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Synthesis of a vanadium analog of siliceous FER

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Transition metal substitution in zeolite frameworks is a very useful modification. Here, we report for the first time, the synthesis of a vanadium analog of siliceous ferrierite (FER) by using an organothermal synthesis route. The presence of vanadium ions in the framework was confirmed by XRD, UV–VIS, EPR and NMR spectroscopic studies. The synthesized V-FER catalyst was tested for toluene oxidation.

Introduction

Transition metal modified zeolites, particularly those containing V^{4+} or Ti^{4+} are well known for their excellent catalytic properties in selective synthesis of various fine chemicals.[1,2] Several reports have dealt with the synthesis, characterization and catalytic properties of vanadium containing zeolites, for example ZSM-5,[3] ZSM-11,[4] ZSM-48,[5] ZSM-12,[6] NCL-1,[7] beta[8] and MCM-41.[9] We report here, the results of the synthesis and characterization of a new vanadium analog of siliceous FER from a non-aqueous alkali free seeded system.

Ferrierite (FER) is a high silica, medium pore zeolite containing linked [5^4] polyhedral units having intersecting channels outlined by 10-membered ring (4.3 × 5.5 Å) and 8-membered ring (3.4 × 4.8 Å) pores. The pure silica derivative of FER topology is known.[10] Recently Ahedi and Kotasthane[11] reported the synthesis of Ti-FER. The synthetic method for the pure silica derivative of FER described by Kuperman *et al.*[10] using HF·pyridine as the mineralizing agent has been used for the synthesis of V-FER.

Synthesis

The organothermal synthesis of vanadium ferrierite was carried out using gels of the following composition:

$$1SiO_2:(0.01-0.001)\ VO_2:5.45\ \text{propylamine}:10.78\ \text{pyridine}:2.67\ H_2O:1.4\ HF \qquad (1)$$

Initially 75.5 g (0.955 mol) of pyridine (SQ, Qualigens) and 31.5 g (0.533 mol) of propylamine (E. Merck) were mixed under stirring. A clear blue solution of vanadyl sulfate (0.506 g, 0.002 mol) in 4.8 g (0.267 mol) of deionised water was then slowly added to the above organic solution. Then 3.6 g (0.018 mol) of HF·pyridine (70%, Aldrich) was mixed very carefully with the above clear solution. Finally 6.0 g (0.1 mol) of Cab-O-Sil (Fluka, USA) were slowly dissolved in the above gel under vigorous stirring. This was followed by addition of 0.2 g of silica-FER seed precursor synthesized according to the procedure described by Kuperman *et al.*[10] under continuous stirring to yield a uniform dispersion. The resulting solution had a pH of 11.0 ± 0.2. This liquid was then transferred to a Teflon lined autoclave for crystallization at 170 °C for 5–7 days under static conditions. The crystalline V-FER product was filtered off, washed with water followed by acetone and dried at 100 °C. The X-ray (Rigaku D max II VC) powder diffraction pattern confirmed the phase purity of the V-FER product. The V-FER product was then calcined at 550 °C for 12 h to decompose the organic compounds. The product yield was 80% by weight (5.0 g). The V-FER sample was treated with 1 M ammonium acetate solution at room temperature for 18 h to remove any possible non-framework vanadium species. Two such vanadium silicates with Si : V ratios of 120 : 1 and 180 : 1 were prepared.

Characterization

The synthesized V-FER catalyst samples were characterized by XRD (Rigaku D max II VC), XRF (Rigaku 3070 X-ray spectrometer), UV–VIS (Shimadzu UV–VIS spectrophotometer 2101Pc), EPR (Bruker EMX EPR) and NMR (Bruker MSL-300) spectrometry.

Catalytic studies

To study the oxidative properties of vanadium within the catalyst the toluene oxidation reaction was studied. In a typical oxidation reaction, the solid catalyst was added to toluene (AR grade, S. D. Fine chemicals, India) in a suitable solvent (*e.g.* acetone). Then the mixture was placed in a steel autoclave (Parr 4842, 300 ml) and *tert*-butylhydroperoxide (TBHP) (AR, 70%, S. D. Fine chemicals, India) was added to the autoclave as an oxidant. The autoclave vessel was pressurized with compressed air up to 200 lb in^{-2}. The autoclave was then heated to a specific temperature. After the reaction was complete, the vessel was cooled, depressurized and the product analysed after centrifugation to recover the solid catalyst.

Product analysis

The products of the oxidation reactions were analyzed using a gas chromatograph (Shimadzu GC-15A) equipped with a packed column (SE-30). The identities of the products were further confirmed by GC–MS (Shimadzu QCMC-QP 2000A).

