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Transition metal-silicate analogs of zeolites

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The synthesis and characterization of three transition metal (Fe^{3+}, Ti^{4+} and V^{4+})-silicate molecular sieves are discussed. The key factors for a successful incorporation of these metal ions in the growing silicate network during gel preparation/hydrothermal synthesis (e.g. avoidance of insoluble/sparingly soluble metal hydroxides/oxyhydroxides (Fe^{3+} and Ti^{4+}) and alkali metal ions (Ti^{4+} and $V^{4+/5+}$)) as well as the effects of post synthesis drying, calcination etc. on the stability of these metal ions in the framework are evaluated. Various spectroscopic and other techniques which are required to provide general as well as specific structural and textural information about the fate of these transition metal ions are discussed.

Keywords: Zeolites; transition metal silicates; zeolites with transition metals; Ti^{4+} silicates; V^{4+} silicates; Fe^{3+} silicates

1. Introduction

Zeolites are tectosilicates with a three-dimensional framework of SiO_2 tetrahedra in which a given tetrahedron shares each of its four oxygens with one each of four other tetrahedra. When the Si atoms are isomorphously replaced by Al, Ga, Fe etc., aluminosilicates, gallosilicates, ferrisilicates etc., with negatively charged framework, are obtained. When tetravalent transition metal ions, like Ti^{4+} are substituted for Si^{4+} a neutral metallosilicate framework is obtained. The transition metal silicate molecular sieves are potential shape selective oxidation catalysts.

The present paper summarizes the work carried out at the National Chemical Laboratory, in the area of ferri-, titanium- and vanadium-silicate analogs of zeolites. An earlier review [1] had dealt with the ferrisilicates. The main part of the review deals with the synthesis and structural characterization of ferri-, titanium- and vanadium-silicate molecular sieves. The catalytic properties of Ti and V silicates in selective oxidation reactions are dealt with in a subsequent paper in this issue by Ramaswamy and Sivasanker [2].

2. Synthesis of metallosilicate zeolites: general features

2.1. GENERAL

When transition metal ions are present in the three-dimensional silicate framework, they may occupy any, some or all of the following locations: (1) lattice framework positions, (2) surface defect sites (Si–O–M) (reaction of the metal ion with the surface silanol groups nay generate such sites i.e. surface grafting), (3) cation exchange sites, (4) finely divided oxide clusters inside/outside the pores of the molecular sieves, and (5) bulk oxides on the external surface. The relative distribution of the transition metal ions amongst these various locations will depend largely on the particular synthesis procedure and drying/calcination conditions adopted. In a basic medium (pH = 9–13), Fe^{3+} and Ti^{4+} form insoluble oxides/hydroxides, while V^{4+}/V^{5+} form soluble oxides in the above-mentioned pH range. Further Ti^{4+} also forms stable alkali metal titanates.

For a successful incorporation of Fe^{3+} and Ti^{4+} ions into the zeolitic framework the precipitation of the metal hydroxides/oxyhydroxides during gel preparation should be avoided, because the latter, once formed, do not lead to the incorporation of the metal in the silicate network. Proper choice of synthesis conditions can ensure that at least in the as-synthesized form, most of the metal ions are incorporated in the framework. An understanding of the interaction of transition metal ions with the various silicate species (present in the solution), organic templates, hydroxide ions, water and other anions is essential to establish a scientific basis for the synthesis of these materials. Such information is inadequate. Drying and calcination (to remove the template) can also play a crucial role in determining the fate of the metal ion. During these processing steps, the ambient atmosphere (vacuum, inert gas, air, H_2 etc.), rates of heating, final temperatures can all influence the distribution of metal ions amongst the different possible locations.

