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Catalytic hydroxylation of phenol over a vanadium silicate molecular sieve with MEL structure

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Abstract

Vanadium silicate molecular sieves with MEL structure (VS-2) are found to be active in the hydroxylation of phenol with hydrogen peroxide, a reaction which is commercially practiced over titanium silicalite (TS-1 and TS-2) catalysts. Among various reaction parameters, the influence of the solvent on the conversion and product selectivity appears to be different from that reported on titanium silicalites. In methanol, for example, no hydroxylation takes place. In water, the phenol conversion as well as the H₂O₂ selectivity follows the order, TS-1 > TS-2 > VS-2. Only those vanadium ions which are in the lattice positions appear to catalyse this reaction.

Keywords: hydroxylation; MEL structure; molecular sieves; phenol hydroxylation; vanadium silicate.

INTRODUCTION

Unlike the conventional aluminosilicate zeolites, the titanium analogs, TS-1 and TS-2 (with MFI [1,2] and MEL [3] structures, respectively) are effective in the oxidation of a number of organic molecules with aqueous hydrogen peroxide as oxidant [4–8]. The first commercial process utilizing titanium silicalite (TS-1) as a catalyst was the hydroxylation of phenol to hydroquinone and catechol introduced by Enichem, Italy [9–13]. Several reports have since appeared on the influence of various parameters, such as the titanium content, phenol to H₂O₂ mole ratio, the solvent used, etc., on the conversion of phenol and various products of hydroxylation [14–16]. TS-2 (with MEL structure) is reported to be equally effective in the hydroxylation of phenol [3,17]. We now report that in addition to the above mentioned titanium silicalites, the vanadium analog of ZSM-11, namely VS-2, also possesses such catalytic properties in the oxidation of phenol to hydroquinone and catechol. The synthesis and structural characterization of vanadium silicate molecular sieves, with MFI

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and MEL structures where vanadium ions are incorporated in the zeolite framework, have recently been reported [18-22]. Our results indicate that as in the case of the titanium silicalites, only those vanadium ions which are in the framework catalyse this reaction.

EXPERIMENTAL

Synthesis of vanadium silicate with MEL structure was carried out using gels of the following molar composition: $\text{SiO}_2:0.2 \text{ TBA-OH}:x\text{VO}_2:30 \text{ H}_2\text{O}$, where $x=0.01-0.03$.

Vanadium silicate samples with three different Si/V (79,116 and 162) ratios were synthesised and characterized by X-ray diffraction (XRD), IR, electron spin resonance (ESR), and adsorption techniques as described in our earlier communications [21,22]. That the vanadium ions in our samples (as V^{5+} ions in the calcined form) are atomically dispersed, immobile and are most probably in the framework positions of silicalite-2 structure is suggested from the data presented therein [21,22].

For comparison titanium silicalites (TS-1 and TS-2) with Si/Ti ratios of 76 and 77 were synthesized according to the procedure given in refs. 2 and 3.

The calcined VS-2 samples were treated with 1 M ammonium acetate and then calcined at 753 K in air for 6 h before use in the hydroxylation reaction, which was performed in batch reactors. In a typical reaction, 100 mg of the catalyst was dispersed in a solution containing 1 g of phenol and 10 g of solvent. The mixture was vigorously stirred and H_2O_2 was then added in one lot using a 0.5 ml graduated syringe. After completion of the reaction, the products were analysed using gas chromatography (GC) (HP 5880), fitted with a 50 m long crosslinked methyl silicone gum capillary column. When water was used as solvent, acetone was added to the products after completion of the reaction and before analysis.

RESULTS AND DISCUSSION

Influence of vanadium content

Hydroxylation of phenol did not take place in the absence of catalyst. Neither pure silicalite-2 nor silicalite-2 impregnated with vanadium was active in this reaction. The introduction of vanadium even at lower concentrations in the silicalite lattice catalysed this reaction. This is similar to the observation made on titanium silicalites, where hydroxylation of phenol and benzene has frequently been used as a test reaction to characterize the presence or absence of Ti^{4+} ions in the framework positions [14]. Table 1 reports the catalytic activity of VS-2 samples with three different V/V+Si mole ratios in the hydroxylation of phenol using water as solvent. Phenol conversion marginally

