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Surface properties of ZSM-5 modified by phosphorus

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Phosphorus modification of ZSM-5 leads to extra framework P^{5+} and probably incorporation of +3 valence state of P in the framework. The resulting system has increased Brønsted acidity. Theoretical calculations also favour the postulate that phosphorus in +3 valence state can be incorporated into the lattice.

Keywords: ZSM-5; pyridine adsorption; Xα method; phosphorus valence state

1. Introduction

Pentasil zeolites have been examined extensively as the active component of the catalysts for a variety of hydrocarbon conversions [1]. The modulation and tuning of the acidity of these catalysts which is mainly responsible for the observed catalytic behaviour, in addition to shape selectivity is associated with the control of the aluminum ions in the zeolite framework. Introduction of metal cations, boron and phosphorus has been used to improve the desired catalytic properties of ZSM-5 [2–5]. Normally, incorporation of different elements in the aluminosilicate lattice is achieved either under the conditions of hydrothermal synthesis or by post treatment or impregnation [6]. Kujima et al. [7] attempted phosphorus incorporation into ZSM-5 by PCl_5 treatment and reported that only aluminum extraction without phosphorus insertion occurred. While isomorphous substitution of phosphorus could be achieved in the zeolite framework when sodium form of zeolites was reacted with PCl_5 under static conditions at 423–873 K. Jentys et al. [8] used three model compounds, namely, phosphoric acid, trimethyl phosphine (TMP) and trimethyl phosphite (TMPT) for modifying HZSM-5 and reported that dealumination, generation of $H_2PO_4^-$ groups and strong chemisorption of TMP are the dominating mechanisms for the decrease in the concentration of the strong Brønsted acid sites. Kaeding and Butter [9] have earlier reported that replacement of bridging hydroxyl groups by $H_2PO_4^-$ group could be responsible for the increased number of acid sites, which are weaker in strength compared to those of the unmodified zeolite. Vedrine et al. [10] however, have preferred the explanation that modification of channel size and increased tortuosity by the phosphorus compounds could account for the higher C_2–C_4 olefin selectivity in the methanol conversion reaction. There are also reports which favour the poisoning of strong Brønsted acid sites by the phosphorus compounds used for modification [11]. Catalytic consequences of ZSM-5 systems modified by phosphorus compounds have been examined by a number of workers [3,10,12–14] especially for methanol to gasoline conversion (MTG), for the alkylation of toluene by methanol, for the isomerization of xylenes as well as cracking of *n*-hexane. The selectivity alterations observed are attributed as either due to changes in channel size [4] or due to alteration of the strength of the Brønsted acid site or to the increase in the number of weak Brønsted acid sites.

The purpose of the present investigation is therefore to address the question of phosphorus incorporation in the ZSM-5 framework as well as to examine the manifestation of this incorporation in the surface properties especially with respect to alteration of the strength of Brønsted acid sites. Most of the reports available in literature seem to favour the extra framework modification by phosphorus in the aluminosilicate framework. Theoretical cluster calculations have also been carried out (by semi-empirical methods of MNDO and $X\alpha$) to ascertain whether isomorphous substitution by phosphorus is feasible in the pentasil zeolite framework. Another question that is addressed is that, if phosphorus substitution were to occur, what is the most probable valence state of phosphorus, i.e. +3 or +5?

2. Experimental

The synthesis of phosphorus containing ZSM-5 zeolites was carried out as follows [3]. Water glass, *n*-propyl amine, aluminum sulphate, phosphoric acid were used as starting materials. *n*-propyl amine was mixed with the source of silica. The solution was stirred vigorously for 1 h at room temperature, then a solution of aluminum sulphate and phosphoric acid was added. Typically the samples were prepared from a gel composition $5.3Na_2O : 60SiO_2 : 1.0Al_2O_3 : 0.54H_3PO_4$: 23.17*n*-propyl amine : $2487.9H_2O$. The amount of phosphoric acid in the gel was adjusted according to the desired level of phosphorus content. The gel was then homogenized for 2 h and then transferred into a stainless steel autoclave and autoclaved at 443 K for 55 h. The zeolite crystals obtained were washed, dried at 383 K overnight and calcined at 723 K in air to remove the template. ZSM-5 without phosphorus was prepared using a similar procedure but without the addition of phosphoric acid. The H-form of the prepared zeolites was obtained by ion exchanging the sodium form with 1 M ammonium chloride. After ion exchange the zeolites were thoroughly washed and dried at 383 K for 1 h. The samples were then calcined at 748 K for 4 h.

XRD patterns of the as-prepared samples were recorded in the range $2\theta = 5-60°$ on a Phillips (model PW 1140) automatic powder diffractometer using Ni filtered Cu K_α radiation at a scanning rate of 3 deg/min.

