Synthesis, characterization and catalytic properties of two novel vanado-aluminosilicates with EU-1 and ZSM-22 structures

Maya Chatterjee, D. Bhattacharya, N. Venkatathri and S. Sivasanker National Chemical Laboratory, Pune 411008, India

Received 20 March 1995; accepted 27 August 1995

The synthesis in the presence of alkali ions of two novel vanadium containing zeolites V-Al-EU-1 and V-Al-ZSM-22 is reported. Both V⁴⁺- and V⁵⁺-ions are present in as-synthe-sized samples. Cyclic voltammograms of the samples reveal the presence of two types of V⁵⁺ in the calcined samples. A weak shoulder at ~980 cm⁻¹ is observed in the IR spectra of the calcined samples. On extraction with acid a sharp band appears at ~960 cm⁻¹. The acid washed samples are more active in the hydroxylation of phenol and the oxidation of toluene (with H₂O₂) than the calcined samples.

Keywords: V-EU-1; V-ZSM-22; vanadosilicates, synthesis of; vanadosilicates, cyclic voltammetry of; phenol, hydroxylation of; toluene, oxidation of

1. Introduction

The introduction of transition metal ions such as V^{4+}/V^{5+} and Ti^{4+} in the lattice of aluminosilicate molecular sieves has been reported to make these materials catalytically active in many selective oxidation reactions involving H₂O₂ [1–10]. Already, the titanosilicate TS-1 is being used commercially in the production of catechol and hydroquinone from phenol [4], while a semi-commercial plant for the ammoximation of cyclohexanone is reported to be under construction [11]. As a consequence, the search for newer transition metal containing molecular sieves with potential industrial applications has assumed importance. The catalytically active vanadosilicates, such as VS-1 (MFI) [6], VS-2 (MEL) [7], V-ZSM-48 [8] and V-Al-Beta [9] have all been synthesized in the absence of alkali metal ions, and using organic templates. The synthesis of V-MCM-41, however, has been carried out in the presence of Na-ions [10]. Bellussi et al. [12] have reported that the VS-1 synthesized in the presence of Na-ions either incorporates too little vanadium or is not stable after calcination. Khouw and Davis [13], on the other hand, have reported that TS-1 prepared in the presence of alkali ions contains significant amount of Ti (Si/Ti = 40 after acid washing) and becomes catalytically active after the acid wash to eliminate the Na-ions. The above findings of Khouw and Davis [13] should enable the synthesis of catalytically active titanosilicates from synthesis gels containing Na-ions.

In this paper, we report the synthesis in the presence of alkali metal ions of two novel vanado-aluminosilicates belonging to the structure groups EUO and TON. The samples have been characterized by physicochemical techniques which reveal the presence of vanadium ions in the lattice. Besides, the vanadosilicates are also active in the oxidation of toluene in the presence of H_2O_2 .

2. Experimental

The syntheses of both V-EU-1 and V-ZSM-22 were carrried out in the presence of Na- and K-ions using hexamethonium bromide (HMBr₂) and 1,6-diaminohexane as the templates. In the absence of alkali ions, both zeolites did not crystallize well. For e.g., when Na-ions were excluded during the synthesis of EU-1, only about 20% crystalline (EU-1) material was obtained after 20 days. This is similar to the observations of Dodwell et al. [14] that the use of HMBr₂ as the template required the use of NaOH to effect crystallization of EU-1 through NaOH could be excluded if HM(OH)₂ was used. Besides, the addition of a small amount of Al to the synthesis gel was necessary to enable structure formation. Interestingly, when Al was absent in the synthesis gel for EU-1, a crystalline material containing predominantly ZSM-48 was obtained. In fact, Dodwell et al.[14] have reported that EU-1 crystallized when SiO₂/Al₂O₃ < 120 and EU-2 (ZSM-48) crystallized when SiO₂/Al₂O₃ > 240.

