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Development of a new model reaction to characterize the weak reactivity of cationic zeolites

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Abstract

A new test in liquid phase using dodecen-1 isomerization as a model reaction was developed to characterize the weak reactivity of cationic zeolites.

Thanks to it, the NaY weak activity can be characterized in conditions close to those of several industrial adsorption and separation processes (temperature around 150–200 °C and in liquid phase). Indeed, characterization by this model reaction of several NaHY prepared from NaY by exchanging some Na^+ by protons and of NaY treated by NaOH allows us to attribute the NaY activity to residual Brönsted acid sites and even to estimate their number. Comparison of NaY before and after passivation of its external by Tetra-EthylOrthoSiloxane (TEOS) deposition enable us to propose that the residual active sites are mainly located at the external surface and/or in the porosity directly connected to this one.
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1. Introduction

Numerous separation or purification processes (separation of *n*-paraffins, xylenes and N_2/O_2) use cationic zeolites as adsorbents [1–9]. They are chosen because of their very weak acidity due to a low number of active sites. However, it can sometimes be sufficient to induce through coke formation, a slow but progressive decrease of the molecular sieve performance and consequently of the processes [10–14]. And in some cases, it would be interesting to neutralize this activity. But before getting a chance to reach this aim, it is necessary to know what kind of acidity is responsible for zeolite reactivity.

Most of the time, the classical techniques used to characterise the zeolite acidity (NMR, IR, etc.) are not sensitive enough to analyze the very weakly acidic cationic zeolites

(too low quantity and/or strength of sites). Moreover, they are often carried out in conditions far from those of some industrial processes [15]. To overcome these disadvantages, adapted model reactions can be used. Several [16–18] have already been developed as the one developed by the International Zeolite Association about the ethylbenzene disproportionation over LaNaY [19]. But they often concern zeolite containing divalent and/or trivalent cations that are well-known to increase zeolite's activity. And as well as physical techniques, most of them are carried out in gas phase.

So, the development of a new test in liquid phase on very weakly active zeolite as NaY would be a useful complement for all the already available methods. This would in particularly give information about zeolite activity in conditions close to those of some industrial processes as xylenes separation for producing paraxylene and/or metaxylene (PAREX from UOP and ELUXYL from IFP) or separation of n-paraffins from kerosene (MOLEX from UOP) that are operated in liquid phase. Therefore, the

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present work has been set up. To be sure to be sensitive to non acidic zeolites, the new test was developed with a reputed inactive zeolite, the NaY. In counterbalance, this implies to choose a very easy reaction as olefin isomerization and a very reactive molecule as a long olefin such as dodecen-1.

By comparing reactivity of NaY with those of NaY partially exchanged with protons, neutralized by NaOH or treated with TetraEthylOrthoSiloxane (TEOS), we will try to characterized as much as possible NaY activity (determination of number and localisation of active sites). Extractions and analysis of adsorbed compounds at the internal and external surfaces after tests allow us to complete the information obtained from the test reaction.

2. Experimental

2.1. Materials

The commercial NaY from *Zeolyst International* (*CBV100*) is used as received and after treatments. It has a bulk Si/Al ratio of 2.50 (determined by ^{29}Si NMR, i.e. corresponding to a bulk elemental analysis), a surface Si/Al ratio of 2.54 (determined by XPS), a BET surface area of 838 m^2/g and a microporous volume of 0.349 cm^3/g calculated using the Dubinin–Radushkevich equation.

In parallel, we synthesised two other NaY in our laboratory. We followed a procedure developed at IFP, inspired from the paper of Hasegawa et al. [20]. To produce 750 ml of precursor gel, 54.94 g of NaOH in pellets with 672.12 g of water were mixed. Under agitation, 78 g of Ludox HS 40 (silicium source) and 6.99 g of $NaAlO_2$ (aluminium and sodium source) were added. The gel is maturated under room temperature in an 1 L autoclave during 24 h. In order to prepare NaY with crystal sizes of around 1000 nm the autoclave is placed under agitation for 12 h at 85 °C muffle furnace. To prepared smaller crystal sizes (500 nm) the procedure is the same but the autoclave is kept static. The crystal sizes were measured by SEM technique.