Infrared studies were carried out in a portable high vacuum IR cell having NaCl windows equipped with a heating section using a Perkin Elmer FTIR model 1760. The cell was connected to a vacuum system (10^{-5} Torr). Self-supporting wafers of H-form of the zeolites were prepared by compressing the samples at a pressure of 8 tons for 1 min. The sample was then loaded into the cell and was activated at 673 K in the heating zone for 3 h in vacuum. The sample was then cooled to room temperature and the IR spectra were recorded. Pyridine vapour was then admitted into the cell for 15 min. The gas phase and physically adsorbed pyridine were removed by evacuating the cell to 10^{-5} Torr and the IR spectra recorded.

XPS of the sample was recorded at room temperature by using VG scientific ESCALAB MK II spectrometer using Mg K_α ($h\nu$ =1253.6 eV) radiation.

The quantum chemical calculations were carried out using the MS-Xα and semi-empirical MNDO methods. The geometrical parameters for the dimeric clusters of the form $[(OH)_3\text{–T–O–T–}(OH)_3]^{n-}$ were from X-ray crystallographic data [15]. The T (Al, Si or P) and the oxygen positions are assigned according to their location in the framework. The hydrogen atoms needed to maintain the electroneutrality of the cluster are located at the nearest neighbour T sites. The cluster charge is zero when Si atoms are present, −1 when Al or P (+3) substitutes Si and +1 when P (+5) substitutes Si.

In the MS-Xα method the radii of the muffin tin spheres surrounding the various atoms are based on the Norman radii. The whole cluster of atomic spheres is surrounded by an outer sphere. In the case of charged species a Watson sphere is used with radius equal to the outer sphere and has the charge opposite to that of the cluster. The atomic exchange parameters (α) are taken from Schwarz's table [16]. Calculations were also done using the semi-empirical MNDO method for these clusters.

3. Results and discussion

The details of the results of MNDO method are available in our earlier communication [17]. The total energies of the clusters considered are given in table 1. The total energies of the same clusters without phosphorus substitution obtained by using the ab initio method as extracted from ref. [18] are also included in table 1. It is seen that our results of the Xα method and the results of ab initio calculations

Table 1
Total energies of the $(OH)_3\text{–T–O–T}'\text{–}(OH)_3$ cluster with TT′ as Si and Si, Si and Al and Si and P

Cluster	Ab initio (Ry)	MNDO (eV)	Xα (Ry)
[SiSi]	−2181.108	−2512.081	−2174.825
$[SiAl]^{-1}$	−2087.619	−2462.567	−2104.787
$[SiP]^{-1}$		−2572.924	−2253.381
$[SiP]^{+1}$		−2565.249	−2243.233

agree well. The results from both MNDO and Xα methods show that phosphorus substituted systems are stable compared to the aluminosilicate cluster considered for the calculation. Between the two possibilities the cluster containing P^{3+} appears to be comparatively more stable than the cluster containing P^{5+}, though the total energies of both the clusters are lower than that of the cluster chosen to represent the zeolite. The cluster calculations thus show that isomorphous substitution in ZSM-5 by phosphorus is feasible and the probable oxidation state of phosphorus in the substituted configuration is P^{3+}.

In order to ascertain whether P^{3+} is really present in the lattice, X-ray photoelectron spectra (XPS) were recorded for the 2p emission of both silicon and phosphorus and the typical spectrum obtained for phosphorus 2p emission is given in fig. 1. There are various other aspects of XPS of zeolites which have been considered in literature [19]. However, our objective in this study is to examine whether phosphorus substitution has any effect on the binding energy of the Si 2p emission (since the charge on the bridging oxygen was found to be quite different for the different clusters, −0.7592 for SiOSi, −0.7239 for SiOAl, and −0.8849 for SiOP (P^{3+}) as deduced from MNDO calculations on typical clusters) as well as to scan phosphorus 2p region to ascertain the valence state of phosphorus. The Si 2p peak had a binding energy value of 103.0 eV with FWHM of 2.2 eV. The binding energy value of Si 2p in ZSM-5 has been reported to be 103.4 eV [4]. It is therefore, not possible to deduce whether phosphorus substitution has occurred from the binding energy value of Si 2p level. The XP spectrum of the P 2p level is shown in fig. 1, wherein there are two peaks with binding energy values of 130.2 and 135.9 eV. The peak around 136 eV is attributed to the presence of phosphorus in the +5 valence state while the lower binding energy peak around 130 eV can be tentatively ascribed to phosphorus in the +3 valence state. Therefore it is presumed that the attempts to incorporate phosphorus using phosphoric acid as source would result in the pres-

