

THE INFLUENCE OF SILICA TO ALUMINA RATIO ON Y ZEOLITE ACTIVITY BY SIMULTANEOUS TG AND DSC ANALYSIS

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Abstract

Simultaneous TG and DSC analyses of *n*-butylamine adsorption/desorption were carried out over several zeolites with different degrees of dealumination. The samples used consisted of high crystalline zeolites, prepared via steam/leaching sequential treatments, and characterized by various techniques. Catalytic activity measured as the initial rate of cracking of 1,3,5-triisopropylbenzene did not correlate with total acidity, however, the energy required to the complete desorption of the probe molecule, determined by integration of DSC curves, correlates with the catalytic activity of zeolites with any or little extra-framework alumina content. High amounts of extra-framework alumina give significant constraint effect to accessibility to acid sites as shown by applying the Crank's method to the TG curves. This method allowed to determine the intra-crystalline diffusivity of the probe molecule, which seems to be the controlling step to the cracking reaction.

Keywords: acidity, DSC, simultaneous analysis, TG, zeolites

Introduction

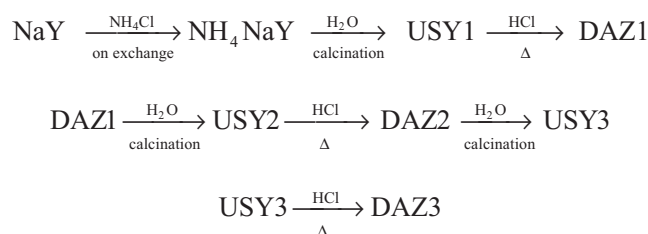
Y zeolites are widely used as the active component for cracking catalysts in petroleum industry. Extensive work has been carried out during the last four decades aiming at correlating the zeolite acidity to its cracking activity [1–3]. Several acidity measurement techniques, such as TPD (Temperature Programmed Desorption), TG and IR analysis, have been investigated but no general correlation has been achieved. Previous studies in our group [4–6], using model reactions of bulky molecules, showed that acid strength and site densities are not the only parameters controlling activity and selectivity during catalytic cracking. The recent advances in thermal analysis equipment, mainly simultaneous analyses apparatus, bring a new perspective to catalyst characterization. The aim of this work is to demonstrate that the use of simultaneous TG/DSC techniques permits to identify the contribution of diffusion to

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cracking mechanism and to properly measure the acid strength of deeply dealuminated Y zeolites, which can be correlated with catalytic activity.

Experimental

Zeolites samples were prepared and characterized by Sobrinho [4] according to the following procedure. Parent NaY (Si/Al=2.8) zeolite was ion-exchanged in a 11 mass% NH_4Cl solution, at 70°C . After the ion exchange, steaming treatments took place in a cylindrical reactor containing 60 g of the zeolite, with 20 g h^{-1} flow rate of saturated steam (200°C), at 650°C for 90 min, generating the USY (Ultra Stable Y zeolite) samples. Acid leachings were carried out at 70°C for 30 min, with pH of ca. 1.0–2.5, generating the analogous DAZ (Dealuminated Y zeolite) samples, according to the following scheme:



X-ray diffraction (XRD) analyses took place in a Philips PW1729 diffractometer with CuK_α radiation and the relative crystallinities of the samples were estimated from the integrated area of the peaks with Miller indexes (220), (311), (331), (333), (440), (533), (642), (660), (751) and (664). The global Si/Al was determined by X-ray fluorescence (XRF) in a Philips PW1407 spectrometer with CrK_α radiation. The framework Si/Al was determined by ^{29}Si NMR spectra obtained in a Varian VXR 300 spectrometer under 7.05 T magnetic field. The main characteristics of the parent NaY zeolite and steam treated and dealuminated samples prepared thereof are given in Table 1.