TABLE 1

Hydroxylation of phenol over VS-2: Influence of vanadium content/catalyst concentration

Reaction conditions: phenol=1 g; solvent=water (10 ml); temp. (K)=353; phenol/H₂O₂ (mole)=3; reaction time (h)=8

V/(V+Si)	Catalyst amount (g)	Phenol conversion ^a (mol-%)	H ₂ O ₂ selectivity ^b (%)	Product distribution (mol-%) ^c		
				HQ	CAT	PBQ
0.0127	0.01	13.4	19.0	13.6	46.4	40.0
0.0127	0.02	18.7	34.5	21.8	56.2	22.0
0.0127	0.05	24.2	53.9	41.0	53.6	5.4
0.0127	0.10	25.8	58.7	42.2	55.5	2.3
0.0127	0.20	27.8	62.9	44.3	52.0	3.7
0.0086	0.10	25.0	58.0	41.1	58.1	0.8
0.0062	0.10	24.1	55.3	36.7	61.5	1.8

^aPhenol conversion = (No. of moles of phenol converted) / (Total no. of moles of Phenol × 100).^bH₂O₂ Selectivity = (No. of moles of H₂O₂ consumed in the formation of dihydroxybenzenes) / (Total no. of moles of H₂O₂ added) × 100; consumption for quinones and tars excluded.^cBreak-up (in mol-%) of products excluding tars. HQ = hydroquinone; CAT = catechol; PBQ = *para*-benzoquinone.

increases from 24.0 to 25.8 mol-% after 8 h reaction time, with H₂O₂ selectivity (defined as mol-% H₂O₂ consumed in the formation of dihydroxybenzenes) of 55.3 to 58.7%. At a given V/V+Si ratio of 0.0127, when the amount of the catalyst is increased from 0.01 g to 0.2 g (for 1 g of phenol) in the reaction mixture, both phenol conversion and efficiency in the utilization of H₂O₂ increase and level off at about 0.1–0.2 g of the catalyst in the reaction mixture. Large amounts of *para*-benzoquinone (PBQ) are present at a catalyst concentration of 0.01 and 0.02 g in the reaction mixture. Depending upon the concentration of the catalyst in the reaction mixture, the amount of the initially formed quinones decreased with time. For a given duration of the run (8 h) the decrease was found to be rapid, when the catalyst concentration was greater than 5% in the reaction mixture, i.e., > 0.05 g for 1 g of phenol. At higher catalyst loadings, the conversion of phenol to dihydroxybenzenes proceeds at a faster rate than further oxidation to quinones depleting the H₂O₂ available for further oxidation. The H₂O₂ selectivity, consequently, increases with increase in catalyst concentration in the reaction mixture. Irrespective of the catalyst concentration, all the H₂O₂ initially taken is transformed and no H₂O₂ was detected after completion of the reaction. As far as the product distribution is concerned, with increase in the concentration of vanadium in the samples and also with the increase in the concentration of catalyst in the reaction mixture, the product distribution shows that the catechol to hydroquinone ratio decreases (i.e. the selectivity shifts towards hydroquinone in products). It is not

clear at the moment why the product selectivity shifts more towards the *para*-isomer with more vanadium in the reaction mixture.

Influence of the solvent

The solvent used in this reaction is known to have a profound influence on the phenol conversion, H₂O₂ selectivity and the ratio of catechol to hydroquinone over titanium silicalites [12,23]. On vanadium silicate-2, the influence of various solvents is illustrated in Table 2. Phenol conversion increases with increase in the polarity of the solvent (7.0, 13.9 and 24.3%, for acetone, acetonitrile and water, respectively) with a corresponding increase in the efficiency of H₂O₂ utilization. Under identical conditions, maximum phenol conversion is observed in water. Interestingly, no hydroxylation products are obtained in methanol. Even an increase in the reaction temperature (up to 353 K) or a higher concentration of the catalyst in the reaction mixture did not lead to the formation of any dihydroxylated product from phenol. Since no hydroxylation took place, no tar formation was observed, the reaction mixture remaining almost colourless. After 8 h of reaction, no hydrogen peroxide was detected in the reaction mixture, indicating that H₂O₂ is decomposed under these conditions. There is, however, no evidence for the oxidation of methanol. This observation is in contrast to that observed with titanium analogs. In the case of the latter, high H₂O₂ selectivity (of the order of 80%) has been observed in methanol solvent [23]. We presume that the formation of vanadium peroxo species, responsible for the oxygenation of organic substrates is either inhibited or destabilized in the presence of methanol, but not when water is used as solvent.

