Catalysis Letters 16 (1992) 1–9

The retention of copper ions by $AlPO_4$-5/VAPO-5 and their effect on reactant access

B.I. Whittington and J.R. Anderson *

Chemistry Department, Monash University, Clayton, Victoria, Australia,
and CSIRO Division of Materials Science and Technology, Clayton, Victoria, Australia

Received 20 April 1992; accepted 29 June 1992

The reaction of copper salts with $AlPO_4$-5 or V^V-VAPO-5 under acidic ($CuCl_2$, pH adjusted to 2) but especially basic conditions ($Cu(NH_3)_4^{2+}$, pH adjusted to 9) gives ion incorporations greater than expected by a simple ion exchange mechanism (both $AlPO_4$-5 and V^V-VAPO-5 could be expected to have no cation exchange capacity). Ion incorporation is proposed to occur initially at defect sites, and examination of the ESR spectrum of a dehydrated, evacuated $CuCl_2$-exchanged $AlPO_4$-5 shows that these defect sites give rise to a number of unique environments upon Cu^{II} incorporation. The $CuCl_2$-exchanged VAPO-5 retains a significant toluene accessibility to the V^V sites in the VAPO-5. However, the toluene accessibility in the $Cu(NH_3)_4^{2+}$-exchanged VAPO-5 is significantly reduced and we propose this is due to a combination of the presence of crystalline CuO and structural collapse from reaction with base (NH_4OH). The ability of treatment with base (NH_4OH, pH ≈ 13) to restrict access of toluene to the V^V sites of the original VAPO-5 was verified in a separate experiment.

Keywords: Ion exchange; $AlPO_4$-5; VAPO-5; defect sites; copper; ESR

1. Introduction

The micropore $AlPO_4$-5, which is nominally electrically neutral, has recently been observed [1] to incorporate metal ions. This ion retention was proposed to occur due to entrapment as a result of partial framework collapse, or from exchange at defect sites. An excess ion incorporation has also been reported with VAPO-5 [2] [☆], and it would be expected that a similar ion incorporation mechanism operates here. While this excess ion incorporation may allow for the introduction of catalytically active ions into the $AlPO_4$-5 family, their accessibil-

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[*] To whom correspondence should be addressed.

[☆] In particular compare the ammonium ion exchange capacities with the "framework" metal ion incorporation.

ity by organic molecules and hence, their potential as effective catalysts remains unclear. This is particularly true of exchange in alkaline media for, although a greater ion incorporation is possible under basic conditions [1], the stability of $AlPO_4$-5 is adversely affected by base [3]. It is the purpose of this study to examine copper ion incorporation in $AlPO_4$-5/VAPO-5, and some of the factors which restrict accessibility of organic molecules into the channels, since we ultimately wished to explore the catalytic properties of these materials.

2. Experimental

$AlPO_4$-5 was prepared by the following procedure. Boehemite (Condea Plural SB, 48.8 g) was added, with stirring, to a solution of phosphoric acid (83.2 g, 85%) in water (215.7 g). The suspension was mechanically stirred (1 h), triethylamine (70 ml) gradually added, and the resultant mixture manually stirred to give a homogeneous gel. After 20 min mechanical stirring, this gel was transferred to a large (700 ml) stirred autoclave, stirred for 2.5 h, then heated at 363 K for 7 h, and finally at 458 K for 9 h. At the end of this time, the autoclave was cooled in water, the solids centrifuged, washed with water (three times), then dried at 363 K for 2 h. Subsequent calcination at 823 K in air for 3.5 h gave the crystalline $AlPO_4$-5.

A VAPO-5 sample, containing 6.6 mmol vanadium/100 g, was prepared from a procedure similar to that reported by Davis and co-workers [4]. A solution of phosphoric acid (40 g, 85%) in water (28 ml) was added, with stirring, to a previously stirred (10 min) suspension of boehemite (Condea Plural SB, 23.4 g) in water (80 ml). This mixture was mechanically stirred (90 min), vanadium pentoxide (0.6 g) added, then stirred for a further 20 min. Tripropylamine (66 ml) was then gradually added and the mixture was manually stirred until a homogeneous gel resulted. This gel was then mechanically stirred (90 min) before being transferred to an unstirred, 100 ml autoclave and heated at 323 K for 21 h. At the end of this time, the autoclave was air cooled, the products centrifuged, washed with water (about five times) until the liquids were colourless and the solids dried at 363 K ($\approx$ 2 h) before being calcined at 823 K in air for 3.5 h.