Table 1 Main characteristics of NaY zeolite and steam treated and dealuminated samples

Sample	Crystallinity/%	Global Si/Al	Framework Si/Al
NaY	100	2.8	2.8
USY1	100	2.8	5.4
USY2	106	3.5	15.2
USY3	132	12.7	36.7
DAZ1	110	3.8	5.6
DAZ2	119	11.2	16.2
DAZ3	126	27.8	33.5

Cracking of 1,3,5-triisopropylbenzene (FLUKA 92075) was carried out in a differential fixed-bed gas phase plug flow reactor, with a 15 mm bed containing 5 mass% zeolite diluted in glass spheres. Reaction products were analysed by GC-MS (HP5890 and HP5970-B), using a HP-PONA column (50 m, 0.3 mm, 0.5 μm) for the liquid phase, and $\text{Al}_2\text{O}_3/\text{KCl}$ column (50 m, 0.2 mm, 0.5 μm) for the gas phase.

Simultaneous TG/DSC analyses of *n*-butylamine adsorption/desorption were carried out on a Netzsch STA 409 analyser with Pt crucible under 60 mL min^{-1} flow rate of nitrogen. The analysis consisted of five basic steps: 1. pre-heating of the sample under nitrogen flow from room temperature up to 650°C, at 10°C min^{-1} ; 2. sample cooling to 100°C; 3. isothermal *n*-butylamine adsorption under flow of nitrogen saturated with *n*-butylamine; 4. isothermal purge under flow of nitrogen; and 5. *n*-butylamine desorption, under flow of nitrogen, with a temperature program from 100 to 650°C, at 10°C min^{-1} . For diffusivities measurements, steps 2 and 3 were repeated at 140 and 180°C.

Results and discussion

Rates of 1,3,5-triisopropylbenzene cracking were previously calculated by Souza–Aguiar *et al.* [5] and Murta–Valle *et al.* [6] assuming differential behaviour. Plots of reactant disappearance against time-on-stream were fit to the classical Voochries equation [7], allowing one to estimate initial reaction rates, which were plotted against the number of aluminum atoms per unit cell (Al/u.c.). Figure 1 presents this graphic for USY and DAZ samples. For DAZ samples, a maximum rate is found for about 11 Al/u.c., while for USY samples, a minimum rate is found for about the same point. Due to the shape of the curve for USY samples, the previous studies [5–6] suggested that diffusion should be the controlling step of reaction rate.

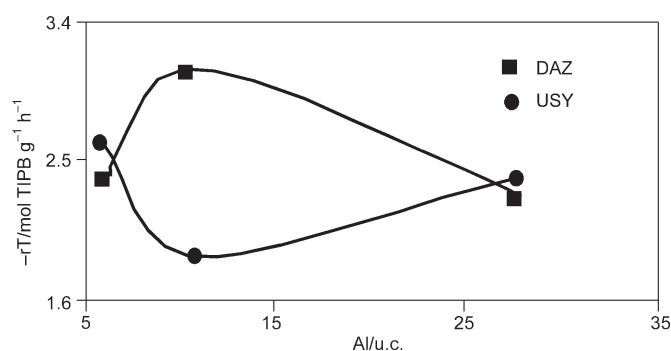


Fig. 1 Initial cracking rates of 1,3,5-TIPB as a function of Al/u.c. at 450°C

The energies of the adsorption bonds of the *n*-butylamine on the zeolite samples were calculated by integration of the DSC curves. The total energy was interpreted as an acid strength, since it includes the contribution of all acid sites involved in the

amine adsorption. The possibility of obtaining a numerical value for this strength is an important breakthrough over traditional methods such as TPD and TG, where acid strength is related only to peak temperatures. Figure 2 shows the total acid strength plotted against Al/u.c. for both families of samples. Comparing with the activity data presented in Fig. 1, it seems that the acid strength measured by the DSC curves gives a precise estimation of zeolite activity to cracking for DAZ samples. The presence of extra-framework alumina, however, seems to block some sites, since acid strength is lower for the USY sample than for the corresponding DAZ sample with the same crystalline structure.

