Carbon-13 solid state MASNMR study on the role of pyrrolidine in various high silica zeolites††

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The $^{13}$C CPMASNMR spectroscopy and thermal analysis of pyrrolidine present in the as-synthesized forms of ZSM-23, ZSM-5 and ZSM-51 zeolites demonstrate that the pyrrolidine is occluded as neutral, chemically intact species in the 10-ring unidimensional, non-intersecting channels of ZSM-23. In ZSM-51 with its 6-membered channels pyrrolidine is located mainly in the large cages (probably as charged species). In ZSM-5, pyrrolidine molecules are present both as neutral molecules (in the channels) and probably as charged species (at the channel intersections).

Nitrogen containing organic compounds such as quaternary ammonium salts or amines are commonly used as templates in the synthesis of zeolite molecular sieves. Lok et al. have reviewed the role of such organic compounds in the synthesis of molecular sieves. These organic molecules may be present in the zeolite void space as neutral species and/or as cations. However, the exact role of organic guest molecules during zeolite formation is not yet clear. The fact that: (i) the same organic compound may lead to the formation of different zeolite structures; and (ii) a particular zeolite structure can be synthesized using a variety of organic molecules having quite different shapes, sizes and structures is yet to be explained properly.

Boxhorn et al. used $^{13}$C MASNMR spectroscopy, to show that tetrapropylammonium (TPA$^+$) ions are chemically intact and are occluded in two different environments in ZSM-5 zeolites. The sensitivity of $^{13}$C NMR chemical shifts of the methyl carbon atoms of tetramethylammonium (TMA$^+$) ions trapped in zeolites towards the environment in various zeolites such as ZK-4, sodalite, faujasite A, offretite, ZSM-4 and omega has also been demonstrated. Since high resolution $^{13}$C solid state NMR using magic angle and cross polarization (CP MASNMR) can provide relevant information on the structure and position/configuration of the organic species trapped in the zeolite pore system, it can be used to have a better understanding of the role of organic templates in the formation of zeolites. In the present paper, we have studied the role of pyrrolidine present in various high silica zeolites: ZSM-5, ZSM-23, and ZSM-51 using high resolution $^{13}$C CP MASNMR spectroscopy and thermal analysis to discern a relationship, if any, between the framework topology of the zeolites and the quantity, position and configuration of the organic guest molecules trapped within the zeolite pores.

Materials and Methods

The synthesis of the zeolites using pyrrolidine was carried out according to the literature method. The X-ray powder diffraction (Philips, PW-1710 Cu-K$_\alpha$) was used for phase identification and phase purity check of the zeolites. Chemical analysis of the zeolite materials was carried out by a combination of wet chemical and atomic absorption (Hitachi, Z-8000) methods. Thermal analysis (DTA/TG/DTG) was performed using a Netzsch (STA-410) thermobalance. The solid state magic angle NMR spectra using cross polarization (CP) were recorded using a MSL 300 spectrometer (Bruker) at 292 K. The chemical shifts are given in ppm with respect to tetramethylsilane as an internal standard. The contact time was 3 ms with the pulse delay of 3s. 6000-8000 FID's were collected before fourier transformation. Scanning electron microscopic examinations were carried out with a Cambridge Instrument (Stereo Scan-150).

Results and Discussion

Crystalline phase purity of samples

The Si/Al and ratios in the as-synthesized forms of ZSM-23, ZSM-5 and ZSM-51 were 54, 53 and 55 respectively. X-ray powder diffraction and scanning electron microscopic measurements confirmed the phase purity of the zeolites and absence of amorphous matter.
Thermal analysis