Results and discussion

Fig. 1 shows XRD patterns of the two vanadium containing samples along with that of Si-FER. The XRD patterns of the V-FER samples are similar to those of siliceous ferrierite. With increased vanadium content, slight changes in the intensities of different peaks were observed. However, the positions of the peaks were not changed which confirms phase purity after vanadium incorporation. The incorporation of V^{4+} ions into the framework caused a unit cell volume expansion as expected.[2] For siliceous FER the unit cell volume is 1947.21 $Å^3$ while after incorporation of vanadium it is increased to 1959.54 (Si/V = 180) and 1973.59 $Å^3$ (Si/V = 120), *i.e.*, the increase in volume is proportional to the vanadium content in the FER structure (Table 1).

The UV–VIS spectrum of calcined V-FER catalysts show intense charge transfer bands in the range 225–250 nm due to V–O bonding [Fig. 2(a)]. The absorption band at 386 nm can

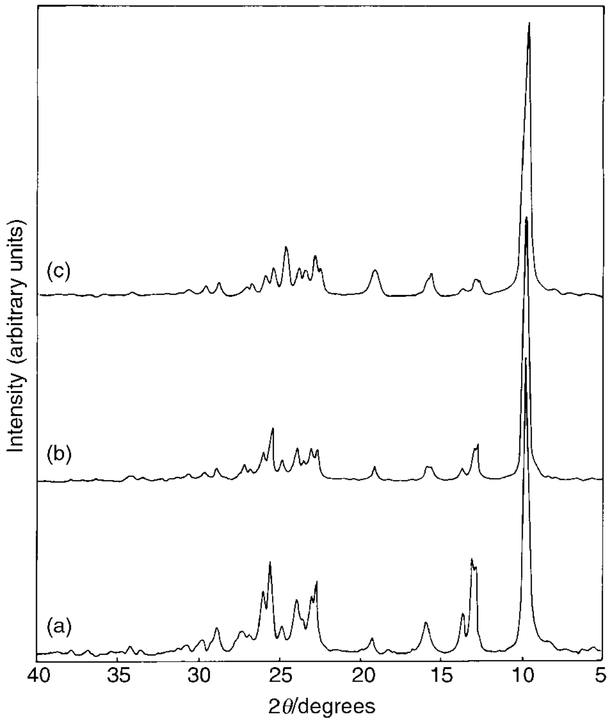

Fig. 1 XRD spectrum of (a) Si-FER, (b) V-FER (sample 2, Si/V = 180) and (c) V-FER (sample 1, Si/V = 120).

Table 1 Unit cell parameter data for various V-FER samples

Sample	Si/V (gel)	Si/V (product) (XRF)	V (wt%) (XRF)	a_0/Å	b_0/Å	c_0/Å	Unit cell volume/ Å^3
1	50	120	0.70	18.83	14.10	7.44	1973.59
2	100	180	0.47	18.75	14.08	7.43	1959.54
Si-FER	—	—	—	18.69	14.06	7.41	1947.21

be assigned to V^{5+} species characterised by a V=O bond[3] [sample 1, Si/V = 120, Fig. 2(a)]. The 336 nm band indicates the presence of V^{5+} species in a tetrahedral environment [sample 2, Si/V = 180, Fig. 2(b)]. It was observed that as the Si/V ratio increased, the proportion of vanadium ions in tetrahedral environments also increased.

Fig. 3 shows EPR spectra of V-FER (samples 1 and 2) and vanadium impregnated Si-FER. The spectra of as-synthesized V-FER [Fig. 3(a), (b)] consist of anisotropic signals with eight equally spaced hyperfine split components indicating the presence of paramagnetic atomically dispersed immobile V^{4+} ions.[3,12,13] The absence of a superimposed broad singlet indicates the absence of clusters of extraframework vanadium species. The g values and hyperfine splitting constants [sample 1 (Si/V = 120): $g_{\parallel} = 1.938$, $g_{\perp} = 2.000$ and $A_{\parallel} = 197.7$, $A_{\perp} = 69.7$ G; sample 2 (Si/V = 180): $g_{\parallel} = 1.935$, $g_{\perp} = 1.975$ and $A_{\parallel} = 186.8$, $A_{\perp} = 76$ G] are characteristic of vanadyl VO^{2+} species.[3,12,13] This indicates that the V^{4+} species in the zeolite may be present in distorted octahedral environments. The spectrum of vanadium impregnated Si-FER [Fig. 3(c)] is totally different from the two V-FER spectra and indicates the presence of extraframework clusters of vanadium species.