2.2. FERRISILICATES

The hydrothermal chemistry of Fe^{3+} ions under conditions of zeolite synthesis had been reviewed earlier [1]. It was observed [1] that, during the first step in the synthesis of ferrisilicate molecular sieves (when iron and silicate species are mixed together at a relatively low pH), polynuclear ferrisilicate species with Si–O–Fe–O–Si–O–Si bonds are formed. Later, when the organic templates and bases are added, these polymeric species give rise to the precursor species necessary for the formation of zeolitic structure. The equilibrium data for various hydrolysis reactions of Fe^{3+} in aqueous media have been reviewed in detail by Flynn [3]. Table 1 summarizes the list of ferrisilicate zeolites prepared in our laboratory by the direct hydrothermal synthesis method along with their physico-chemical characteristics. The detailed recipes for the synthesis of various ferrisilicates of table 1 are given in

Table 1
Physico-chemical characterization of ferrisilicate molecular sieves

	Si/Fe molar ratio	Magnetic moment[a] (BM)		Mössbauer IS[a] (mm/s)		K/Fe[b] molar ratio	Adsorption[b,c] (wt%)		
		298 K	97 K	295 K	4.2 K		H_2O	n-Hx	c-Hx
MFI	36	5.7	5.6	0.25	0.35	0.79	9.8	11.0	5.1
MEL	35	5.8	5.6	0.22	–	0.82	8.5	11.3	5.2
MTT	59	5.9	5.6	–	–	0.86	5.8	8.5	3.5
TON	65	5.4	5.7	–	–	0.92	4.9	8.5	4.0
ZSM-48	69	5.8	5.6	0.22	–	0.86	–	8.5	4.0
EUO	18	5.9	5.5	0.26	0.33	0.76	9.4	11.0	5.7
MTW	65	5.8	5.6	–	–	0.91	5.9	12.0	6.7
MOR[d]	09	5.8	5.7	0.24	0.34	–	7.2	4.1	4.8
BETA	17	5.8	5.6	0.22	0.32	0.75	23.6	18.0	18.7
FAU[d]	17	–	–	–	–	–	28.0	–	–

[a] Measurements done on as-synthesized samples.
[b] Measurements done on calcined samples.
[c] $p/p_0 = 0.5$, $T = 298$ K; n-Hx = normal hexane, c-Hx = cyclohexane.
[d] MOR: Si/Al = 5; FAU: Si/Al = 3.

our earlier review [1]. The white color of the solid (absence of brown hydroxide/oxide of iron), and the values of magnetic moment (5.6–5.9 BM), Mössbauer isomer shift (0.2–0.3 mm s^{-1} at room temperature and 0.3–0.4 mm s^{-1} at 4.2 K) and ion-exchange capacity ($K^+/MO_2^- = 0.9 \pm 0.1$) are necessary requirements to establish that most of the iron, if not all, is present in tetrahedral zeolitic framework.

2.3. TITANIUM SILICATES

The incorporation of Ti^{4+} ions in MFI (ZSM-5) framework (TS-1), first claimed by Taramasso et al. [4], has opened a new area in selective oxidation reactions in zeolitic environment. The use of TS-1 in oxyfunctionalization of carbon [4–7] as well as sulfur [8,9] in a number of organic substrates, has generated considerable interest among researchers. We have reported detailed studies on the synthesis of Ti-rich, TS-1 zeolites [10–12]. Recently, we have also synthesized [13–15] a new Ti silicate with MEL (ZSM-11) topology (TS-2).

Since, like Fe^{3+}, Ti^{4+} also produces insoluble/sparingly soluble oxide/hydroxides, the most crucial factor in the successful incorporation of Ti in the silica framework is to avoid the formation of the white precipitate of titanium oxide/hydroxide. This is achieved [10–14] by carefully adding $Ti(OBu)_4/Ti(OEt)_4$ (Bu = butyl, Et = ethyl) solution in dry alcohol (preferably isopropylalcohol) to a mixture of $Si(OC_2H_5)_4$ and tetrapropyl ammonium hydroxide solution (having mainly monomeric Si^{4+} ions in solution) [10,11]. This method leads to quite efficient synthesis of TS-1 with high Ti content. Based upon the crystallization kinetics and high resolution NMR studies, Thangaraj and Sivasanker [10,11] have drawn the following conclusions:

(1) A mismatch between the hydrolysis rates of $Ti(OBu)_4$ and the polymerization rate of Si^{4+} may lead to non-inclusion of Ti^{4+} in the framework.

(2) Tetraethylorthosilicate is hydrolyzed by aqueous TPAOH to mainly monomeric and lower branched silicate ions (Q^0 and Q^1).