2.1. SYNTHESIS OF V-EUO

V-EU-1 (A) and V-EU-1 (B) with different Si : V and Si : Al molar ratios were synthesized hydrothermally. The molar gel composition used was $SiO_2 : xVO_2 : 0.4Na_2O : yAl_2O_3 : .041HMBr_2 : 50H_2O (x and y values for samples$ $A and B were 0.05, 0.02 and 0.01, 0.03, respectively) where HMBr_2 refers to the$ organic template hexamethonium bromidemonohydrate. In a typical synthesis,12.3 g sodium silicate (30% silica, Loba Chemie, Bombay) was dissolved in 30 ml $water. A solution of 0.13 g of <math>Al_2(SO_4)_3$, 0.53 g NaOH and 0.4 g VOSO₄ dissolved in 20 ml water was added to the sodium silicate solution and stirred for 1 h. Next, 0.95 g hexamethonium bromide monohydrate (Aldrich) was added followed by water (10 ml). The completely homogeneous mixture was then stirred for another 1/2 h. The resulting gel was loaded into a stainless steel autoclave, capped tightly and tumbled at 50 rpm in an oven at 433 K for 10 days.

After crystallization, the products were filtered, washed thoroughly with doubly distilled water, dried at 373 K and calcined in air at 823 K for 12 h. The solids

were white before calcination but were greyish after calcination due to the presence of unburnt carbonaceous matter. The carbonaceous residue was completely oxidized by successive treatments with H_2O_2 [13]. The samples were washed, dried and calcined at 773 K (6 h) to get white materials.

2.2. SYNTHESIS OF V-TON

Three V-ZSM-22 samples with different vanadium contents and the same aluminium content were synthesized. In a typical synthesis, the gel was prepared by stirring a solution of silica sol, vanadyl sulphate trihydrate, aluminium sulphate, alkali and 1,6-diaminohexane in water. 10.2 g silica sol (28% silica) was diluted with 12.4 g water. To this sol, a solution containing 0.33 g of aluminium sulphate, 0.45 g potassium hydroxide and the required amount of vanadyl sulphate trihydrate in 10 g water was added with vigorous stirring. Next, 1.69 g of 1,6-diaminohexane (Aldrich) in 7.7 g water was added to the above gel. The molar composition of the above gel was $27[NH_2(CH_2)_6NH_2]: 13K_2O: xAl_2O_3: yVO_2: 91SiO_2: 3670H_2O [x = 0.01, y = 0.008-0.012]. The hydrothermal synthesis was carried out in a teflon coated stainless steel autoclave at 433 K for 10 days under agitation. The solid material was filtered and washed with deionized water. The samples were dried at 383 K (12 h) and calcined in air at 873 K for 16 h.$

To remove extralattice vanadium species, if any, the calcined samples were treated with 1 M ammonium acetate solution at room temperature under agitation for 18 h. Acid treatment was carried out with 1 M H₂SO₄ solution at room temperature under agitation for 12 h to exchange the alkali ions. After NH_4^+ exchange or acid treatments, the samples were washed well and calcined at 823 K for 8 h. Table 1 reports the composition of the samples.

2.3. PHYSICOCHEMICAL CHARACTERIZATION

Chemical analyses of all the samples were performed by atomic absorption using a Hitachi Z-8000 instrument.

Sample	Gel		Crystalline (as-synthesized) samples ^a								
	Si/V	Si/A1	Si	Al	v	Na/K ^b	template ^c	Si/V	Si/Al		
EU-1 (A)	38.1	100.0	0.985	0.0072	0.0081	0.0210	0.021	121.6	136.8		
EU-1 (B)	102.0	60.0	0.985	0.0074	0.0032	0.0142	0.019	307.8	133.1		
ZSM-22(A)	45.8	91.0	0.989	0.0073	0.0057	0.0038	0.040	173.5	135.4		
ZSM-22 (B)	80.4	91.0	0.982	0.0091	0.0052	0.0040	_	188.8	107.9		
ZSM-22 (C)	130.2	91.0	0.986	0.0095	0.0040	0.0025	_	246.5	103.8		

Table 1 Composition of the V-EU-1 and V-ZSM-22 samples

^a Composition reported as gram atom.

^b Na in EU-1 and K in ZSM-22.

^c Molar ratios of HMBr₂ (EU-1) and 1,6-diaminohexane (ZSM-22) determined by TGA (weight loss between 573 and 973 K).

X-ray diffraction patterns of the samples were recorded on a Rigaku D-MAX III VC X-ray diffractrometer using nickel filtered Cu K α radiation ($\lambda = 1.5406$ Å).