The influence of the solvent on the product distribution is more complex. *Para*-benzoquinone is obtained (4 to 5%) in all the three solvents (acetone,

TABLE 2

Hydroxylation of phenol over VS-2: Influence of the solvent

Reaction conditions: catalyst = VS-2 (Si/V = 79); temp. (K) = 333; phenol/VS-2 = 10; phenol/H₂O₂ (mole) = 3; reaction time (h) = 8; 10 ml solvent

Solvent	Phenol conversion ^a (mol-%)	H ₂ O ₂ selectivity ^b (%)	Product distribution (mol-%) ^c		
			HQ	CAT	PBQ
Water	24.3	55.7	44.1	52.0	3.9
Acetonitrile	13.9	29.7	55.4	39.8	4.8
Acetone	7.0	12.7	95.1	0	4.9
Methanol	0	0	-	-	-

^{a-c}As defined in Table 1.

acetonitrile and water). Surprisingly, only hydroquinone is observed when acetone was used as solvent. The products of hydroxylation of phenol on titanium silicalites, on the other hand, consist of almost an equimolar mixture of catechol and hydroquinone [9-11,1]. Tuel et al. [23] have recently reported enhanced yields of catechol in this reaction over TS-1, on changing the solvent from methanol to acetone. Apparently, the influence of the solvent on the product distribution is a complex phenomenon requiring further investigation.

Influence of the phenol to H₂O₂ ratio

The results of the influence of concentration of hydrogen peroxide on the conversion of phenol and utilization of H₂O₂ are presented in Table 3. As expected, the efficiency of utilization of H₂O₂ increases at higher phenol to H₂O₂ molar ratios and the conversion decreases. Conversion and efficiency of H₂O₂ have opposite trends in the presence of optimum amounts of catalyst in the reaction medium. A H₂O₂ selectivity of 71.5% was observed at the phenol to H₂O₂ ratio of 10 in water as solvent. The ratio of hydroquinone to catechol shifted marginally in favour of hydroquinone with an increase in the phenol to H₂O₂ ratio.

Comparison with titanium silicalites

A comparison of the activities of VS-2 and the titanium silicalites, TS-1 and TS-2 in the hydroxylation of phenol under similar operating conditions has been made. The phenol conversion, H₂O₂ selectivity and the product distributions as a function of time on VS-2, TS-2 and TS-1 are presented in Fig. 1 A, B and C, respectively. The reactions were carried out using water as solvent at 353 K and at phenol to H₂O₂ mole ratio of 3.0. 100 mg Each of the three catalysts having almost similar Si/M ratios was used in the batch reaction. At

TABLE 3

Hydroxylation of phenol over VS-2: Influence of H₂O₂ concentration

Reaction conditions: catalyst = VS-2 (Si/V = 79); temp. (K) = 353; phenol/VS-2 = 10; solvent = water (10 ml); reaction time (h) = 8

Phenol/H ₂ O ₂ mole ratio	Phenol conversion ^a (mol-%)	H ₂ O ₂ selectivity ^b (%)	Product distribution (mol-%) ^c		
			HQ	CAT	PBQ
3	25.8	58.7	42.2	55.5	2.3
5	17.4	65.7	45.0	53.4	1.6
10	9.5	71.5	49.6	48.7	1.7

^{a-c}As defined in Table 1.

