Spectroscopy, energetics and siting of NH+4 in zeolites; theory and experiment

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specific role of the indium sites formed after hydrogen or hydrocarbon reduction. Both acidity and catalytic activity gradually decrease with the indium content until all zeolite acid sites are covered by In. It seems that the main difference between In and Ga/zeolite systems consists in the specific properties of the cationic species introduced by the solid state reaction under discussion. The replacement of zeolite protons by indium, existing probably as a In^+ cation results in a strong suppression of the whole acidic function of the zeolite. In contrast, the intrinsic activity of the Ga^+ cation as a Lewis acid site,through water dissociation route or by facilitating the hydrogen transfer seems to be high enough to attain a high catalytic activity in carbocationic transformations of hydrocarbons. The combination of both cations in one and the same zeolite offers also interesting possibilities for regulating the catalytic properties as it is briefly shown in the case of n-pentane conversion.

Finally, our claim is that a novel zeolite is obtained through stabilization of indium as In^+ in the interior of the zeolite crystallites. Further research is still necessary in order to elucidate whether the unusual oxidation state of the indium cation and its very high content in various zeolite structures may be utilized for appropriate catalytic transformations.

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REFERENCES

1. Price, G.L. and Kanazirev, V.,J.Catal.,126,267(1990).
2. Kanazirev ,V., Price, G.L.and Dooley, K.M.,in: *Zeolite Chemistry and Catalysis,* Eds.Jacobs, P.A. et al., Elsevier Science Publishers B.V., Amsterdam,p.277(1991).
3. Kanazirev, V.,Dimitrova, R.,Price ,G.L.,Khodakov, A.Yu. ,Kustov L.M. and Kazansky V., J.Mol.Catal., 70, 111 (1991)
4. Kanazirev,V.,Mavrodinova, V.,Kozova and Price, G.L.,Catal.Lett.,9,35 (1991).
5. Zatorski, L.W., Wierzchowski, P.T. and Ciochowlas,A.A.,*Proceedings of the 6th International Symposium of Heterogeneous Catalysis,* Eds. Shopov ,D.et al.,p.205(1987).
6. Zatorski, L.W., Bull.Polish.Acad.Sci.Chem.,35,325 (1987)
7. Kanazirev, V. and Borisova, N., Zeolites, 2, 23 (1982).
8. Kanazirev, V., Tsoncheva, T. and Minchev, Ch.,Z.Phys.Chem.N.F., 149, 237 (1986).
9. Breck, D.W.,*Zeolite Molecular Sieves,* Willy, J. and Sons, New York (1974).
10. Barin, I., *Thermodinamical Data of Pure Substances,* VCH Weinheim, 1989.
11. Kanazirev,V. and Foerster, H., in preparation.

SPECTROSCOPY, ENERGETICS AND SITING OF NH_4^+ IN ZEOLITES; THEORY AND EXPERIMENT

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ABSTRACT:

The adsorption of an ammonia molecule onto an acidic zeolite and the proton transfer from the zeolite to the ammonia are studied by quantum chemical methods. The NH_4^+ is adsorbed with two or three hydrogen bonds to the zeolite. The calculated vibrational frequencies explain the experimental infra–red spectra.

INTRODUCTION

One of the most interesting applications of zeolites is their use as a catalyst [1]. Many of the catalytic properties stem from the acidic properties of the zeolites and much research has been carried out on the properties of the acidic group [2]. The interaction between the acidic hydroxyl group and the base ammonia has been studied by many techniques, like infra red spectroscopy, NMR–spectroscopy, Temperature–Programmed Desorption (TPD), X–Ray Diffraction (XRD), inelastic neutron scattering or theoretically by quantum–chemical calculations [3–40].