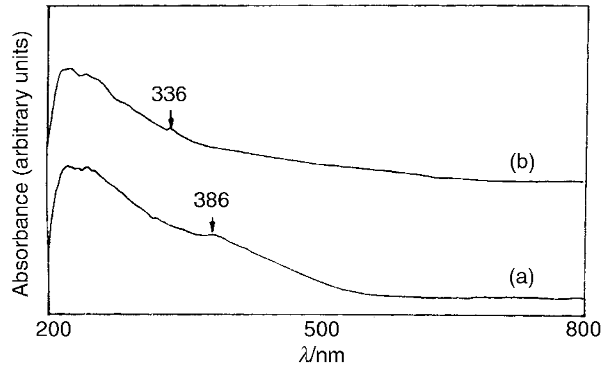

Fig. 2 UV–VIS spectrum of V-FER calcined samples. (a) sample 1, Si/V = 120 and (b) sample 2, Si/V = 180.

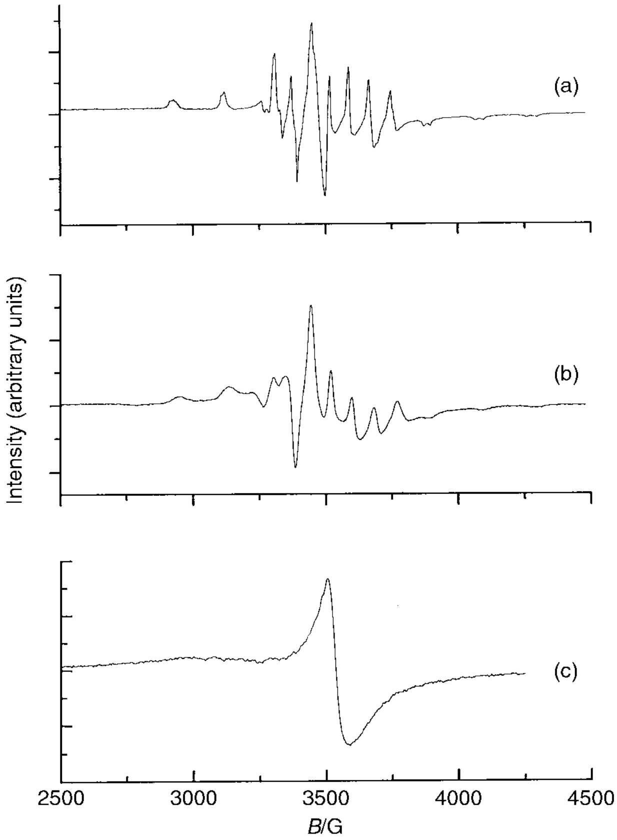

Fig. 3 EPR spectrum of V-FER as-synthesized samples: (a) sample 2, Si/V = 180; (b) sample 1, Si/V = 120 and (c) V-Si-FER [impregnated (Si/V = 120)].

The solid state MAS ^{51}V NMR spectra of calcined V-FER samples show two different peak positions. One at δ *ca.* −300 corresponds to V^{5+} in a square pyramidal environment,[3,13] while the other at δ *ca.* −530 corresponds to tetrahedral V^{5+}. Fig. 4 shows that at high vanadium content [sample 1, Si/V =

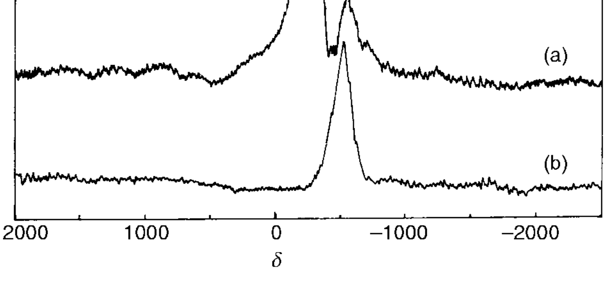

Fig. 4 ^{51}V MAS NMR spectra of V-FER calcined samples: (a)

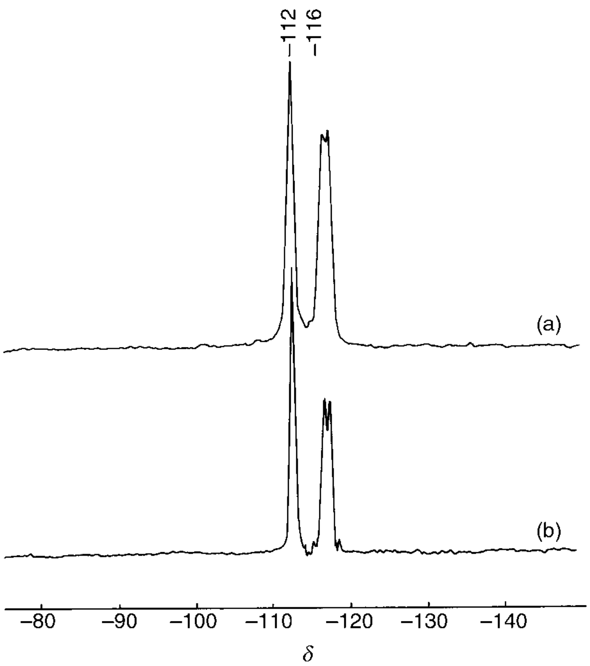

Fig. 5 ^{29}Si MAS NMR of V-FER calcined samples; (a) sample 2, Si/V = 180 and (b) sample 1, Si/V = 120.