Table 1 shows the per cent mass loss due to removal of water and organic compounds after calcination of as-synthesized zeolites in air in the temperature range of 393-973 K. The number of molecules of H₂O/pyrrolidine per unit cell of the zeolite (Table 1) has been calculated from the observed mass loss, and molecular weights and chemical composition of the zeolites. Table 2 summarizes the structural features of these three high silica zeolites. ZSM-23 is a medium pore zeolite with unidimensional noninterconnected channels, while ZSM-5, a medium pore (10-ring) zeolite, possesses interconnected channel system. ZSM-51 is, however, a clathrasil having very large cavities connected through narrow (6-ring) channels. The extra void space available at the channel intersections in ZSM-5 is responsible for the larger amount of pyrrolidine occluded in it (6.5 mol/u.c) compared to that in ZSM-23 (1.1 mol/u.c). Since the unit cell of ZSM-5 contains 4 channel intersections, the observed value of 6.5 pyrrolidine mol/u.c., indicates that these organic molecules may be present both in the channels as well as at the channel intersections. In the case of ZSM-23 the organic molecules are present only in the channels as there are no channel intersections. In ZSM-51, pyrrolidine can be accommodated in the 19-hedra cavities only. According to its structure, a maximum cage filling of one pyrrolidine molecule per [59 61] large cage is possible, in reasonable agreement with observed results in Table 1.

13C-NMR spectra

Figure 1 illustrates the 13C NMR spectra of pyrrolidine in various environments. Pure liquid pyrrolidine as well as that adsorbed on silica gel showed essentially similar chemical shifts values, 47.1 and 25.7 ppm respectively for C-1 and C-2 of the pyrrolidine molecule. The 13C NMR spectrum of the as-synthesized ZSM-23 exhibits corresponding signals at 46.8 and 24.6 ppm (Fig. 1B) indicating that the chemically intact pyrrolidine is present is physically adsorbed form in the monodimensional channels of zeolite ZSM-23. However, much broader linewidths of the spectra of pyrrolidine present in ZSM-23 (Fig. 1B) indicate the restricted translational and rotational mobility of pyrrolidine molecules in the zeolitic environment. The 13C spectrum of as-synthesized ZSM-5 exhibits two strong peaks

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<th>Zeolite</th>
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<td>ZSM-51</td>
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Fig. 1—13C CP MAS NMR spectra of pyrrolidine physically adsorbed on silica gel (curve A) and present in the as-synthesized form of ZSM-23, ZSM-5 and ZSM-51 (curves B-D respectively).
at 64 and 22 ppm (probably corresponding to C-1 and C-2 of pyrrolidine), in addition to those due to adsorbed pyrrolidine (Fig. 1C). The intense peaks at 64 and 22 ppm are also present in the spectrum of as-synthesized ZSM-51 (Fig. 1D).

In the teardrop shaped 10-ring unidimensional pores of ZSM-23\(^9\) pyrrolidine is present only as adsorbed species performing the role of pore-filling/stabilizing agent. The slight upfield shift (to around 46 and 24 ppm compared to that around 48 and 26 ppm, for liquid state) of signals due to C-1 and C-2 is due to the greater interaction of the pyrrolidine molecules with their surroundings.

In ZSM-51, with large cavities connected through narrow (6-ring) channels\(^10\), pyrrolidine can be present only in the large cavities and it cannot be accommodated in the narrow channels of ZSM-51 in accordance with the thermal analysis results (Table 1). The \(^{13}\)C spectrum of ZSM-51 (Fig. 1D) exhibits two main peaks at 64 and 22 ppm (probably corresponding to C-1 and C-2 carbons of pyrrolidine respectively) indicating that pyrrolidine is mainly present in its charge form (due to the interaction with acid sites of the zeolite). It is known\(^11\) that a charge developed on nitrogen induces a downfield shift in the \(^{13}\)C NMR line of C-1 atom and an upfield shift in the C-2 signal. The availability of large void space around acid sites probably facilitates this.

In ZSM-5, which possesses both 10-ring channels (like ZSM-23) as well as large void space at the channel intersections\(^8\), the pyrrolidine molecules are present both in the channels (adsorbed/occluded, as in the case of ZSM-23) and in the extra void space at channel intersections (charged/reacted form, as in the case of ZSM-51). Thermal analysis data also support the presence of pyrrolidine molecules in the channels and at the channel intersections of ZSM-5.

It is well known that in ZSM-5 the acid sites are mainly located at the channel intersections. The availability of both acidic centres and void volume in their neighbourhood, perhaps, leads to the formation of charged forms of pyrrolidine during the synthesis of ZSM-5, and ZSM-51.

Acknowledgement
This work was partly funded by U.N.D.P.

References