Scanning electron microscopy was performed on a JEOL-840A instrument.

IR spectra were recorded in the range $1300-400 \text{ cm}^{-1}$ (Perkin Elmer; model 1620) using KBr pellets.

UV-VIS spectroscopy was carried out using a spectrometer (Shimadzu; UV-2101 PC) interfaced with an IBM PC and using barium sulphate as a standard.

ESR spectra of the samples were obtained on a Bruker (ER 200) spectrometer at 9.73 GHz (X band) with a rectangular cavity (ST 8424). A standard sample (weak pitch, Varian, g = 2.0029) was used for calibration purposes.

Cyclic voltammetric measurements [15,16] were carried out using a Pt-electrode (6 mm dia) coated with a paste made up of 100 mg of the molecular sieve, 100 mg of graphite and 10 mg of polystyrene in 2 ml tetrahydrofuran. The electrode was polished with diamond paste before coating with the molecular sieve paste. The paste was then allowed to dry in vacuum. The experiments were carried out using a three-electrode single compartment cell with the molecular sieve coated Pt-electrode as the working electrode, Pt-foil as the counter electrode and standard calomel as the reference electrode in 1.0 M aqueous KCl (pH = 5.24). The experiments were carried out at 298 K in a EG&G Princeton Applied Research potentiostat (PAR 173) coupled with a function generator (PA 173) along with an X - Y recorder. The supporting electrolytes were deoxygenated before measurements by purging with argon.

2.4. CATALYTIC STUDIES

The reactions of toluene and phenol with H_2O_2 (30% aqueous solution) were carried out in a batch reactor. In a typical reaction, 100 mg of the catalyst was dispersed in 1 gm of toluene (phenol) and 10 ml of the solvent, acetonitrile. The mixture was stirred vigorously after the addition of the required amount of H_2O_2 corresponding to the molar ratio, substrate: $H_2O_2 = 3$. Reactions were carried out at 353 K for 18 h. The products were analyzed by gas chromatography (HP 5880; capillary column HP1, 50 m; oven temperature: 433 K for phenol reaction and 393 K for toluene reaction).

3. Results and discussion

3.1. CHEMICAL ANALYSIS

Two EU-1 samples were prepared with different V- and Al-inputs in the gel (table 1). The incorporation of V in the crystalline materials is about 30%, while the incorporation of Al is 75 and 45% for the two samples. As a result, the two samples

EU-1 (A) and (B) possess nearly the same amount of Al (Si/Al \approx 135) but different amounts of V (Si/V = 122 and 308). The three ZSM-22 samples were synthesized using the same amount of Al but different V-contents. Increasing the V-content in the gel increases the V-pickup, being 26, 43 and 53% for the three samples (A, B and C). We again have three ZSM-22 samples with nearly the same amount of Al and different V-contents (Si/V = 174, 189 and 247). Earlier workers [17] have reported that extralattice V can be removed from vanadosilicates by extracting with 1 M NH₄OAc solution at room temperature. V-loss from the EU-1 samples after the above treatment is marginal but the V-content decreases by 10 and 15% in the cases of ZSM-22 (A) and (B), respectively. When leaching of the samples with 1 M H₂SO₄ (298 K; 12 h) was carried out, the V-loss in all the cases was small (< 5%). The V in the calcined samples are probably present in the lattice or are strongly anchored to the lattice of the zeolites. The H₂SO₄ treatment significantly decreased the alkali content of the samples.

3.2. XRD

The XRD patterns of the V-EU-1 and V-ZSM-22 along with those of the Al-analogs are presented in figs. 1 and 2, respectively. The X-ray patterns reveal that the samples are highly crystalline. Though the patterns are generally similar for the Vfree and V-containing samples, changes in intensities of some lines are noticed. Such changes probably are a result of V-incorporation in the samples. V^{4+} and V^{5+} ions are larger than Si⁴⁺ ions, and hence their incorporation in the lattice of a zeolite



Fig. 1. XRD patterns of (A) EU-1 and (B) V-EU-1.