(3) The silicate monomers then oligomerize into Q^2 and Q^3 units when a solution of titanium tetrabutoxide in isopropyl alcohol is added. The titanium tetrabutoxide hydrolyzes rapidly but does not precipitate as TiO_2. Titanium is probably incorporated into the silicate species during the oligomerization process.

(4) As the aging time increases, the Q^3 silicate/titanium-silicate species (mainly DSR units) are predominant, indicating that the most favored silicate and titanium-silicate species to form active nuclei are the Q^3 species. Since silicate and titanium silicate are crystallized directly from a clear medium, soluble silicate/titanium-silicate ions should be the reactive species responsible for nuclei formation.

2.4. VANADIUM SILICATES

There are three Al-free, vanadium-silicate zeolites synthesized so far where the presence of V in framework is well documented. The first, well-characterized vanadium containing zeolite was V-MFI [16]. Recently, we have reported the synthesis of V-MEL (vanadium silicate with ZSM-11 (MEL) topology) [17,18]. Further, for the first time, a vanadium silicate analog of a large pore high silica zeolite, NCL-1 (V–NCL-1) was also synthesized [19]. Incidentally, NCL-1, a novel high silica large pore zeolite was also invented in our laboratories [20]. The incorporation of vanadium in a large pore zeolite has enhanced the potential utility of vanadium silicates in oxidation/hydroxylation reactions involving bulky organic compounds.

Fig. 1 depicts the X-ray diffraction (powder) patterns of Al-free, pure silica polymorph (Si–NCL-1, curve a, sample A) and vanadium silicates with varying V-contents (curves b–d refer to Si/V molar ratios = 400, 250 and 150 respectively). The molar gel compositions used in the syntheses were as follows: Si/V = 175, 96 and 48 (for samples B–D, respectively, fig. 1), $Na^+/Si = 0.15$, $OH^-/Si = 0.12$, $RBr_2/Si = 0.05$ (where RBr_2 is an organic template, hexamethylene bis (triethylammonium bromide)), and $H_2O/SiO_2 = 50$. The crystallization was carried out in a stainless steel autoclave under agitation at 443 K. The crystallization time for samples A–D was 4, 9, 12 and 16 days respectively.

Table 2 summarizes the physicochemical properties of samples A–E. It is seen that the vanadium uptake from the gel during the crystallization is far from complete. The efficiency of vanadium incorporation in the crystalline phase decreases with increasing vanadium content in the gel. Sample E (obtained from D by extraction with 1 M solution of ammonium acetate) had a Si/V ratio of 262 (compared

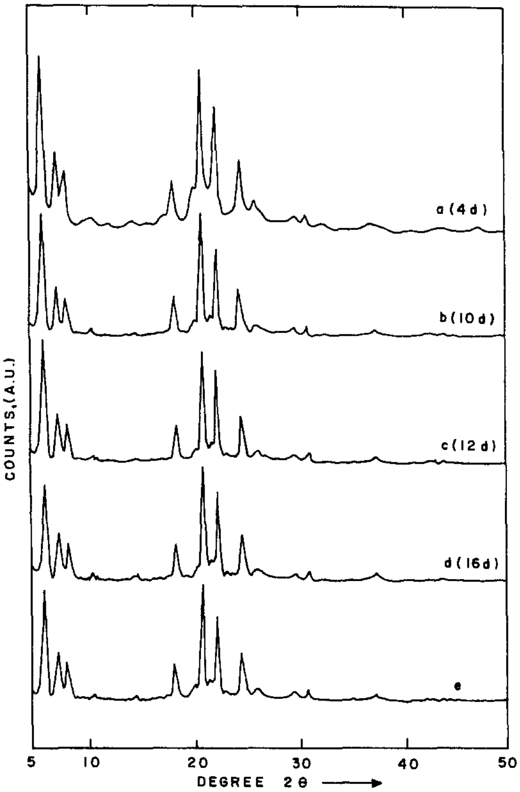

Fig. 1. X-ray diffraction patterns of fully crystalline NCL-1 zeolites. Curve a: Si–NCL-1, curves b–d: V–NCL-1 with Si/V = 400, 250 and 150, respectively, curve e: Si/V = 262, obtained after treating sample D (Si/V = 150) with ammonium acetate. The crystallization time (in days) is given in parentheses.