Basic $Cu(NH_3)_4(NO_3)_2$ (0.4 M, pH adjusted to 9 with $HCl_{(aq)}$), ammonium hydroxide (0.28 M, $pH \approx 13$) and $CuCl_2$ (0.24 M, pH adjusted to 2 with $HCl_{(aq)}$) were used as the exchange solutions, and a typical reaction procedure involved shaking the calcined micropore (2.0 g; calcined at 823 K for 3.5 h) for approximately 16 h with 50 ml of the exchange solution (6 ml for $CuCl_{2(aq)}$) before filtering, washing with 500 ml of distilled water, and drying. With care, greater than 85% of the solid phase could be recovered. The uncalcined $Cu(NH_3)_4^{2+}$/VAPO-5 sample gave an XRD pattern with a much reduced intensity and changed unit cell dimensions similar to those observed by Meinhold and Tapp [1]. Copper exchanged H-mordenite (Conteka SBV 30, calcined at 823 K for 16 h, Si/Al = 70, ≈ 74% Cu^{II} exchange for H^+) was prepared from a 0.12 M $CuCl_2$ solution (pH 2) in a manner similar to the $CuCl_2/AlPO_4$-5 sample. Deammination of the solids from the $Cu(NH_3)_4^{2+}$ and ammonium hydroxide reactions involved calcination in air at 823 K for 3 h.

Some samples were additionally treated with refluxing toluene (≈ 500 mg solid : 10 ml toluene) for approximately 10 h, then filtered, washed with toluene, and dried at 343 K for 40 min.

Electron spin resonance (ESR) spectra were recorded in the X band (≈ 9.15 GHz) on a Varian E-12 spectrometer with an E-101 microwave bridge using, unless otherwise stated, unevacuated hydrated samples. The V^{IV} vanadyl concentrations were determined by numerical double integration, using a frozen $VOSO_4$ aqueous solution as a reference standard. The same volume of sample (accurately weighed) was used for each spectral measurement to minimise inaccuracies due to variation of ESR sensitivity with position in the ESR cavity.

ESR spectra of the Cu/mordenite and Cu/$AlPO_4$-5 were recorded after the samples were evacuated to 7×10^{-2} Torr, then heated under vacuum at 373 K for 31.5 h.

3. Results and discussion

3.1. CHARACTERISATION OF VAPO-5 AND $AlPO_4$-5

The XRD patterns of VAPO-5 and $AlPO_4$-5 indicated a crystalline material, with the VAPO-5/$AlPO_4$-5 micropore patterns accounting for the majority of the total area (≈ 92% for $AlPO_4$-5 and ≈ 96% for the VAPO-5 sample). In both instances, the main contaminant gave a broad peak for d spacings between 2.6 and 4.5 Å, suggesting a small amount of amorphous material was present. The unit cell dimensions were calculated by assuming hexagonal symmetry, and the values for our calcined, partially hydrated $AlPO_4$-5 ($a = 13.74 \pm 0.03$ Å; $c = 8.42 \pm 0.03$ Å) and VAPO-5 ($a = 13.79 \pm 0.03$ Å; $c = 8.41 \pm 0.03$ Å) compared favourably with those of the calcined $AlPO_4$-5 samples ($a = 13.71$–13.78 Å; $c = 8.44$–8.38 Å) previously reported [1]. Partial overlap between the vanadium pentoxide and VAPO-5 patterns in the XRD, and the low concentration of vanadium present, made it difficult to detect the presence of crystalline vanadium pentoxide in this sample. However, since we were unable to observe any separate vanadium phases by SEM/EDAX, all the vanadium is associated with the VAPO-5 crystals. The $A(V/Al)_{xps}/A(V/Al)_{bulk}$ ratio close to unity obtained by Davis and co-workers [4] additionally indicated this vanadium is distributed throughout the crystal, and not just present on the external VAPO-5 surfaces. Comparison of the $AlPO_4$-5 and VAPO-5 pore volumes (table 1) with the average value of 14.2 ml/100 g reported for $AlPO_4$-5 [5] indicated minimal