In this paper we will study the interaction of the zeolite acidic site and the NH_3 molecule by quantum chemical methods. Although there are methods and programs available to do calculations on periodic systems [41-43] in this paper, as in most, the zeolite is modelled by a small cluster. The cluster approach has the disadvantage that the hydroxyl–group, modelled by the cluster does not always behave the same towards adorbents or bases as in the crystalline case, as has been shown by a recent ab–initio study on the chabazite–NH_3 system [44]. The advantage of cluster calculations, however, is that a high quality basis set can be used, that geometries can be optimized, and that a normal mode analysis can be carried out. Also intensities for infra–red specta can be calculated by ab initio methods.

From ^{15}N NMR spectroscopy it is known that at low temperatures the ammonium cation is located near the aluminum tetrahedra [32]. At low temperatures the NH_4^+ is tumbling around the aluminum tetrahedrons [17,31,32]. Thus the clusters are chosen such that the siting of the ammonium tetrahedron can be described.

METHODS

The choice of the clusters

When doing quantum chemical calculations on clusters there are two choices to be made: the choice of the cluster and the choice of the basis set. In an earlier paper we have shown that the system is not described very well when a small basis set is used [39]. Thus we have to use a large basis set. The disadavantage of this is that the size of the cluster is limited.

In figure 1 the clusters that are used to model the zeolite are shown. For each coordination of the ammonium cation onto the zeolite wall a different cluster is used. In figure 1a the cluster is shown which is used if the ammonium cation is bonded to the zeolite with a single hydrogen bond. This cluster contains the characteristic acidic site, namely the Si–OH–Al group. In figure 1b the cluster is shown for the ammonium cation adsorbed onto the zeolitic cluster with two hydrogen bonds. In figure 1c the cluster is shown that is used if the ammonium cation is adsorbed with three hydrogen bonds. Finally in figure 1d the case is shown in which two ammonia molecules are co–adsorbed on one single site.

Quantum–chemical methods

The quantum–chemical calculations are done at the ab initio SCF–level. We use a mixed basis set with a minimal basis set on the hydrogens that are saturating the dangling bonds, a 6-31G(D) basis set on the silicon and aluminum atoms, a 6-311G(d) basis set on the nitrogen atom, a 31G(p) set on the hydrogen molecules that are attached to the nitrogen, and a 6-311+G(d) basis set on the anionic oxygens. It has been shown that the anionic oxygen needs a large basis set because of its diffuse character [39]. If a only slightly smaller basis set is used, e.g. 6-31G(d) the proton transfer energy is overestimated by about 40 kJ/mol [39]. Inclusion of electron correlation energy by means of second order Møller–Plesset perturbation theory [45] and the use of the counterpoise correction [46,47] for the binding energies increases the calculation time tenfold and it decreases the proton transfer energy by 20 kJ/mol. For all the clusters the geometries are fully optimized at the SCF–level using gradient techniques. This geometry optimization is necessary. There is experimental and theoretical evidence that the zeolite lattice is very flexible [48]. Once the geometries are optimized that infra–red spectra can be calculated using analytical second derivatives.

Experimental

The spectra of the ammonium loaded zeolites were recorded in transmission mode at a resolution of 1 cm^{-1}, with a Bruker IFS 113v spectrometer. 250 scans were coadded. Spectra were recorded using self–supporting discs of zeolite sample (4.5 mg/cm^2). The samples were obtained by exchange of the sodium form of the zeolites at 80°C. Then the samples, a 6.3:1 Si/Al mordenite and a 2.7:1 Si/Al Y zeolite, were placed in an in–situ cell which was connected to a vacuum–system and a gasdosing system. The sample was dehydrated and deammoniated at 500°C in vacuo, after this anhydrous NH_3 was adsorbed at room temperature. Before the spectra were recorded any physisorbed NH_3 was removed by evacuation at room temperature.

RESULTS AND DISCUSSION

Heats of adsorption

For the adsorption sites shown in figure 1 the adsorption energies have been calculated (Table I).