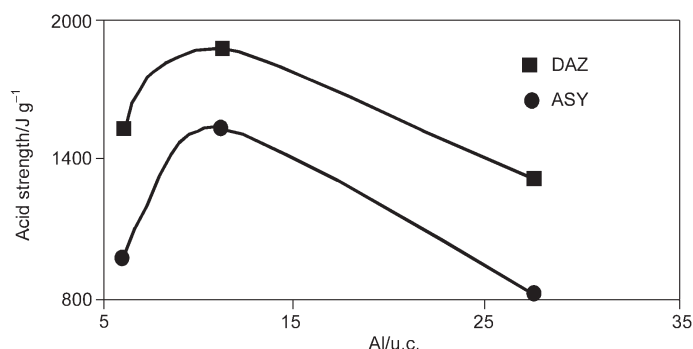


Fig. 2 Acid strength determined by integration of *n*-butylamine desorption DSC curves as a function of Al/u.c.

Apparent diffusivities were calculated by applying the method proposed by Crank [8] for apparent diffusion in spherical particles. During isothermal purge step of TG analysis, pairs of values of the amount diffused and the time required are obtained and plotted against each other. The apparent diffusivities were calculated by means of linear regression of the following equation, where M_t is the amount of the probe molecule diffused at time t , M_∞ is the total amount which may diffuse, R is the radius of the molecule and D_{ap} is the apparent diffusivity.

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{D_{ap}}{R^2}\right)$$

Repeating the procedure at three different temperatures and applying Arrhenius law, apparent diffusivity may be estimated for any temperature. These three temperatures should be low enough to avoid desorption of chemisorbed probe molecule which may lead to misinterpretation of the results. Figure 3 presents the values obtained for apparent diffusivities at 450°C for both families of samples. The plot of diffusivities against Al/u.c. shows that diffusion plays an important role in determining the reaction rate controlling step. In this procedure, the diffusivities are calculated at the desorption step. Thus, they represent the behaviour of reactants and products trying to leave the micropores of the zeolite. For DAZ samples, for instance, the mini-

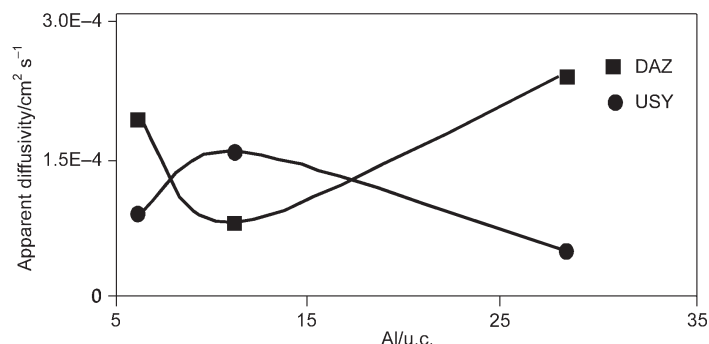


Fig. 3 Apparent diffusivity estimated from TG curves at 450°C as a function of Al/u.c.

imum diffusivity found at 11 Al/u.c. means that, at this point, the reactants will spend more time in contact with the acid sites, which leads to an increase in the catalytic activity. The higher acid strength and the longer contact time (lower diffusivity) at 11 Al/u.c. result in a maximum activity as seen in Fig. 2. For USY samples, diffusivity presents a maximum at 11 Al/u.c., hence the reactants will have less contact with the acid sites at this point. This behaviour leads to an activity opposite to that obtained by DSC curves (Fig. 2). As the catalytic activity shows a minimum at 11 Al/u.c. (Fig. 2), it seems that diffusion, rather than acidity, is controlling the reaction rate.

Conclusions

Simultaneous TG/DSC analyses were employed as a tool to predict the zeolite activity by measuring the energy of the adsorption bond between the probe molecule and zeolite samples. The use of DSC curves to measure acid strength led to a new method to estimate catalytic activity of Y zeolite samples with neither or few extra-framework alumina content. For samples with higher extra-framework alumina contents, diffusion seems to be the rate-controlling step for acid catalytic reactions.

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