Table 1
Physical properties of treated VAPO-5 micropores

Sample and treatment	Vanadium and copper concentrations (mmol/100 g)	N_2 sorption capacity [a] (ml liq.N_2 /100 g)
VAPO-5	6.6 (V)	14.8
$AlPO_4$-5		14.0
VAPO-5 + 0.24 M $CuCl_2$ (pH adjusted to 2) after washing and drying at 363 K	6.9 (V) 5.6 (Cu)	13.9
VAPO-5 + 0.4 M $Cu(NH_3)_4^{2+}$ (pH adjusted to 9) after washing and calcining at 823 K	6.5 (V) 46 (Cu)	11.7
$AlPO_4$-5 + 0.24 M $CuCl_2$ (pH adjusted to 2) after washing and drying at 363 K	1.6 (Cu)	15.6
VAPO-5 + 0.28 M NH_4OH (pH ≈ 13) after washing and calcining at 823 K	6.2 (V)	13.7

[a] Obtained from nitrogen sorption data at 77 K: analyses by the *t*-plot method and by BET gave essentially the same values for sorption capacity.

channel blockage of our samples by amorphous material or, for VAPO-5, extra-framework vanadium.

3.2. INCORPORATION OF CUPRIC SALTS INTO VAPO-5 AND $AlPO_4$-5

The metal ion incorporations resulting from reaction of cupric chloride (0.24 M, pH adjusted to 2) and $Cu(NH_3)_4^{2+}$ (0.4 M, pH adjusted to 9) with calcined V^V VAPO-5 and from reaction of cupric chloride with calcined $AlPO_4$-5 are shown in table 1. Comparison of the the XRD patterns of the original microporous samples with those of the calcined $Cu(NH_3)_4^{2+}$/VAPO-5 and $CuCl_2$ treated $AlPO_4$-5 and VAPO-5 indicated a bulk retention of crystallinity by the micropore. The ESR spectra of the hydrated Cu/VAPO-5 samples contained peaks due to octahedrally coordinated, hydrated Cu^{II} [6], with additional peaks from the small amounts of isolated, immobile VAPO-5 vanadyls.

A reduction in the Cu^{II} ESR peak area by a factor of 2.7 was observed upon calcination of the $Cu(NH_3)_4^{2+}$-exchanged VAPO-5 and we suggest this is due to the formation of copper oxide, which has a weak ESR signal [7]. The XRD of this calcined sample also showed a very weak pattern from copper oxide crystals, consistent with a crystallite size greater than about 100 Å. However, the presence of these crystallites on the external VAPO-5 surface could not explain the decreased pore volume of the calcined $Cu(NH_3)_4^{2+}$/VAPO-5 and indicated limited structural collapse of the VAPO-5 or the existence of small copper oxide particles, undetectable by XRD, within the VAPO-5 pores. In contrast to the calcined, base treated, VAPO-5 sample there was no evidence for the presence of crystalline copper oxide upon treatment of $AlPO_4$-5 or VAPO-5 with $CuCl_2$ and the nitrogen sorption capacities (table 1) deviated less from the sorption capacities of the parent micropores ($AlPO_4$-5 or VAPO-5).

Simple isomorphous substitution of vanadium(V) for phosphorous would not be expected to generate any exchange sites at the vanadium [4] and we therefore suggest initial copper incorporation at the defect sites, or some unknown occluded species. The defect sites are thought to be AlOH and POH groups formed by loss of Al or P atoms from the $AlPO_4$-5 framework [8], and are comparable in nature to the silanol nests of ZSM-5/silicalite [9]. Approximately 0.6 defect sites/unit cell (41 mmol defect sites/100 g) have been observed in $AlPO_4$-5 [8], and it is not unreasonable to assume their presence in VAPO-5.

At present the reason for the greater Cu^{II} incorporation from the basic exchange solution, as compared with that from the acidic exchange solutions, is unknown. However, two mechanisms, operating either together or independently, can be proposed. The first requires formation of a copper hydroxide species upon washing the VAPO-5 sample, in a manner similar to that observed by Kohler et al. [10]. Subsequent calcination would then be expected to form copper oxide particles, as observed here by XRD and also observed on a $Cu(NH_3)_4^{2+}$ exchanged silica [10]. Alternatively, the higher pH of the $Cu(NH_3)_4^{2+}$ solution could allow more extensive deprotonation of the defect sites to AlO^- or PO^- groups *, and it may be that these groups are responsible for the increased cation retention at the higher pH.