Table I. The calculated heats of adsorption (kJ/mol). * The energy refers to the adsorption of the two ammonia molecules; i.e. 30 kJ/mol each.

parameter	value
singly coordinated	–57
doubly coordinated	–110
triply coordinated	–112
coadsorbed structure	-60 *

In the case of the singly bonded structure the favorable structure is the one in which the proton is attached to the zeolitic cluster. Because the ionic structure was not a minimum the geometry could not be optimized for this case [39]. If the geometry is fixed however the difference between the hydrogen bonded form and the ionic form is 65 kJ/mol [39]. Clearly the favorable structures are those in which the ammonium cation is bonded with two or three hydrogen bonds. The calculated heats of adsorption compare very well with experimental heats of adsorption. If the heat of adsorption is measured with TPD the values for the heats of adsorption are in the range 112 ± 33 kJ/mol. [11,18,20,21,22,26,28]. With Micro-Calorimety these values are in the range of 146 ± 146 kJ/mol. [9,12,13,14,27].

The experimental spectra

Spectra have been recorded for two samples. In figure 2a the N–H stretching region of a spectrum of a NH_4^+ mordenite with a Si/Al ratio of 6.3 is shown. In figure 2b, the spectrum for a NH_4^+–Y zeolite is shown with a Si/Al ratio of 2.7. Although the spectra were recorded for different zeolites they show the same features. There are three broad overlapping bands and one sharp peak in the 2700–3500 cm^{-1} region. Also spectra of other ammonium containing zeolites like zeolite beta [4], and erionite [5] shows these characteristics.

The calculated spectra

For the clusters shown in figure 1 the spectra have been calculated. They are shown in figure 3. Analytical second derivatives were used. The frequencies were scaled by 0.92. If this scaling factor is used the calculated N–H strectching frequencies of NH_3 matches the experimental ones.

The spectra of the hydrogen bonded form and of the structure where two NH_3–molecules are coadsorbed are dominated by one single peak. The spectra of the doubly bonded structure show two intense peaks and two smaller ones that are hardly visible. The structure with the triply coordinated ammonium, shows two intens peaks very close to each other and one less intense peak. From the heats of adsorption it may be expected that the latter two structures will dominate the spectrum of the ammonia loaded zeolite. The experimental spectra can be explained quite easily from the calculated ones. The two broad bands on the left side can stem from the doubly coordinated ammonium, the triply coordinated structure causes the two peaks on the right, the broad band around 3000 cm^{-1} and the relative sharp one around 3400 cm^{-1}. This sharp one is the N–H stetching of the proton pointing away from the zeolitic site.

CONCLUSIONS

The proton of the zeolite is completely transfered to the base NH_3. NH_4^+ is bonded to the zeolite wall with two or three hydrogen bonds. The calculated heats of adsorption are good agreement with the experimental ones. The calculated spectra explain the experimental ones.

References

[1] D.W. Breck, Zeolite molecular sieves, Wiley Interscience, New York (1974).

[2] 'Introduction to zeolite science and practice', H. van Bekkum, E.M. Flanigan and J.C. Jansen (eds.), Stud. in Surface Sci. and Catal. **58**, Elsevier Amsterdam (1991).

[3] W.L. Earl, P.O. Fritz, A.A.V. Gibson and J.H. Lunsford, J. Phys. Chem. **91** , 2091 (1987).

[4] S.G. Hegde, R. Kumar, R.N. Bhat and P. Ratnasamy, Zeolites **9**, 230 (1989).

[5] A. Kogelbauer, J.A. Lercher, K.-H. Steinberg, F.Roessner, A. Soellner and R.V. Dmitriev, **9**, 224 (1989).

[6] G.A. Ozin, M.D. Baker, J.Godber and C.J. Gil, J. Phys. Chem. **93**, 2899 (1989).

[7] G.A.Ozin, M.D. Baker, K. Helwig and J. Godber, J. Phys. Chem. **89**, 1846 (1985).

[8] E.A. Paukshtis, Y.D. Pankrat' ev, A.G. Pel' menschikov, E.B. Burgina, V.M. Turkov, E.N. Yurchenko and G.M. Zhidomirov, Kinetika i Kataliz **27**, 1440 (1986).