to 150 for sample D) indicating that in sample D part of the vanadium was extractable, and hence, most probably in non-framework positions. Further treatments of sample E with ammonium acetate did not lead to an increase in the Si/V ratio of the sample. The remaining vanadium is apparently firmly bound to the lattice framework and, hence, cannot be removed by treatment with ammonium acetate. The sorption capacity of samples B, C and D is similar to that of the V-free sample A. The unit cell volume increases linearly with the ratio V/(V + Si) (fig. 2). When sample D was treated with steam (100%) at 823 K for 4 h, the resulting material (sample F) had the same unit cell volume as the V-free silica polymorph (table 2). The contraction in the unit cell volume on hydrothermal treatment has occurred probably due to the migration of the vanadium ions, originally present in framework positions in sample D, to non-framework positions. The structural identity and location of vanadium in V–NCL-1 is discussed below.

Table 2
Physico-chemical properties of Si–NCL-1 and V–NCL-1 samples

Samples	Si/V gel	Si/V solid	Total surface area (m^2/g)	ESR intensity area (m^2/g)	Unit cell volume ($Å^3$)	Sorption capacity	
						o-xylene	mesitylene
A	–	–	339	–	2864	7.31	4.77
B	175	400	298	272	2883	7.28	4.68
C	96	250	310	371	2896	7.20	4.63
D	48	150	301	462	2912	7.26	4.59
E[c]	48	262	311	161	2891	–	–
F[f]	48	–	–	–	2862	–	–

[a] At liquid nitrogen temperature and at $p/p_0 = 0.1$.
[b] Integrated intensity in arbitrary units.
[c] Calculated from the XRD data.
[d] At 298 K and at $p/p_0 = 0.5$.
[e] Sample D treated at 298 K for 24 h with ammonium acetate (50 ml of 0.1 M solution/g catalyst), washed and calcined in air at 723 K.
[f] Sample D treated with steam (100%) at 923 K for 4 h.

3. Characterization studies

A crucial question is whether the transition metal ion is indeed in framework positions (substituting Si^{4+} ions) or is present in non-framework positions? A wide variety of techniques have been utilized to obtain such information. There is conclusive evidence, now, that when synthesized carefully, Fe^{3+} occurs in lattice positions isomorphously substituting for Si^{4+} [1]. The situation is not so clear for

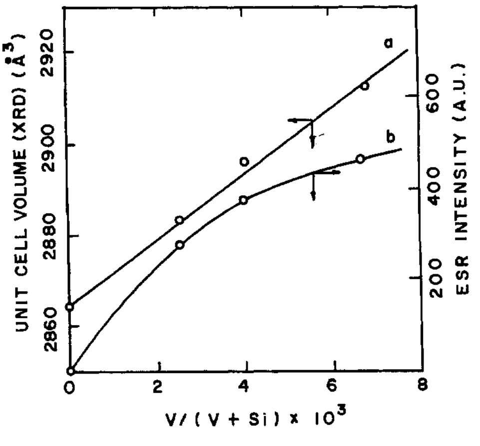

Fig. 2. Correlation between the vanadium content in V–NCL-1 sample and XRD unit cell volume (curve a) and ESR intensity (curve b).

titanium and vanadium. Firstly, all the Ti and V silicates synthesized and characterized in some detail, so far, belong to systems like MFI, MEL (for TS-1/VS-1 and TS-2/VS-2, respectively) or NCL-1 (for V–NCL-1) in which the Al or transition metal-free pure silica polymorph is also known. Hence, there is always the possibility that what is synthesized is the silica polymorph containing the transition metal ion in non-framework positions. Secondly, when trivalent ions (like Al^{3+} or Fe^{3+}) substitute for Si^{4+} in the lattice, they generate cation exchange capacity in the molecular sieve whose existence can be utilized to confirm the isomorphous substitution. Ti^{4+} and V^{4+}, however, do not possess this property. Hence, a powerful chemical tool, like exchange capacity cannot be used to characterize these latter silicates. Another conceptual difficulty in dealing with these systems, in the absence of single crystal studies, is the precise meaning of "framework positions". If the XRD and framework IR patterns of powder crystals (of average diameter of about 1 micron) indicate that the unit cell parameters and the ratio of IR intensities of 960–550 cm^{-1} bands (1) increase regularly and linearly with Ti (or V) content (fig. 3) and (2) attain the values of the pure silica polymorph when subjected to severe hydrothermal treatment (presumably all the transition metal ions are