120, Fig. 4(a)] the V^{5+} species present in the structure are mostly in a square pyramidal environment along with a small amount in a tetrahedral environment. When the vanadium content was lower [sample 2, Si/V = 180, Fig. 4(b)], all the V^{5+} species were present in tetrahedral environments. This confirms that as the vanadium content in FER is reduced, the probability of vanadium ions being tetrahedrally coordinated in the framework is increased. These results are complementary to those obtained from the UV–VIS studies.

^{29}Si MAS NMR spectra of samples 1 and 2 are shown in Fig. 5. The doublet at δ −116 corresponds to Q^4 species and the sharp single peak at δ −112 corresponds to Q^3 species. It was observed that the intensity of the Q^4 species band in the sample 2 (Si/V = 180) was higher than that of sample 1 (Si/V = 120) owing to increased vanadium (tetrahedral or square pyramidal) content in sample 1 relative to sample 2.

From the characterization techniques, the presence of vanadium in the framework was confirmed (XRD, unit cell expansion; UV, tetrahedral vanadium species; NMR, square pyramidal vanadium species). The vanadium species are totally different from those in the impregnated extraframework sample (as shown by EPR) for which Moudrakovski *et al.*[13] and Kornatowski *et al.*[14] suggested a 'V=O' species within the framework.

Catalysis

The V-FER samples were catalytically active in the oxidation of toluene and mixtures of benzaldehyde, benzyl alcohol and benzoic acid were formed. Results for different reaction conditions are given in Table 2. The reaction was faster (conversion of toluene) in a polar solvent such as acetone as compared to non-polar solvents. At high vanadium loading the conversion was higher as compared to low loading. The vanadium impregnated sample [V-Si-FER(Si/V = 120)] showed less activity during the reaction as compared to the V-FER(Si/V = 120) sample. The high activity of vanadosilicates may be due to the oxyfunctionalization of toluene only by those vanadium species which are in framework positions. Similar results have been observed for titanosilicates and vanadosilicates by Tatsmul *et al.*[15] and P. R. H. P. Rao and Ramaswamy,[16] respectively.

Conclusion

Novel medium pore vanadium silicates with the FER structure have been synthesized. Unit cell volume information and XRD patterns confirm the phase purity and incorporation of vanadium in the frameworks. EPR spectroscopy confirmed that some of the V^{4+} present is in distorted octahedral positions. UV–VIS and NMR spectroscopy confirmed the presence of tetrahedral V^{5+} species in the frameworks.

It was also observed that as vanadium content in the catalyst increased, the proportion of non-tetrahedral framework species increased. All the spectroscopic information indicated the presence of isolated, well dispersed vanadium ions stabilized within the zeolitic lattice. V-FER acts as a good oxidation catalyst in mild reactions and the activity of the catalyst was found to be higher in polar solvents such as acetone. The level of incorporated vanadium affects product formation and the nature of vanadium species in the catalyst affects the selectivity towards products.

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Table 2 Reaction conditions and product distribution for the toluene oxidation reaction[a]

					Product selectivity (%)			
Catalyst[b]	Toluene/TBHP (mol/mol)	*T*/C	Solvent	Conv. (%)	Benzaldehyde	Benzyl alcohol	Benzoic acid	Others[c]
V-FER (120)	20	60	Acetone	1.47	32.9	—	—	67.1
V-FER (120)	20	90	Acetone	7.89	22.0	12.1	8.6	57.3
V-FER (120)	20	110	Acetone	5.17	29.0	20.7	21.1	29.2
V-FER (120)	20	90	Acetonitrile	5.10	39.5	24.5	12.0	24.0
V-FER (120)	20	90	*n*-Hexane	5.19	11.4	13.1	15.6	59.9
V-FER (120)	2	90	Acetone	23.83	16.9	7.5	33.9	42.2
V-FER (180)	20	90	Acetone	3.65	20.1	15.5	6.4	58.0
V-Si-FER (120) impregnated	20	90	Acetone	2.76	—	38.9	5.6	55.5
Si-FER	20	90	Acetone	0.70	—	42.9	4.1	53.0

[a]Reaction parameters: catalyst (V-FER) = 0.025 g, time = 1.0 h, pressure = 200 lb in^{-2}. [b]Number in parentheses is the Si/V ratio. [c]High boiling components formed during the reaction.

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