[9] R.D. Shannon, R.H. Staley, A.J. Vega, R.X. Fischer, W.H. Baur and A. Auroux, J. Phys. Chem. **93**, 2019 (1989).

[10] T. Stock, D. Dombrowski, J. Fruwert and H. Ratajczak J.C.S. Farad. Trans I,**79**, 2773 (1983).

[11] N.-Y. Topsøe, K. Pedersen and E.G. Derouane, J. Catal **70**, 41 (1990).

[12] K. Tsutumi, Y. Mitani, H. Takahashi, Bull. Chem . Soc. Jpn **56**, 1912 (1983).

[13] J.C. Vedrine, A. Auroux, V. Bolis, P. Dejaifve, C. Naccache, P. Wierzchowski, E.G. Derouane, J.B. Nagy, J.-P. Gilson, J.H.C. van Hooff, J.P. van den Berg and J. Wolthuizen, J. Catal **50**, 248 (1979).

[14] A. Auroux and J.C. Vedrine, Stud. in Surf. Sci. and Catal **20**, 311 (1985).

[15] D.R. Corbin, L. Abrams, G.A. Jones, M.M. Eddy, W.T.A. Harrison, G.D. Stucky and D.E.Cox, J. Am. Chem. Soc **112**, 4821 (1990).

[16] L.B. McCusker, Zeolites **4** , 50 (1990).

[17] D.Deininger and B. Reïmann, Z. phys. Chemie **251**, 353 (1972).

[18] E. Dima and L.V.C. Rees, Zeolites **8**, 10 (1990).

[19] B.P. Embaid, M. Hunger, M.M. Landrove and R. Martin, Z. phys. Chemie **166** (neue folge), 109 (1990).

[20] C.V. Hidalgo, H. Itoh, T. Hattori, M. Niwa and Y. Murakumi, J. Catal. **85**, 362 (1984).

[21] H.G. Karge and V. Dondur, J. Phys. Chem. **94**, 765 (1990).

[22] H.G. Karge, V. Dondur and J. Weitkamp, J. Phys. Chem **95**, 283 (1991).

[23] M.M. Mestdagh, W.E.E. Stone and J.J. Fripiat, J. Catal. **38**, 358 (1975).

[24] D. Michel, A. Germanus and H. Pfeifer, J.C.S. Farad. Trans. I, **78**, 237 (1982).

[25] L.M. Parker, D.M. Bibby and R.H. Meinhold, Zeolites **5**, 384 (1985).

[26] J.G. Post and J.H.C. van Hooff, Zeolites **8**, 9 (1984).

[27] Z.C.Shi, A. Auroux and Y.B. Taarit, Can. J. Chem **66**, 1012 (1988).

[28] W. Schirmer, H. Stach, K. Fiedler, W. Rudzinski and J. Jagiello, Zeolites **3**, 199 (1983).

[29] H. Kriegsman, A. Reklat, E. Löffler and Th. Steiger, Z. phys. Chemie **271**, 61 (1990).

[30] H. Itoh, C.V. Hidalgo, T. Hattori, M. Niwa and Y. Murakumi, J. Catal. **85**, 521 (1984).

[31] T.J. Udovic, R.R. Cavanagh, J.J. Rush, M.J. Wax, G.D. Stucky, G.A. Jones and D.R. Corbin , J. Phys. Chem **91**, 5968 (1987).

[32] A.J. Vega and Z. Luz, J. Phys. Chem **91**, 365 (1987).

[33] G.P. Babu, S.G. Hegde, S.B. Kulkarni and P. Ratnasamy, J. Catal **81**, 471 (1983).

[34] P. Dejaifve, A. Auroux, P.C. Gravelle, J.C. Vedrine, Z. Gabelica and E.G. Derouane, J. Catal **70**, 123 (1981).

[35] S.-Y. Zhang, O.Talu and D.T. Hayhurst, J. Phys. Chem **95**, 1722 (1991).

[36] M. Allavena, K. Seiti, E. Kassab, Gy. Frenczy and J.G. Ángyán, Chem. Phys. Lett. **168**, 461 (1990).