To further study the Cu^{II} environment in the $CuCl_2/AlPO_4$-5, an ESR study of the dehydrated, evacuated Cu/$AlPO_4$-5 sample was undertaken, using a copper exchanged H-mordenite for comparison. The absence of any hyperfine splitting in the perpendicular peak component ($\approx$ 3200 G) and the large linewidths for the parallel components in the ESR spectrum of the dehydrated, evacuated Cu/$AlPO_4$–5 (fig. 1a) indicated the $AlPO_4$-5 defect sites gave rise to a number of unique Cu^{II} environments upon Cu^{II} incorporation from an acid solution. This contrasts with the Cu/H-mordenite (fig. 2a), in which only two unique Cu^{II} environments are observed. Exposure of both Cu/$AlPO_4$-5 and Cu/H-mordenite to air resulted in a significant peak broadening (figs. 2b and 3b) from oxygen–Cu^{II} dipole–dipole interactions [12].

3.3. TOLUENE TREATMENT OF THE Cu/VAPO-5 SAMPLES

Reduction of the Cu/VAPO-5 samples with refluxing toluene gave an indication of the apparent toluene accessibility to V^V vanadium. While treatment of

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* For cation retention at the SiO^-/SiOH groups of ZSM-5 see ref. [11].

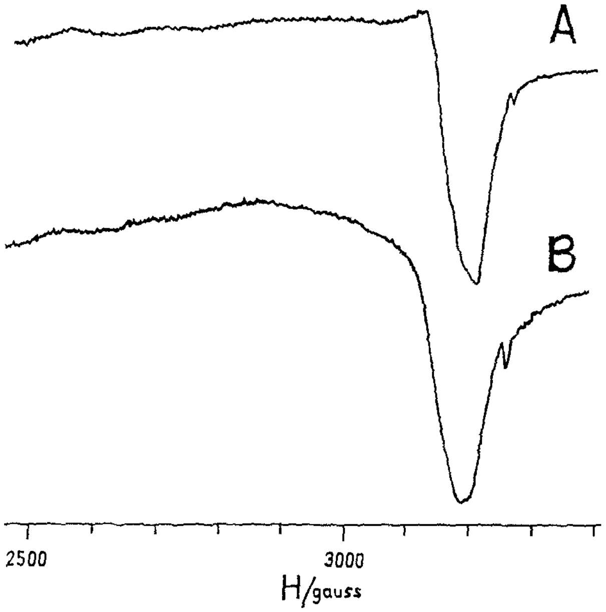

Fig. 1. ESR spectrum (130 K) of $CuCl_2$ exchanged AlPO$_4$-5 (a) evacuated and dehydrated at 373 K and (b) after the admission of air.

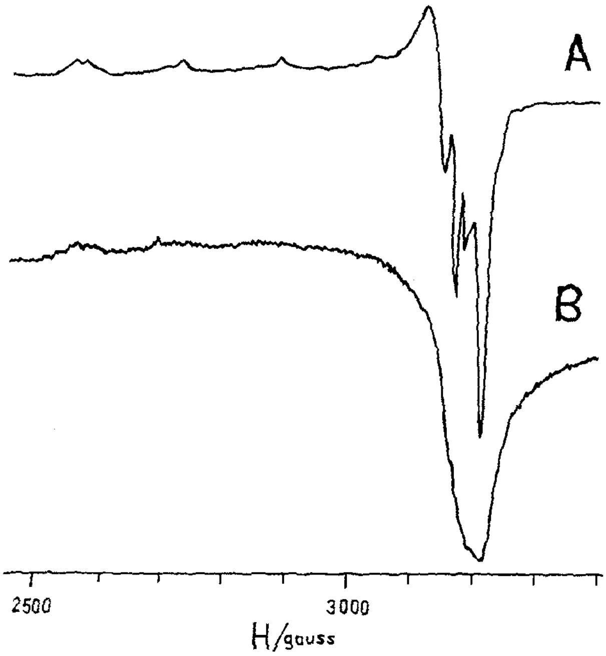

Fig. 2. ESR spectrum (130 K) of $CuCl_2$ exchanged mordenite (a) evacuated and dehydrated at 373 K and (b) after the admission of air.

Table 2
The ability of refluxing toluene to reduce the vanadium (V) in VAPO-5 after various treatments

Sample and treatment	% V^{IV}=O/V_{total} [a]
1 VAPO-5	≈ 3
2 dried $CuCl_2$/VAPO-5 treated with refluxing toluene/10 h	46
3 calcined $Cu(NH_3)_4^{2+}$/VAPO-5 treated with refluxing toluene/10 h	12
4 VAPO-5 + 0.28 M NH_4OH/washed/dried at 338 K	3
5 sample 4 calcined at 823 K/3.5 h	3
6 sample 5 treated with refluxing toluene/5 h	19
7 VAPO-5 treated with refluxing toluene (a) 4 h	66
(b) 10 h	72
8 sample 7a + 0.28 M NH_4OH/ washed/dried at 333 K	54
9 sample 8 calcined at 823 K/3.5 h	3

