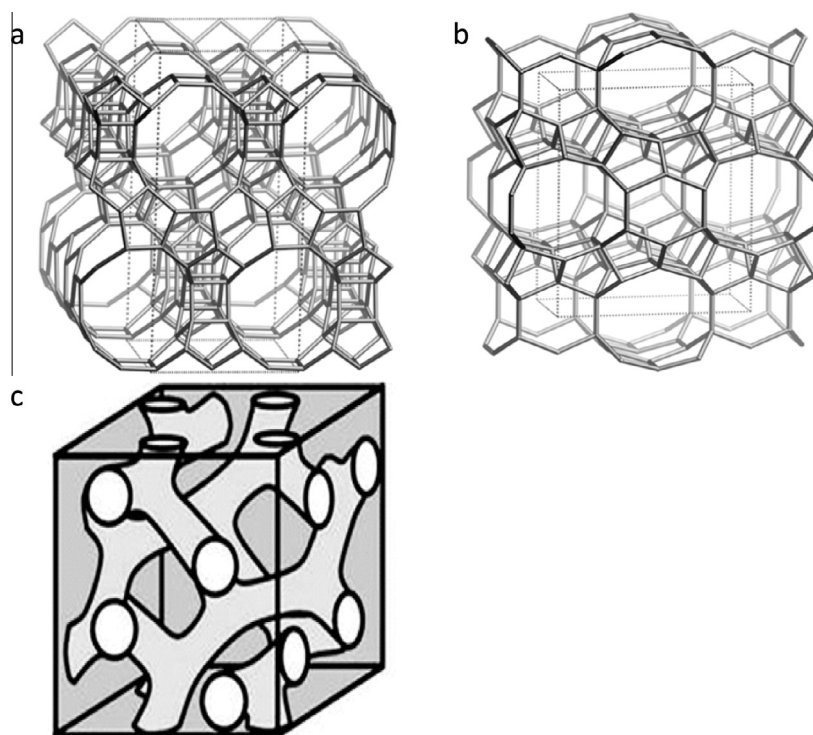


Fig. 1. Framework structure of zeolites, (a) Beta, (b) Ferrierite and (c) Si-MCM-48.

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