Fig. 2. XRD patterns of (A) ZSM-22 and (B) V-ZSM-22.

generally increases its unit cell size [7,8]. We have examined the change in the *d*-value of a typical intense line at $2\theta \approx 20^{\circ}$ in the XRD patterns of samples with and without vanadium in the EUO and TON systems. In both systems, a systematic increase in the *d*-value of the line was found to take place with increasing V-content. For EUO, the *d*-value increased from 0.4303 nm for the Al-only (Si/Al = 100) sample to 0.4341 nm for sample A (Si/V = 121.6). Similarly, for TON, the *d*-value increase was from 0.4333 nm for the Al-only (Si/Al = 60) sample to 0.4376 nm for sample A (Si/V = 188.3). The above results suggest that V has probably entered the lattice positions in both systems.

3.3. SEM

SEM pictures did not reveal noticeable differences in morphology or size between the V-free and V-containing samples. The EU-1 crystals were generally narrow ellipsoids ($\sim 1 \mu m$ long) and the ZSM-22 crystals were needles ($\sim 1 \mu m$ long).

3.4. IR

The IR spectra of calcined samples of EU-1 (A) and ZSM-22 (A) before and after extraction with 1 M H₂SO₄ are presented in fig. 3. A weak shoulder at ~ 980 cm⁻¹ is observed in both EU-1 (A) and ZSM-22 (A) in the calcined samples. On extraction with dilute H₂SO₄ and recalcination, a prominent band is observed at ~ 960 cm⁻¹. The origin of the band at 960–970 cm⁻¹ which has been observed in



Fig. 3. IR spectra of V-EU-1 (A) and V-ZSM-22 (A). A: calcined; A (E): acid extracted.

titano and vanadosilicates has been discussed by numerous workers [1,18,19]. It was earlier believed to be due to Si–O–V (or Si–O–Ti) vibrations. However, the recent work by Camblor et al. [19] and Khouw and Davis [13] suggests that it is more likely to be due to Si–O[–] vibrations. Khouw and Davis [13] have observed that calcined samples of TS-1 synthesized in the presence of alkali ions exhibited a weak shoulder at ~ 985 cm⁻¹ after calcination and a moderately strong absorption at ~ 960 cm⁻¹ after extraction with acid. Our results (fig. 3) of the vanadium samples synthesized in the presence of Na/K-ions are very similar to their results. In analogy with their suggestion for TS-1, we believe that the V-ions are present in defect structures in the lattice along with the alkali (say K) ions as shown below:



The above scheme suggests that one alkali metal ion is incorporated along with a V^{5+} -ion. A V^{4+} -ion, on the other hand, can be incorporated in two ways as shown below:



Species I exists in a T_d environment and is expected to be ESR active only at liquid N_2 temperature, while species II possesses a square pyramidal symmetry. The ESR data reveals an orthorhombic symmetry for the V⁴⁺-ions. Species II could give such ESR spectra. Besides, the observation of similar ESR spectra both at RT and liquid N_2 temperature suggests that the spectra cannot be attributed to species I.

Earlier studies [20] on the V-MEL system (alkali-free synthesis) have revealed that V^{5+} -ions are present in the framework while V^{4+} -ions are present as discrete ions, loosely bound to the framework. However, the exact location of the V^{5+} - and V^{4+} -ions in V-EU-1 and V-ZSM-22 is not known. As these samples are structurally different from V-MEL and also have been synthesized in the presence of alkali ions, the assignment of structures for the V-ions in these samples based on the V-MEL studies may not be justified.

An examination of table 1 reveals that the charge compensating ions are in excess (based on Al-content) in EU-1 and less in ZSM-22. The structures suggested for the V-ions will also lead to the presence of additional alkali ions in the samples. Thus, though the excess alkali ions present in EU-1 may be partly accounted for, the reasons for the lower alkali content in V-ZSM-22 samples are not clear. In fact, Casci et al. [21] have reported excess cations in the case of EU-1. They have attributed this to the presence of associated hydroxide ions or occluded anions such as bromide, silicate etc. Again, Araya and Lowe [22] have observed that the cations are less than the Al³⁺-ions in as-synthesized NU-10 (equivalent to ZSM-22) samples. They believe that charge balance is achieved in the system via protonation of the template (1,6-diaminohexane).