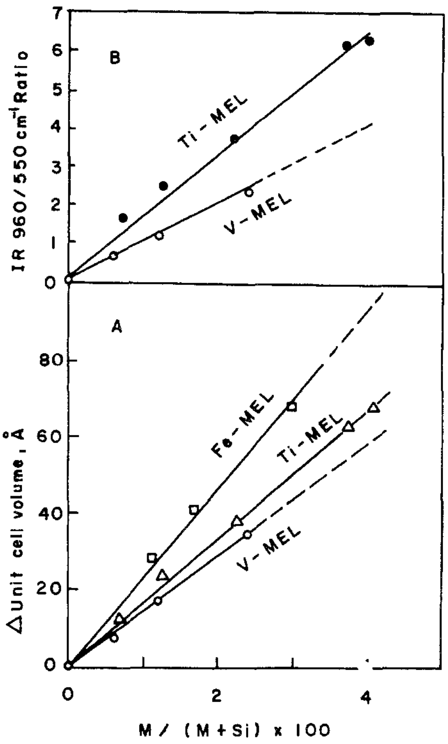

Fig. 3. Correlation between transition metal (M) content and A: Δ unit cell volume ($Å^3$) obtained by subtracting unit cell volume of pure MEL silicalite-2 from that of MEL metallosilicates (M = Fe, Ti or V); (B) ratio of IR intensity of 960 cm^{-1} to 550 cm^{-1} band (M = Ti or V).

expelled from the lattice to non-framework positions during the process), does it constitute conclusive evidence that the Ti (or V) ions are originally in framework positions? Can the same observations be explained if it is assumed that the Ti (or V) ions react with the internal silanol groups forming surface Si–O–M–O–Si bonds (surface "capping" or "grafting")? In such small crystals, with obviously a high concentration of defect sites (including silanol groups), it is difficult to provide, at present, an unambiguous answer to the above question. Studies on large, single crystals can, perhaps provide an answer. Table 3 summarizes the various techniques used in the structural and textural characterization of the titanium and vanadium silicate analogs of zeolites along with the relevant information obtained from each one of them.

A significant contribution to the structural characterization of Ti in titanium sili-

Table 3
Characterization of titanium and vanadium silicate analogs of zeolites

Techniques	Relevant information
1. Chemical analysis	Ti, V and Al content.
2. XRD	Crystallinity/phase purity; lattice expansion due to Ti/V incorporation (fig. 3).
3. Electron microscopy/EDAX	Average size of crystals; presence of amorphous matter; Ti/V distribution.
4. Adsorption	Amorphous matter within pores.
5. Thermal analysis	Crystal stability; distribution of organics in different locations.
6. IR spectra	
framework	Band around 960 cm^{-1} due to Si–O–Ti/V.
hydroxyl bands	Broad band at 3400–3500 (Ti) or 3200–3600 (V) cm^{-1}.
7. ESR	No peaks in the case of Ti^{4+}/V^{5+}. V^{4+} – 8 line spectrum ($g = 1.932$; $g = 1.981$; $A = 185$ G; $A = 72$ G).
8. NMR	
Ti	Broad ^{29}Si signal.
V	^{51}V peak at −573 ppm, $H = 50$ ppm.
9. Ion exchange capacity	
Ti	No ion exchange capacity.
V	Exchangeable protons (Na/V = 0.5–0.7).
10. Acidity	
Ti	Weak Lewis acidity; no Brønsted acidity
V	Medium Lewis and Brønsted acidity.
11. UV-VIS spectra	
Ti	210 nm due to Ti^{4+} in T_d; 238 nm due to Ti^{4+} in O_h (influenced by H_2O adsorption).
V	CT band below 400 nm and absence of 550 nm band indicate V^{4+} in T_d coordination.
12. ESCA	Surface composition, absence of extra O_{1s} peak due to Ti/V oxides.
13. EXAFS/XANES Ti	Ti in defect, not regular T site
14. Catalytic activity in oxidation reactions	V-silicates activate the primary carbon atom while Ti- analogs do not.