[37] A.S. Medin, V.Y. Borovkov, V.B. Kazansky, A.G. Pelmenschikov and G.M. Zhidomirov, Zeolites **10**, 668 (1990).

[38] P. Geerlings, N. Tariel, A. Botrel, R. Lissillour and W.J. Mortier, J. Phys. Chem. **88**, 5752 (1984).

[39] E.H. Teunissen, F.B. van Duijneveldt and R.A. van Santen, J. Phys. Chem. **96**, 366 (1992).

[40] E. Kassab, K. Seiti and M. Allavena, J. Phys. Chem. **95**, 9425 (1991).

[41] C. Pisani, R. Dovesi and C. Roetti, '*Hartree–Fock Ab–initio Treatment of Crystalline Systems*, Lecture Notes in Chemistry **48**, Springer Verlag, Berlin **1988**.

[42] C. Pisani and R. Dovesi, Int. J. Quantum Chem. **17**, 501 (1980). R. Dovesi, C. Pisani, C. Roetti and V.R. Saunders, Phys. Rev. B **28**, 5781 (1983). R. Dovesi, Int. J. Quantum Chem. **29**, 1755 (1986).

[43] G. te Velde, Numerical Integration and other methodological aspects of bansdtructure calcluation, pHD–thesis VU Amsterdam (1990).

[44] E.H. Teunissen, C. Roetti, C. Pisani, A.J.M. de Man, A.P.J. Jansen, R. Orlando, R.A. van Santen and R. Dovesi, to be published.

[45] C. Møller and M.S. Plesset, Phys. Rev. **46**, 618 (1934).

[46] S.F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[47] J.H. van Lenthe, J.G.C.M. van Duijneveldt–van de Rijdt and F.B. van Duijneveldt, Adv. in Chem. Phys. **69**, 521 (1987).

[48] R.A. van Santen, A.J.M. de Man, W.P.J.H. Jacobs, E.H. Teunissen and G.J. Kramer, Catal. Lett. **9**, 273 (1991), and references therein.