3.5. UV-VIS

The UV-Vis reflectance spectra of the as-synthesized and calcined samples are presented in fig. 4. Centi et al. [17] have reported that the low-energy charge transfer (LCT) bands of V⁵⁺ in O_h and T_d environments appear around 333–500 and 285–333 nm, respectively; the V⁴⁺-ions produce bands in the region 250–285 nm. In the as-synthesized samples, the prominent adsorption occurs below 250 nm along with minor absorption at around 280 nm for both V-EU-1 and V-ZSM-22. An additional weak band at ~ 380 nm is observed for V-EU-1 and ~ 450 nm for V-ZSM-22. The < 250 nm band has been attributed by Tuel and Taarit [23] to the charge



Fig. 4. UV-Vis reflectance spectra of the V-samples. A: V-EU-1 (A) (as-synthesized); B: V-EU-1 (A) (calcined); C: V-ZSM-22 (A) (as-synthesized); D: V-ZSM-22 (A) (calcined).

transfer between V⁴⁺-ions and the Si-atoms of the lattice. The bands at ~ 280 and ~ 380 nm have been suggested by Kornatowski et al. [24] to be due V⁵⁺-ions in T_d arrangements. The 450 nm band observed in V-ZSM-22 can be assigned to V⁵⁺-ions in a O_h symmetry [17]. Sen et al. [9] have reported that V⁵⁺-ions are present in the as-synthesized samples of V-Al-Beta. The calcined samples of both zeolites give broad bands mainly around 260–280 and 380–400 nm attributed to V⁵⁺ in T_d and O_h symmetries, respectively. A broad weak band at ~ 680 nm due to bulk V₂O₅ is also observed in the calcined samples. On NH₄OAc exchange and calcination, the 680 nm band disappears. The UV-Vis results suggest that the V-ions are present both as V⁴⁺- and V⁵⁺-ions in the as-synthesized samples, and mainly as V⁵⁺ (O_h and T_d) in the calcined samples.

3.6. ESR

The as-synthesized V-EU-1 and V-ZSM-22 samples exhibit V⁴⁺ ESR spectra at room temperature (figs. 5 and 6). The spectral parameters (V-EU-1: $g_{\parallel} = 1.924$, $g_{\perp} = 1.965$, $A_{\parallel} = 193.4$ G; $A_{\perp} = 66.4$ G and V-ZSM-22: $g_{\parallel} = 1.924$, $g_{\perp} = 1.969$; $A_{\parallel} = 193.0$ G, $A_{\perp} = 66.0$ G), suggest that the V⁴⁺-ions are present in an orthorhombic symmetry. The spectral parameters are not significantly altered at liquid N₂ temperature. On calcination, V-EU-1 does not give any spectral line attributable to V⁴⁺-ions either at RT or at liquid N₂ temperature. In the case of V-ZSM-22, the calcined samples give ESR spectra at RT and liquid N₂ temperature with a reduced intensity (intensity < 10% of as the as-synthesized sample). The ESR spectral parameters are similar to those of the as-synthesized sample suggesting that a



Fig. 5. ESR spectra of V-EU-1 (A). A: as-synthesized (RT); B: as-synthesized (liquid N₂ temp.); C: calcined (liquid N₂ temp.).

small amount of V⁴⁺-ions are not oxidised to V⁵⁺ at the calcination temperature of 823 K. On leaching the calcined sample with NH₄OAc the V⁴⁺ spectrum disappears and a sharp single line spectrum (g = 2.002) is obtained at liquid N₂ temperature. The origin of this line is not clear, and is probably due to O₂⁻ radicals associated with the V-ions [25].

3.7. CYCLIC VOLTAMMETRIC STUDIES

Transition metal ions such as Ti^{4+} and V^{5+} possess reversible reduction-oxidation (redox) characteristics. The redox properties of these ions can conveniently be studied by cyclic voltammetric experiments. Castro-Martins et al. [26] have reported that only the Ti^{4+} -ions present in lattice positions in TS-1 undergo redox cycles and not the extraneous Ti ions present in the samples. Similarly in the case of vanadosilicates, Venkatathri et al. [16] have reported that only the V⁵⁺-ions present in the lattice positions undergo redox cycles and not the extralattice vanadium species. The cyclic voltammograms of the calcined samples of V-EU-1 and V-ZSM-22 are presented in fig. 7. Two sets of redox signals (V⁵⁺/V⁴⁺) corresponding to two different V⁵⁺ are observed. The peak positions of these signals (table 2) are similar



Fig. 6. ESR spectra of V-ZSM-22 (A). A: as-synthesized (RT); B: as-synthesized (liquid N_2 temp.); C: calcined/NH₄OAc extracted (liquid N_2 temp.).