cates was made, recently, by Kaliaguine et al. [21]. They investigated titanium silicates with MEL structure (TS-2) by near edge and extended X-ray absorption fine structure (XANES and EXAFS, respectively) techniques. The experiments were conducted on air-exposed samples. They found that titanium species are present in these zeolites as monomeric and dimeric species and have three types of coordination: tetrahedral, square pyramidal and octahedral. The relative content of these species depends on the overall Ti loading. They also found that TiO_x units and SiO_4 tetrahedra are linked through an edge rather than via the usual corner-sharing mode common in zeolites. Hence, they concluded that Ti species are better described as structural defects rather than T atoms isomorphously substituted for Si in the zeolite lattice. The pentacoordinated, square pyramidal titanium detected by EXAFS is probably derived from the tetrahedral sites by adsorption of water molecules. Similarly, Lopez et al. [22] using the first shell EXAFS analysis found a strong dehydration dependence of the coordination of Ti leading to a transformation from octahedral to tetrahedral sites on dehydration.

In the case of the vanadium silicates, there is a linear and progressive increase in the XRD unit cell parameters and the ratio of the intensities of the 960–550 cm^{-1} bands (characteristic of Si–O–V bands and the pentasil framework, respectively) (fig. 3) with increasing V content [17]. The vanadium ions could not be exchanged by other cations. However, the material contained exchangeable protons, which participated in typical Brønsted acid catalyzed reactions like xylene isomerization. ESR experiments indicated that in the as-synthesized samples, the vanadium occurs as atomically dispersed V^{4+} ions in a non-tetrahedral symmetric location. On calcining in air the spectra disappeared indicating the oxidation of V^{4+} to V^{5+} species. Reduction in H_2 restored the original spectra. The V ions are, hence, accessible to gas molecules and the V^{4+}–V^{5+} transition is reversible. The complete oxidation of V^{4+} ions to V^{5+} indicates the absence of any clustered vanadium [23]. Rao et al. [17] also observed that there were no absorption bands in the 400–800 nm range indicating the absence of vanadyl groups or V^{4+} ions in T_d symmetry in the calcined vanadium silicates. In carefully prepared samples, ^{51}V MAS NMR studies revealed the presence of only a single vanadium species with a chemical shift parameter ($\delta = -573$ ppm) and a signal linewidth (50 ppm) similar to those observed in monomeric orthovanadates having tetrahedrally coordinated vanadium ions. It is probable that V is coordinated at defect sites wherein the concentration of SiOH groups is likely to be high. More detailed investigation of the vanadium silicates by techniques such as EXAFS/XANES is desirable if more definitive conclusions are to be drawn.

4. Catalytic properties

The catalytic properties of the titanium and vanadium silicate molecular sieves are described in more detail in another paper from this laboratory by Ramaswamy and Sivasanker [2] and hence will not be dealt with in this article.

The ferrisilicate molecular sieves have potential utility both as acidic or redox catalysts. Analogous to Al^{3+}, the isomorphous substitution of Si^{4+} by Fe^{3+} generates Brønsted acidity. Owing to their lower acid strength [24], Fe-zeolites (vis-a-vis Al-analogs) are more selective in C_8 aromatic reactions due to the suppression of secondary reactions like disproportionation. In acid catalyzed reactions, the differences in catalytic activity, selectivity and stability between the alumino- and ferrisilicate zeolites (due to the presence of weaker acid sites in the latter) have been well documented [1,25–27].

The potential of Fe-zeolites as bifunctional or redox catalysts (e.g. dehydrogenation of ethylbenzene to styrene or methylethylbenzene to methylstyrene [1,28]) is due to the fact that under controlled steaming conditions, part or all of the Fe can be removed from the lattice framework and dispersed as finely divided iron oxide particles within the restricted environment of zeolite pores and/or on the external surface of the crystals.

5. Conclusions

Some transition metals like Fe, Ti, V etc. can be incorporated in zeolitic framework provided proper care is taken during synthesis as well as post-synthesis treatments. Even though, all the transition metal-silicate analogs of zeolites may not contain the transition ions in isomorphous substitution positions, they are sites linked to the crystalline silicate framework in a manner not fully understood at present. However, due to the atomic dispersion achieved thereby they hold interesting potential as novel, shape selective oxidation catalysts.

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