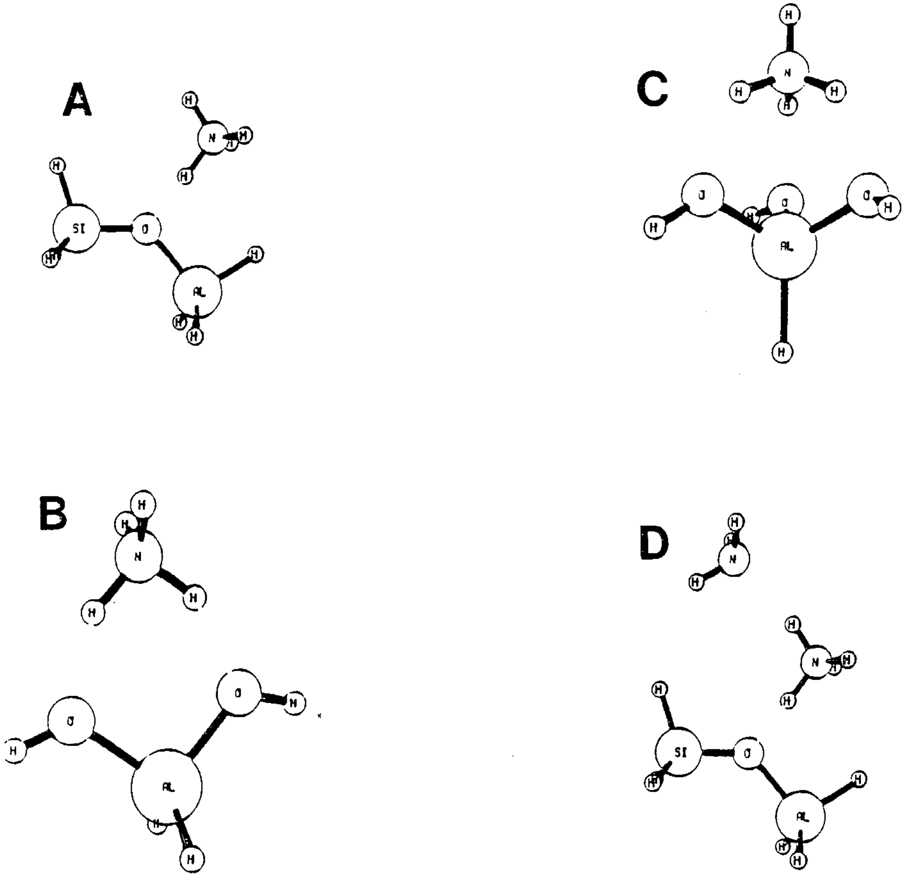

Figure 1. The clusters used to model the adsorption sites; a: the singly bonded structure, b: the doubly bonded structure, c: the triply bonded structure, d: the coadsorbed structure.

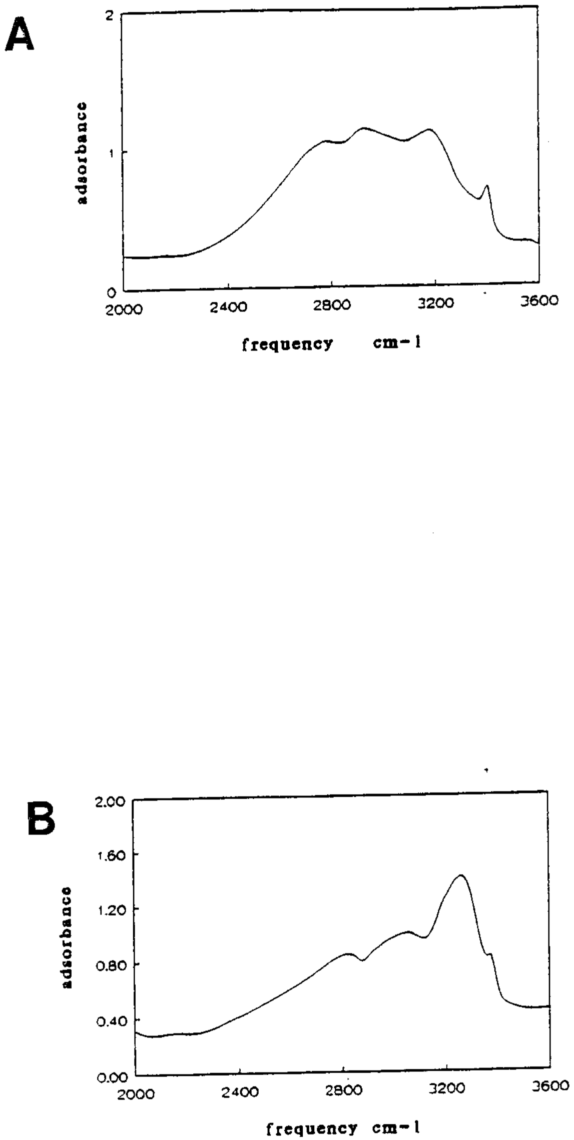

Figure 2. The experimental spectra of the ammonia reconstituted form of mordenite (a) and zeolite Y (b).