[a] Obtained by numerical double integration of the ESR spectrum (130 K) using a $VOSO_4$ spin standard. Estimated error ±10%.

the $CuCl_2$/VAPO-5 (table 2, sample 2) or the calcined $Cu(NH_3)_4^{2+}$/VAPO-5 (table 2, sample 3) with refluxing toluene gave lower V^{IV} vanadyl contents than a similarly treated VAPO-5 sample (table 2, sample 7b), the decrease in V^{IV} vanadyl content was more pronounced for the toluene treated calcined $Cu(NH_3)_4^{2+}$/VAPO-5. In both instances, treatment with refluxing toluene gave no change in the relative amounts of ESR detectable Cu^{II}.

Comparison of the V^{IV} vanadyl contents from the VAPO-5 and $CuCl_2$/VAPO-5 samples after treatment with refluxing toluene (table 2, samples 2 and 7b) could indicate minor channel blockage, either from limited structural collapse or the presence of copper ions. Alternatively, a strong interaction between the paramagnetic Cu^{II} and V^{IV} vanadyls could quench the V^{IV} vanadyl signal [13] *, in which case the vanadyl concentration shown (table 2, sample 2) represents the lower limit for the toluene accessibility. While a similar mechanism may be responsible for the low V^{IV} vanadyl concentration of the toluene treated, calcined, $Cu(NH_3)_4^{2+}$/VAPO-5 (cf. table 2, samples 3 and 7b), the nitrogen sorption capacity is significantly lower than that of the original VAPO-5 sample (table 1) and together, these two observations suggest channel blockage has occurred. As mentioned previously, this could arise from localised framework destruction (by NH_4OH attack: see later) or the presence of small copper oxide particles in the VAPO-5 pores. The bulk retention of crystallinity in the calcined sample shows that the VAPO-5 framework is substantially intact, and

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* In the V^{IV}–V^{IV} system, a distance of less than 4 Å is required.

that if any destruction of the framework occurred, it is probably localised at the channel entrances.

3.4. REACTIONS OF VAPO-5 WITH AMMONIUM HYDROXIDE

It is known that the presence of base has a detrimental effect on the stability of $AlPO_4$-5 [3]. The reaction of the original VAPO-5 with NH_4OH (pH ≈ 13) was therefore examined to determine its effect on the accessibility of toluene into the channel structure.

Calcination of the base-treated VAPO-5 (table 2, sample 5), subsequent treatment with refluxing toluene (table 2, sample 6), and comparison with a vanadyl-containing VAPO-5 (table 2, sample 7) showed the combination of base and heat treatment produced channel blockage and suggested that ammonium hydroxide was at least partly responsible for the channel blockage present in the $Cu(NH_3)_4^{2+}$/VAPO-5 system at the lower reaction pH. Very little vanadium was lost from the VAPO-5 as a result of these treatments (table 1).

Treatment of the vanadyl-containing VAPO-5 with NH_4OH (table 2, sample 8) and subsequent calcination (table 2, sample 9) significantly reduced the V^{IV} vanadyl ion concentration, but not the total vanadium content, and indicated that while toluene was unable to enter the channels, oxygen had access to the vanadyl groups. The similar vanadyl concentrations for the vanadyl containing VAPO-5 sample 7a and the base-treated sample 7a indicated the treatment with NH_4OH did not oxidise the V^{IV}=O, nor extract it from the framework and allow it to react to ESR silent dimers *.

Incomplete reduction of V^V-VAPO-5 by refluxing toluene (table 2, sample 6) and toluene at 373 K [16] has been observed, and comparison with results from as-synthesized VAPO-5 samples [16] suggests the ESR silent vanadium to be a V^V species which is not easily reduced because of restricted reductant access. Both chemical and ESR analysis of the as-synthesized, vanadyl-containing, VAPO-5 samples have been found to give similar V^{IV} contents [16], indicating framework substitution of $V^{IV}-O-V^{IV}$ species cannot be responsible for the ESR silent vanadium at these vanadium contents.

Acknowledgement

We thank Professor Pilbrow for allowing us use of the Physics Department ESR spectrometer.

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* $VOSO_4(aq)$ + egta chelates at pH > 5.5 gave a reduction in the observed ESR signal intensity at 300 K due to the formation of dimers [14]. However, at pH 14, there is evidence to suggest that ESR detectable $VO(OH)_3^-$ are present [15].

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