Novel Large-pore Vanadium Alumino- and Boro-silicates With BEA Structure

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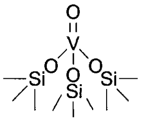
New large-pore vanadium alumino- and boro-silicates with beta (BEA) structure are synthesized; ESR, IR data and catalytic oxidation properties indicate that vanadium is incorporated as V^{5+} in the lattice.

The use of titanium and vanadium modified molecular sieves belonging to the MFI and MEL structure types as catalysts in liquid-phase oxidation with H_2O_2 as the oxidant has been well documented.[1,2] So far the vanadium analogues of only two large-pore molecular sieves, NCL-1,[3] ZSM-12[4] and one mesoporous material, MCM-41[5] have been reported. We now report the synthesis of vanadium-containing large-pore molecular sieves having BEA structure. A small amount of Al^{3+} or B^{3+} to assist BEA structure development has also been incorporated. Corma and coworkers[6] have similarly incorporated Al^{3+} to synthesize Ti-analogues of beta.

It is generally believed that the incorporation of vanadium takes place as V^{4+} during hydrothermal synthesis. The V^{4+} has been reported to transform into V^{5+} on calcination (the calcination step being essential to remove the organic template) and these V^{5+} ions have been suggested to be the active centres in oxidation catalysis.[1b,3] Recently, Kornatowski *et al.*[7] have reported that vanadium is incorporated both as V^{5+} and V^{4+} in the MFI-zeolite lattice. The V–Al-beta and V–B-beta synthesized by us possess only V^{5+} in the lattice. As V^{5+} are the stable species in alkaline medium at high temperatures, especially in the presence of air, they are more likely to be incorporated in the lattice of alumino- or boro-silicates which are synthesized at high pH (> 12). On the other hand, vanadium-containing AlPO molecular sieves which are synthesized in acidic (pH < 7) medium tend to incorporate more V^{4+} ions in the lattice.[8] Besides, the incorporation of the smaller V^{5+} ions (crystal ionic radii: V^{5+} = 0.059 nm; V^{4+} = 0.063 nm; Si^{4+} = 0.042 nm) in the silicate lattice should be more favourable. Presumably, the V^{5+} ions are present as vanadate like species (shown below) with three Si–O–V linkages.



The hydrothermal synthesis of vanadium alumino- or borosilicates was carried out using gels of the following molar composition; $SiO_2 : xM_2O_3 : y\ VO_2 : 0.52\ NEt_4OH : 21\ H_2O$, where M = Al or B and $x > 0.0025$, $y < 0.033$.

In a typical synthesis, NEt_4OH (40% aqueous solution, Aldrich) was added to tetraethyl orthosilicate (Aldrich) at 295 K. After stirring the mixture for 40 min, an aqueous solution of $VOSO_4 \cdot 3H_2O$ (Aldrich) in deionized water was added slowly under stirring. This mixture was stirred for 30 min, then a solution of $Al_2(SO_4)_3 \cdot 16H_2O$ (or H_3BO_3) in deionized water was added slowly under vigorous stirring. The resultant mixture was stirred for another 4 h. The colourless clear gel (pH = 12.4–12.8) was charged into a stainless-steel autoclave and heated at 413 K for 8 days under static conditions. After crystallization, the product was filtered, washed with deionized water, dried at 373 K and calcined in air at 773 K for 10 h. The material was white before and after calcination. The XRD patterns of V–Al-beta and V–B-beta was similar to Al-beta. The samples were highly crystalline. SEM pictures showed that the crystallites were spherical in shape and were 0.2–0.3 μm in size. No vanadium was leached out after treatment of the V–Al-beta and V–B-beta samples with an aqueous solution of NH_4OAc (1 mol dm^{-3}) at 298 K for 12 h. This treatment has been shown by earlier workers[9] to remove the extralattice vanadium. The chemical compositions of V–Al-beta and V–B-beta are given in Table 1. Chemical analysis were performed by wet chemical methods and ICP (John Yuon-JY VHR) spectrometry. The vanadium analysis were verified titrimetrically with standard iron(II) ammonium sulfate solution. Sodium diphenyl amine sulfonate was used as an indicator.

The location of V in the lattice is suggested from the observation of an IR band at around 960 cm^{-1} for both the V–Al-beta and V–B-beta samples (Fig. 1). Vanadium-free samples of Al-beta and B-beta well as those in which vanadium was deposited by impregnation procedures did not exhibit this band.

Table 1 Compositions (atom ratio) of gel and crystalline products (M = Al or B)

			Crystalline Products			
	Gel phase		Calcined		NH_4OAc treated	
Sample	Si/V	Si/M	Si/V	Si/M	Si/V	Si/M
V–Al-beta	80	200	245	80	251	80
V–B-beta	80	200	225	130	229	116
Al-Beta	∞	200	∞	69	—	—