Fig. 7. Cyclic voltammograms of calcined samples of V-EU-1 (A) and V-ZSM-22 (A).

Sample	Peak po	Peak currents (µA)						
	$\overline{E_{a}}$ 1	E _a 2	E _c 1	$E_{\rm c}2$	$\overline{I_a 1}$	I _a 2	<i>I</i> c1	I _c 2
V-ZSM-22	0.48	0.20	0.20	-0.14	44	52	84	16
V-EU-1	0.51	0.26	0.14	-0.11	88	52	24	24
VS-1 ^a	0.38	0.16	0.02	-0.21	91	19	44	50

Table 2
Cyclic voltammogram data of V-ZSM-22 and V-EU-1: peak potentials and peak currents

^a Data from ref. [16].

to those obtained for the known and well studied vanadosilicate, VS-1 [16]. The cyclic voltammetric results, therefore, confirm that V-ions are present in the lattice position of both V-EU-1 and V-ZSM-22. Also, these studies indicate the presence of at least two types of V^{5+} -ions in calcined samples.

3.8. CATALYTIC ACTIVITIES

The results of the oxidation of toluene and the hydroxylation of phenol in the presence of H_2O_2 over V-EU-1 and V-ZSM-22 samples are presented in table 3. Blank experiments carried out in the absence of the catalysts did not reveal measurable conversions. The activities of the calcined samples and the NH4OAc extracted samples are reasonably similar. Considering the fact that some amount of V-was extracted by NH_4OAc (especially in V-ZSM-22 samples; see table 1), it is apparent that only the non-extractable vanadium (V in the framework) has been catalytically active. However, when the samples are acid washed, their activities increase manyfold. These observations are similar to those of Khouw and Davis [13] on TS-1 samples containing alkali ions. The reason for the increased oxidation activity of the

Oxidation of toluene and hydroxylation of phenol over V-EU-1 (A) and V-ZSM-22 (A)										
Sample	Pretreatment	Toluene o	oxidation		Phenol hydroxylation					
		conv. (TON) ^a	products (mol%)			conv.	products (mol%)			
			BAL ^b	ВОН ^в	cresols	(100)*	НО₽	CAT ^b	BQ⁵	
V-EU-1	calcined	0.7	48.7	51.3	_	0.5		2.0	98.0	
V-EU-1	NH ₄ OAc treated	0.6	46.7	53.3	-	0.4	-	3.0	97.0	
V-EU-1	acid treated	3.4	45.3	36.6	18.1	5.4	38.5	58.6	2.9	
V-ZSM-22	calcined	2.3	84.9	15.1		0.9	-	11.5	88.5	
V-ZSM-22	NH ₄ OAc treated	2.8	85.2	14.8	-	1.0		12.8	87.2	
V-ZSM-22	acid treated	4.0	43.3	40.4	16.3	4.2	30.0	64.7	5.3	

Table 3

^a TON = No. of molecules of substrate consumed per hour per V ion.

^b BAL, benzaldehyde; BOH, benzylalcohol; HQ, hydroquinone; CAT, catechol; BQ, benzoquinones.

washed samples is not clear, although Khouw and Davis [13] have suggested that the unwashed samples may be decomposing the H_2O_2 more rapidly than catalysing the oxidation of the substrates.

4. Conclusions

The synthesis of V-containing samples of EU-1 and ZSM-22 is possible in the presence of alkali ions. The synthesized samples are highly crystalline and thermally stable. Both V^{5+} - and V^{4+} -ions are present in the as-synthesized samples. At least two types of V^{5+} -ions are present in the calcined samples. The ions appear to be present in the lattice and undergo easy redox cycles. Acid washed samples give an absorption band ~ 960 cm⁻¹ attributable to Si-O⁻ vibrations. Acid washing also increases the catalytic activity of the samples in the oxidation of toluene and hydroxylation of phenol.