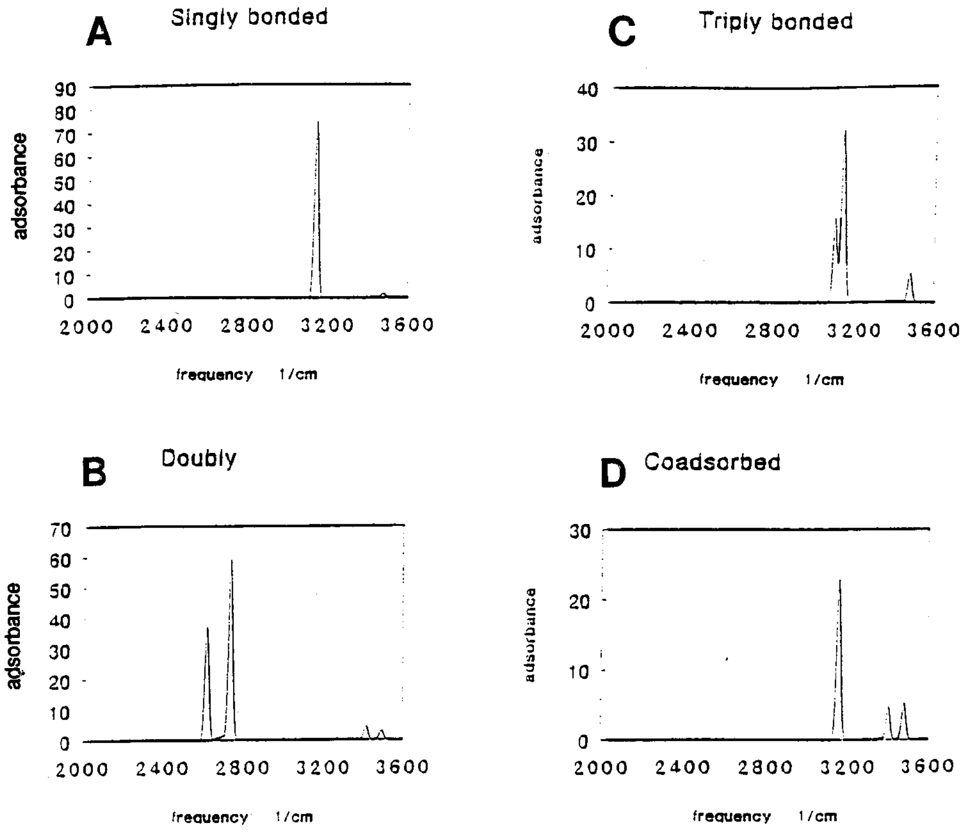

Figure 3. The calculated spectra; a: the singly bonded structure, b: the doubly bonded structure, c: the triply bonded structure, d: the coadsorbed structure.

STUDIES ON TEMPLATE MOLECULES: LOCATION,ORIENTATION,PROTONATION AND INTERACTION WITH FRAMEWORK IN HIGH SILICA ZEOLITES

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ABSTRACT

Template molecule of TMEDA (tetramethylethylenediamine) trapped in the channel or the cage of high silica zeolites of mordenite,ZSM-5, ZSM-35, ZSM-39, and CF-3 were characterized by ^{13}C CP MAS and HPDEC MAS n.m.r. spectra, IR spectra, TG/DTA and chemical analysis. Linear relations between ^{13}C chemical shift (δ) for $-CH_3$ and $-C_2H_4-$ groups of TMEDA, and the free diameter (l) of the channel or the cage have been determined. It was found that an obvious difference in relative intensity of ^{13}C CP and HPDEC resonance, line narrowness, and great division from the δ-l linear relations can be used to deduce the position, the orientation of template molecule in the channel or the cage of the zeolites, and its interaction with framework.

INTRODUCTION

The study on the location and state of the organic template molecules trapped in the zeolite framework plays very important role in revealing the process of the crystallization of the zeolites. ^{13}C MAS n.m.r. is one of the most useful methods for such a study. Position of template [1-4], dependence of its ^{13}C chemical shift on the size of the cage and its dynamic behaviour[5,6], the protonation state[7-9], the presentation of complexes [10], and the configuration [11] have been studied.

In system of TMEDA-Na_2O-SiO_2-Al_2O_3-H_2O, mordenite(Md.), ZSM-5,ZSM-35, and clathrate zeolites ZSM-39, and CF-3 [12,13] were hydrothermally synthesized[14]. In this study, ^{13}C CP MAS and HPDEC MAS n.m.r.,IR, TG/DTA, and chemical analysis have been used to investigate the position, the orientation, the occupancy percentage, and the protonation of TMEDA in the channel or the cage, and its interaction with the framework of the zeolites.