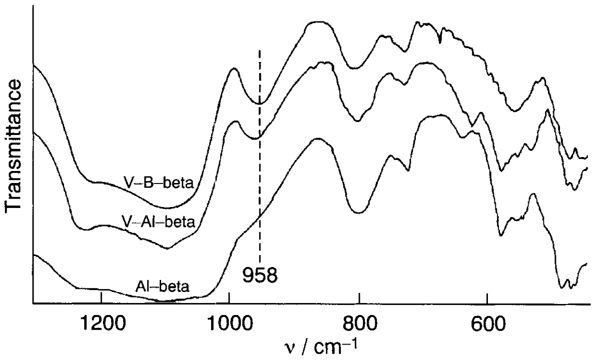


Fig. 1 IR spectra of different beta samples

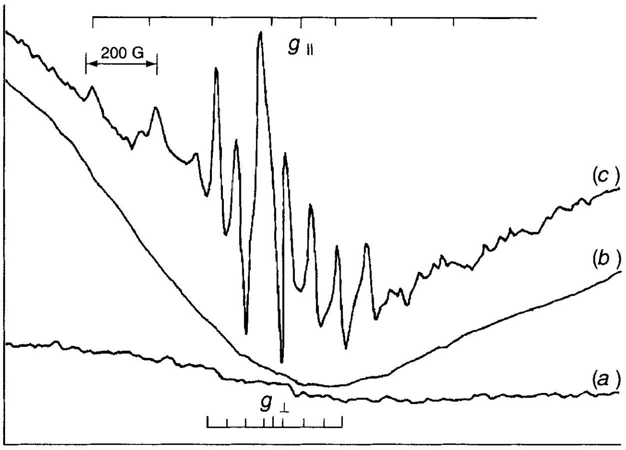


Fig. 2 ESR spectra of V–Al-beta samples at 77 K; (*a*) as-synthesized; (*b*) calcined and (*c*) after reduction (H_2/723 K, 5 h)

Table 2 Oxidation of toluene over the V-analogues of beta

			Products (mole %)				
				Cresol			
Sample	Conv. (%)	H_2O_2 selectivity (%)	Benzaldehyde	*ortho*	*para*	Benzyl alcohol	Others
V–Al-beta	14.0	64.8	56.0	21.0	17.0	4.0	2.0
V–Al-beta[a]	13.8	64.6	56.8	20.8	17.0	3.2	0.6
Al-beta[b]	1.9	10.6	90.0	—	—	7.0	3.0
V–B-beta	12.8	61.0	59.0	18.5	17.8	3.2	1.5
V–B-beta[a]	13.2	63.8	61.2	17.4	18.5	2.5	0.4
B-beta[b]	1.2	6.6	89.6	—	—	5.9	4.5
Al-beta	< 0.1	—	—	—	—	—	—
B-beta	< 0.1	—	—	—	—	—	—
No catalyst	Nil	—	—	—	—	—	—

[a] NH_4OAc treated sample. [b] V_2O_5 impregnated samples; *Reaction conditions*: 100 mg catalyst; toluene : H_2O_2 mol ratio = 3 : 1; toluene : catalyst = 10 : 1 (wt : wt); 348 K; 10 g solvent (acetonitrile); reaction time = 24 h; reaction carried out in a 100 ml batch reactor.

The above band (960 cm^{-1}) has also been observed in the case of titanium and vanadium silicalites (MFI, MEL and ZSM-48)[10–13] and has been attributed to Si–O–Ti (or V) vibrations due to the presence of Ti (or V) in the lattice. Besides, the intensity of the 960 cm^{-1} band did not decrease on extraction with NH_4OAc suggesting strong bonding of the V-ions with the lattice.

The synthesis gel (pH = 12.4–12.8), the as-synthesized samples and the calcined samples did not exhibit any ESR signal (77 K) indicating the absence of paramagnetic vanadium ions (V^{4+}). The absence of ESR activity of the synthesis gel even though V^{4+} ions ($VOSO_4$) were used is due to the easy oxidation of V^{4+} ions to V^{5+} at high pH in the presence of air.[14] After reduction of the calcined samples in H_2 or after use in oxidation of toluene (*vide infra*), the material exhibited a very weak ESR signal at 298 K and an intense 8 line hyperfine spectra at 77 K (Fig. 2). The g and A parameters calculated from the spectra ($g_{\parallel} = 1.938$, $g_{\perp} = 1.992$, $A_{\parallel} = 190.5$ G, $A_{\perp} = 71.4$ G) correspond to square-pyramidal environments similar to those reported for VS-1 vanadosilicates.[15] The diffuse reflectance spectra of as-synthesized and calcined samples of V–Al-beta and V–B-beta show a very weak absorption at about 330 nm attributed to V^{5+} in a tetradehdral environment.[16] The intensity of the band is low because of the low concentration of vanadium present in the samples.

Oxidation of toluene was carried out on V–Al-beta, V–B-beta as well as NH_4OAc treated samples and V_2O_5 impregnated Al-beta and B-beta (Table 2). Negligible conversion (< 0.1%) was observed when the reaction was carried out in the presence of Al-beta, B-beta and when no catalyst was used. Oxidation of toluene gave benzaldehyde and cresol as the major products. In the oxidation of the large molecule *m*-xylene over V–Al-beta, the products were mainly 3-methyl benzaldehyde (60%), benzoic acid (29%) and 2,6-dimethyl phenol (6%) with 6% conversion and 39% H_2O_2 selectivity. V-MEL was inactive in the above reaction.

In conclusion, we report for the first time the synthesis of V-containing molecular sieves with BEA structure. Besides, we show that the vanadium can be incorporated only as a V^{5+} in the beta lattice. This V^{5+} is easily reducible and the materials are good catalysts for selective oxidation reactions.

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