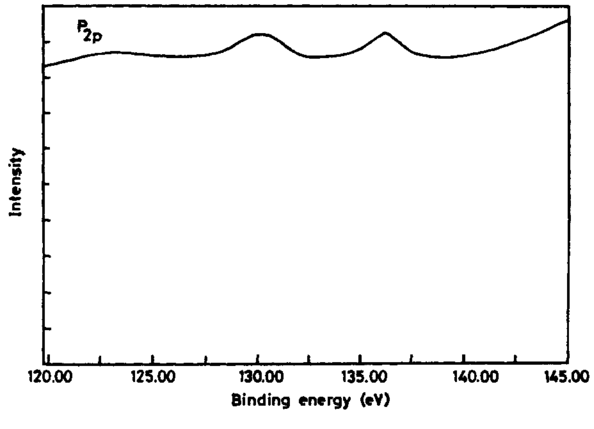

Fig. 1. X-ray photoelectron spectra of P (2p) emission of P-ZSM (Al/P)=6.

Table 2
Values of unit cell parameters and unit cell volume for phosphorus containing zeolite ZSM-5

System	*a* (Å)	*b* (Å)	*c* (Å)	Unit cell volume ($Å^3$)
ZSM-5	20.1061	19.8564	13.4192	5357.41
ZSM Al/P = 6	20.1069	19.8962	13.4087	5364.16
ZSM Al/P = 4	20.1061	19.8848	13.4522	5378.27
ZSM Al/P = 2	20.1158	19.8654	13.4578	5377.85
TPA ZSM-5 [a]	20.022	19.899	13.383	5332.02

[a] Data deduced from XRD pattern given in ref. [21].

ence of phosphorus both in +3 and +5 valence states. In order to ascertain the nature of framework species if present XRD spectra of the samples synthesized were recorded and the data obtained are given in table 2. It is seen that the unit cell volume increases with decrease in Al/P ratio and the unit cell volume attains a constant value around Al/P = 4, indicating that if at all phosphorus incorporation were to occur it takes place to a certain extent. The IR spectra of the samples synthesized given in fig. 2 together with that of pure ZSM-5 show that crystallization of phosphorus containing zeolites in the ZSM-5 structure.

The acidity of the phosphorus containing zeolites was evaluated by the adsorption of pyridine which gave IR absorptions at 1545 and 1450 cm^{-1} corresponding

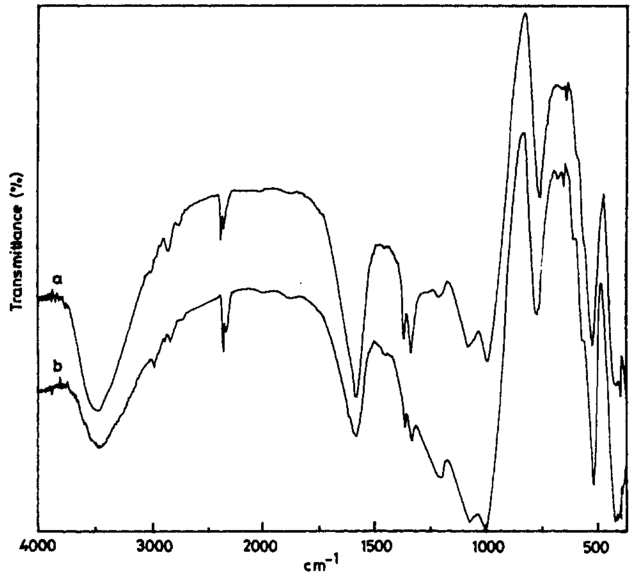

Fig. 2. Infrared spectra of the synthesized zeolites, (a) ZSM-5; (b) ZSM-5 (Al/P) = 6.

Table 3
IR data of pyridine adsorbed on phosphorus containing zeolites

System	$\nu_{\text{Brønsted}}$ (B) (cm^{-1})	ν_{Lewis} (L) (cm^{-1})	$\nu_{\text{B and L}}$ (cm^{-1})	B/L[a]
ZSM	1547	1446.3	1490.7	1.2236
ZSM Al/P = 6	1547	1445.6	1490.6	1.4222
ZSM Al/P = 2	1547.4	1446	1490.8	1.444

[a] $B/L = A_B/A_L(\epsilon_L/\epsilon_B)$; $\epsilon_L/\epsilon_B = 1.5$ for zeolites having silica/alumina ratio > 15 from ref. [20].

to adsorption on Brønsted and Lewis acid sites respectively [20]. The data extracted from these IR measurements are assembled in table 3. It is seen that with phosphorus addition the proportion of Brønsted acid sites increases. This effect which is in agreement with the reported results [9] does not anyway provide clues whether phosphorus is in the framework or not. Based on the observations, we are tempted to propose that phosphorus if present in the framework is in +3 state and extra framework phosphorus is in +5 state with a limitation over the extent of phosphorus incorporation in the lattice.

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