To obtain partially exchanged zeolites (series NaHY), 50 g of saturated commercial NaY sample (water content: 25 wt.%) were suspended in 250 ml of NH_4Cl solution at different concentrations (*VWR International- Prolabo*) (0.40, 0.75, 1.10, 1.50, 1.80, 2.20, 2.60 and 5.20 g/l) at 90 °C for 4 h under magnetic stirring. After this, the hot mixtures are filtered and washed with 1 L of deionised water at 90 °C. The obtained filtration cakes are dried at 100 °C in a muffle furnace during 12 h. The recovered solids are then calcinated under air at 550 °C for 4 h to remove the NH_3 (creation of H^+) and the water molecules. The resulting solids are called NaHY-a%, with a corresponding to the obtained exchange level in proton comprise between 0.9 and 13.8. These exchange levels were determined using the Na^+ content measured by ICP–AES (induced coupled plasma–absorption emission spectroscopy).

TEOS deposition by CVD (chemical vapor deposition) leads to the substitution of acid sites at the zeolite's exter-

nal surface by supposed non acidic silanol groups. This kind of silanation only affects the external surface due to the bulky configuration of the TEOS. Indeed, as its kinetic molecular diameter is 0.96 nm, i.e. larger than the NaY supercage's aperture that is about 0.75 nm [21], it could not enter the microporosity of the zeolite. After being pre-treated under air in a cylindrical reactor at 550 °C (10 °C/min during 1 h) (3 l/h/g), the NaY is maintained at 150 °C. An up-flow of TEOS diluted in nitrogen (3 l/h/g) at 58 °C is injected through the zeolite for 1 h. In order to stabilize the TEOS coating at the zeolites's surface, the modified zeolite is calcinated at 550 °C (10 °C/min $Q_{N_2} = 2.5$ l/h/g) for 4 h ($Q_{air} = 2.5$ l/h/g)) so that the silicic groups are transformed into silanol groups. The obtained solid will be noted as NaY–TEOS. XPS analysis shows an increase of the Si/Al ratio at the external surface from 2.54 for NaY to 2.60. It was also verified that this treatment does not lead to a drop neither of the surface area nor of the zeolite microporous volume (surface area = 823 m^2/g and microporous volume = 0.340 cm^3/g determined from nitrogen adsorption isotherm using the Dubinin–Radushkevich equation). Finally, it was checked that this kind of treatment does not narrow the pore's aperture by following the metaxylene (MX) adsorption on a thermobalance (*Setaram*). As the adsorption front is similar between NaY and NaY–TEOS and as the capacity has hardly decreased (0.308 cm^3/g for NaY against 0.295 cm^3/g for NaY–TEOS), it was considered that in NaY–TEOS the pores are still accessible.

The NaOH washing was performed by suspending 10 g of the parent commercial NaY zeolite samples in 250 ml of NaOH aqueous solutions. Different concentrations of base were prepared: 0.1, 0.5 and 1 M. After 3 h stirring at room temperature, the recovered solid is filtered, washed with deionised water and dried at 100 °C in a muffle furnace for 12 h. The resulting samples are referenced as NaY–NaOH 0.1 M, NaY–NaOH 0.5 M and NaY–NaOH 1 M. In order to check the influence of this kind of treatment on the zeolite's structure, several characterization have been performed. The degree of crystallinity, defined as the ratio of areas of the X-Ray diffraction main peak for the samples before (NaY) and after treatments, is 0.97 for all samples. The BET surface area and the microporous volume are really close to those of NaY (822 m^2/g and 0.340 cm^3/g for NaY–NaOH 1 M, 859 m^2/g and 0.355 cm^3/g for NaY–NaOH 0.5 M and 800 m^2/g and 0.333 cm^3/g for NaY–NaOH 0.1 M). These results confirm that alkaline treatments did not destroy the zeolite structure.

2.2. Physical methods

The bulk chemical composition is measured by ICP–AES with a *ThermoJarrell ASH IRIS 200 ADV HR* device. The samples are first mineralised with concentrated solutions of hydrofluoric acid (HF) and nitric acid (HNO_3). The surface composition is determined by XPS.