

Chapter 6

Conclusions

The modifications made to the zeolites studied have improved the adsorption and catalytic properties in the following ways:

- Mordenite can adsorb slightly higher volumes of N_2 maintaining a good N_2/O_2 adsorption selectivity, even though its Si/Al ratio is higher than the normally used faujasite-type zeolites. The results are so good because the porous structure of the zeolite based in channels makes the cations more accessible. Therefore, this natural zeolite is a good alternative to the synthetic zeolite X for the N_2/O_2 separation process.
- In mordenites prepared by cationic exchange, the N_2 adsorbed volume increases in the way $Li^+ > Ag^+ > Na^+$ and the N_2/O_2 adsorption selectivity in the way $Ag^+ > Li^+ > Na^+$. Therefore, in the mordenite structure, the combination of different cations enabled equilibrium to be reached between the adsorbed volume and the interaction strength.
- The introduction of small amounts of fluorine into the mordenite framework was found to have a positive effect on the N_2/O_2 adsorption selectivity. The presence of the fluorine atoms means that the framework structure shields the cations less and, therefore, increases the electrostatic interaction between cations and the quadrupolar moment of N_2 molecules. This leads to an increase in the N_2/O_2 adsorption selectivity at lower pressures. On the other hand, the introduction of higher amounts of

fluorine causes some dealumination in the structure and decreases adsorption properties.

- Although Ag_m^{n+} clusters did not form inside the mordenite structure, probably due to the high Si/Al ratio of mordenite, they did on zeolite A. The N_2 and O_2 adsorption properties of these Ag_m^{n+} samples were studied and the results indicate that the sample prepared with high concentrations of Ag cations, (Na/Ag(1M)-A), has a higher adsorption capacity than Na-A when the activation conditions were suitable. Nevertheless, when the sample was prepared with a low concentration of silver cations (Na/Ag(0.01M)-A), silver metallic particles were formed during the sample activation process, which partially hindered the entrance of the gas molecules to the cavities of the zeolite, and therefore lower adsorption capacity than the Na-A zeolite was obtained.
- In the styrene oxide isomerisation, commercial mordenite (NaM), unlike the acidic mordenites, showed hardly any activity. The introduction of fluorine into the mordenite structure framework had a notable effect on its acidic properties. When a low amount of fluorine was introduced (HM1F sample), the Brønsted acidity was greater than that of the HM sample and the structure was not affected. This stronger acidity increased the isomerisation reaction when conventional heating was used but the deactivation was fast when microwave heating was used. On the other hand, when higher amounts of fluorine were introduced (HM10F sample) some dealumination and the appearance of Lewis acid sites are observed, and this meant that the isomerisation activity did not increase as much as in the HM1F sample.
- The use of microwaves as a heating source in the styrene oxide isomerisation reaction accelerated the reaction rates and also the formation of

condensation and coke products. These products are responsible for a faster catalyst deactivation, especially in the most acidic catalyst HM1F.

- The reaction products depend on the solvent used. When hexane is used, the main product of the reaction is phenylacetaldehyde, but when methanol is used, the styrene oxide ring breaks to give 2-methoxy-2-phenylethanol. While the first reaction is mainly favoured by the presence of Brønsted acid sites, the second reaction is favoured by the presence of Brønsted and Lewis acid sites.

Some of the systems used were characterized in depth by means of FTIR spectroscopy adsorbing different probe molecules. The main conclusions that can be drawn are:

- Low temperature CO and room temperature nitrile adsorption experiments on the various zeolite samples form $M^+ \cdots CO$ and $M^+ \cdots NC-R$ complexes (“usual” species) characterized by higher IR frequencies than the free or liquid molecule.
- However at lower frequencies than in the free molecule, a third, new interaction (“unusual” species) was observed in some of the zeolites tested. This interaction is more stable to outgassing processes than the “usual” species and the frequency observed for these species on the alkali mordenites follows the tendency $LiMOR \approx NaMOR < KMOR < CsMOR$.
- We propose that a stronger interaction whose stretching frequency is lower than that of free CO can only be explained by a multiple interaction. These species probably involve two cations, or one cation and one framework oxygen. The former should be more favored in zeolites because the most basic oxygens are most hindered by cations, which should impede some interaction with probe molecules.

- The relative intensity between the “unusual” and the “usual” species grows in the sense $\text{CO} < \text{less hindered nitriles} < \text{more hindered nitriles}$, and $\text{LiMOR} < \text{NaMOR} < \text{KMOR} < \text{CsMOR}$. This, therefore, indicates that the interaction takes place on the outer surface or on the mouths of the main channels.
- The distance between cations also seems to play an important role in the formation of the “unusual species”. On NaX and NaY zeolites, the formation of these species is not as favored as in mordenite samples, possibly because of the larger dimensions of the supercages.