Acknowledgement

The financial support of IFCPAR, New Delhi is gratefully acknowledged.

References

- G. Perego, G. Bellussi, C. Corno, M. Taramasso, F. Buonomo and A. Esposito, Stud. Surf. Sci. Catal. 28 (1986) 129.
- [2] T. Tatsumi, M. Nakamura, S. Nagishi and H. Tominaga, J. Chem. Soc. Chem. Commun. (1990) 476.
- [3] D.R.C. Huybrechts, P.I. Buskens and P.A. Jacobs, J. Mol. Catal. 71 (1992) 129.
- [4] B. Notari, Stud. Surf. Sci. Catal. 37 (1988) 413.
- [5] J.S. Reddy and S. Sivasanker, Ind. J. Technol. 30 (1992) 64.
- [6] M.S. Rigutto and H. van Bekkum, Appl. Catal. 68 (1991) L1.
- [7] P.R.H.P. Rao, A.V. Ramaswamy and P. Ratnasamy, J. Catal. 137 (1992) 225.
- [8] A. Tuel and Y. Ben Taarit, Appl. Catal. A 102 (1993) 201.
- [9] T. Sen, M. Chatterjee and S. Sivasanker, J. Chem. Soc. Chem. Commun. (1995) 207.
- [10] K.M. Reddy, I. Moudrakovski and A. Sayari, J. Chem. Soc. Chem. Commun. (1994) 1059.
- [11] Chemical Week 156 (3) (1995) 20; European Chemical News 63 (1653) (1995) 23.
- [12] G. Bellussi, I. Maddinelli, A. Carati, A. Gervasini and R. Millini, in: Proc. 9th Int. Zeolite Congr., 1992, Vol. 1, eds. R. von Ballmoos, J.B. Higgins and M.M.J. Treacy (Butteworth-Heinemann, Boston, 1993) p. 207.
- [13] C.B. Khouw and M.E. Davis, J. Catal. 151 (1995) 77.
- [14] G.W. Dodwell, R.P. Denkewicz and L.B. Sand, Zeolites 5 (1985) 153.
- [15] N.E. Murr, M.A. Kerkeni, A. Sellami and Y. Ben Taarit, J. Electroanal. Chem. 246 (1988) 461.
- [16] N. Venkatathri, M.P. Vinod, K. Vijayamohanan and S. Sivasanker, J. Chem. Soc. Faraday Trans., submitted.
- [17] G. Centi, S. Perathoner, F. Trifirò, A. Aboukais, C.F. Aissi and M. Guelton, J. Phys. Chem. 96 (1992) 2617.

- 326 M. Chatterjee et al. / Novel vanado-aluminosilicates with EU-1 and ZSM-22 structures
- [18] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti and G. Petrini, Stud. Surf. Sci. Catal. 48 (1988) 133.
- [19] M.A. Camblor, A. Corma and J. Pérez-Pariente, J. Chem. Soc. Chem. Commun. (1993) 1557.
- [20] T. Sen, V. Ramaswamy, S. Ganapathy, P.R. Rajamohanan and S. Sivasanker, J. Phys. Chem., submitted.
- [21] J.L. Casci, T.V. Whittam and B.M. Lowe, in: Proc. 6th Int. Conf. on Zeolites, Reno 1983, p. 894.
- [22] A. Araya and B.M. Lowe, Zeolites 4 (1984) 280.
- [23] A. Tuel and Y. Ben Taarit, Zeolites 14 (1994) 18.
- [24] J. Koranatowski, B. Wichterlova, M. Rozwadowski and W.H. Baur, Stud. Surf. Sci. Catal. 84 (1994) 117.
- [25] P. Fejes, I. Marsi, I. Kiricsi, J. Halasz, I. Hannus, A. Rokenbauer, Gy. Tasi, L. Korecz and Gy. Schobel, Stud. Surf. Sci. Catal. 69 (1991) 173.
- [26] S.D. Castro-Martins, S. Khouzami, A. Tuel, Y. Ben Taarit, N. El Murr and A. Sellami, J. Electroanal. Chem. 350 (1993) 15.