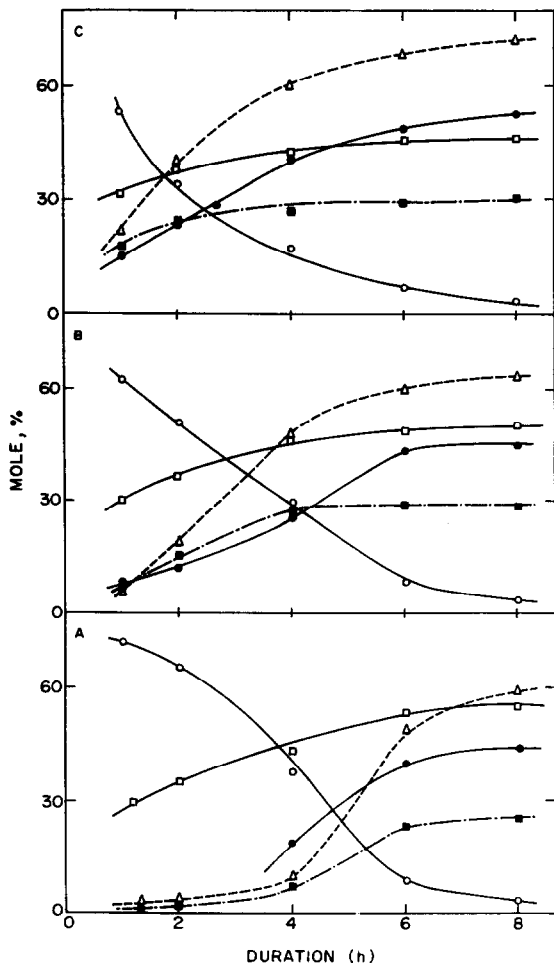


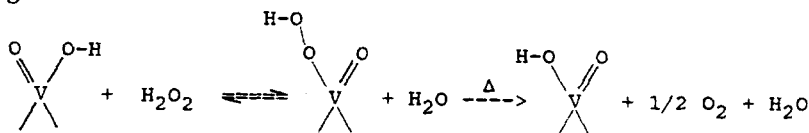
Fig. 1. Comparison of the hydroxylation of phenol over VS-2 (A), TS-2 (B) and TS-1 (C) catalysts. Solvent=water; temp. (K)=353; phenol/ H_2O_2 (moles)=3. (■): phenol conversion; (Δ): H_2O_2 selectivity; (\circ): *para*-benzoquinone; (\square): catechol; (\bullet): hydroquinone.

the end of 8 h run, the phenol conversions were 25.8, 26.7, 30.1 mol-% with H_2O_2 selectivities of 58.7, 62.3, 72.2% for VS-2, TS-2 and TS-1, respectively. A fairly large difference observed in phenol conversions on VS-2 on the one hand and the titanium silicates on the other, in solvent acetone is not discernible when the reactions were carried out in a protic solvent such as water. The figure shows that the initial activity of VS-2 is much lower (upto 4 h) compared to those of TS-1 and TS-2 and that the rates follow the order TS-1 > TS-2 > VS-2. The difference in the product distributions at the end of the run on the three

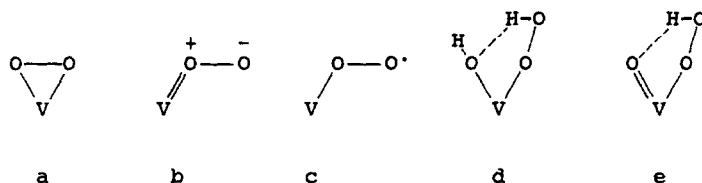
catalysts is seen from the catechol to hydroquinone ratios, which are 1.3, 1.1 and 0.9 for VS-2, TS-2 and TS-1, respectively.

Vanadium peroxo intermediates

The formation of vanadium-peroxo complexes by chemisorption of H_2O_2 on the isolated vanadium species of the type recently postulated to be part of the MFI and MEL structures in vanadium silicates [19-21] could be envisaged as given below.



The following possible active forms of V^{5+} peroxidic reagents are well known as the actual oxygen donors in many oxygenation reactions [24]:



The intramolecular hydrogen-bonded forms of the type 'e' are quite likely to be formed in vanadium silicates upon H_2O_2 chemisorption. The stability of the peroxo complexes depends on the nature of the solvent and the nature of the ligands bonded to the metal [24]. The marked difference observed in the hydroxylation rates in protic and aprotic solvents is indeed related to the stabilization of the peroxo intermediates. Further work is in progress to understand the solvent influence on the rates and mechanism of this reaction.

CONCLUSIONS

Our results demonstrate that (a) vanadium silicate molecular sieves are also good catalysts in the hydroxylation of phenol as are titanium silicates, (b) the influence of solvent on the product selectivity is significantly different from that observed on titanium silicates needing further detailed studies, and that (c) only those vanadium ions that are in the framework positions are involved in the hydroxylation reaction.

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