Oxidation of primary amines over vanadium silicalite molecular sieve, VS-1

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The mild oxidation of various primary amines with diluted hydrogen peroxide has been studied over vanadium silicalite molecular sieve, VS-1. The reaction leads to the corresponding oximes and imines. The nature of solvent was found to have a strong influence on the product selectivity. The use of chloroform favors the formation of nitroalkanes. Under similar conditions primary amines with no α-hydrogen, such as aniline, were oxidized mainly to the corresponding azoxy derivatives.

Keywords: mild oxidation; amines; vanadium silicalites; VS-1

1. Introduction

The oxidation of amines to a variety of nitrogen containing compounds like nitroalkanes, hydroxylamines, amine N-oxides and nitrones has been carried out in the presence of both homogeneous and heterogeneous catalysts [1]. Titanium silicalite molecular sieves, TS-1 and TS-2, are well known catalysts for their academic and industrial importance due to their potential in various oxidation reactions [2]. They have been used for the oxidation at carbon [2,3] as well as at sulfur moieties [4]. Patent literature also claims that TS-1 catalyzes the oxidation of secondary amines to the corresponding hydroxylamines [5]. Recently, Reddy and Jacobs have reported the oxidation of various aliphatic primary amines to their corresponding oximes over titanium silicalites [6].

The incorporation of vanadium into the zeolite framework also enabled the oxidation of a number of organic substrates [7]. Vanadium silicalites were found to be stronger oxidation catalysts than titanium silicalites. Contrary to their titanium counterparts, vanadium silicalites can catalyze the oxidation of alkenes at primary carbon atoms to give alcohols [8] and the oxidation of primary alcohols to car-

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boxylic acids [9]. Because of the differences between these catalysts in hydrocarbon oxidation, it was expected that the oxidation of primary amines over vanadium and titanium silicalites will also lead to different product patterns. This paper reports on the oxidation of various primary amines over vanadium silicalite, VS-1.

2. Experimental

The hydrothermal synthesis of VS-1 was carried out using tetraethylorthosilicate, TEOS (Aldrich), vanadium sulfate (Aldrich) and tetrapropylammonium hydroxide, TPA-OH. To make sure that the template TPA-OH is alkali free, it was prepared by reacting the corresponding bromide with silver oxide. The gel composition was as follows:

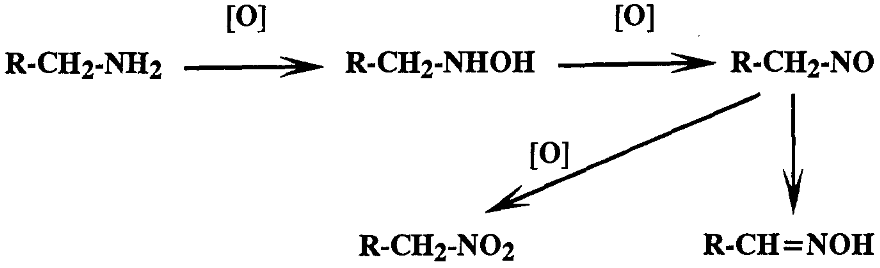
$$0.20(TPA)_2O : SiO_2 : 0.02VO_2 : 30H_2O\,.$$

Chemical analysis of the obtained VS-1 sample gave a Si/V ratio of 195. This sample was further characterized using XRD, IR, ESR and NMR techniques. It was confirmed that the vanadium is located in the zeolite framework. Catalytic reactions were carried out batchwise in a 250 ml two-necked round bottom flask. In a typical reaction, the required amount of amine, hydrogen peroxide, 25 ml solvent and 0.2 g of catalyst were mixed. The reaction mixture was stirred continuously at 338 K. Products were analyzed using a gas chromatograph (Hewlett Packard 5890 series II) equipped with a HP-1 (methylsilicon gum) capillary column (50 m × 0.25 i.d.). Product identification was achieved with GCMS and by comparison to authentic compounds.

3. Results and discussion

The activity of the VS-1 catalyst in the oxidation of different primary amines is reported in table 1. Data were collected after 4 h of reaction time. It was observed that at this time most of the hydrogen peroxide was converted. The reaction conditions were similar to the conditions used for titanium silicalites [6]. In the TS-1 catalyzed oxidation of aliphatic primary amines, the major products were the corresponding oximes. The titanium silicalite also gave significant amounts of hydrazone. Nitroalkanes and nitroso dimers were obtained in small quantities. As shown in table 1, a different product distribution was obtained in the presence of VS-1. The main products were oxime and imine. Depending on the nature of the amine substrate, the combined selectivity towards these two products varied from 27 to 72% and the ratio of imine to oxime varied from 0.6 to 4.2.

In general, the oxidation of aliphatic primary amines over vanadium silicalites takes place according to scheme 1. Amine is first oxidized to hydroxylamine and



Scheme 1.

then to nitrosoalkane. Nitrosoalkane will then either tautomerize to the corresponding oxime or further oxidize to nitroalkane. Formation of the imine takes place according to scheme 2. Oxime is oxidized to a carbonyl compound, which

$$\text{R-CH=NOH} \xrightarrow{[O]} \text{R-CHO} \xrightarrow{\text{R-CH}_2\text{-NH}_2} \text{R-CH=N-CH}_2\text{-R}$$

Scheme 2.

readily reacts with the substrate to give imine. Detailed studies on the oxidation of oximes over titanium and vanadium silicalites showed that the latter is more efficient for the oxidation of oximes to carbonyl compounds [10]. This explains why large amounts of imines are formed in the presence of VS-1, while hardly any imine forms over TS-1. Moreover, in the presence of titanium silicalite, the oxidation of amines to oximes takes place more rapidly than in the presence of vanadium silicalite, so that no hydrogen peroxide is left to oxidize the oxime into a carbonyl com-

Table 1
Oxidation of different primary amines over VS-1 [a]

Substrate	Catalyst	TON [b]	Conv. (%)	Product distribution (wt%)	
				oxime	imine
n-propylamine	VS-1	351	17	35	53
n-propylamine	TS-1 [c]	255	24	70	3
i-propylamine	VS-1	227	11	43	27
n-butylamine	VS-1	351	17	40	45
n-octylamine	VS-1	247	12	16	45
cyclohexylamine	VS-1	103	5	35	39
benzylamine	VS-1	268	13	17	72
aniline [d]	VS-1	247	12	90 [e]	–

[a] Reaction conditions: catalyst weight (g) = 0.2; amine (mmol) = 35; molar amine to hydrogen peroxide ratio = 2; temperature (K) = 338; solvent = methanol (25 ml); reaction time (h) = 4.

[b] TON = turnover number in moles of amine converted per mole of vanadium or titanium.

[c] Si/Ti = 100.

[d] Reaction time (h) = 10.

[e] Azoxybenzene.

pound. On the contrary, when vanadium silicalite is used as a catalyst, the oxidation of amines is slow and the resulting oximes react further leading to imines as shown in scheme 2.

When the oxidation of amines is carried out without any catalyst, very low conversions are obtained. It was also observed that even in the presence of TS-1 or VS-1, no reaction occurs without hydrogen peroxide. The purpose of this test was to check whether any reaction takes place between the amine substrate and the solvent. Note that there are significant amounts of unidentified compounds, which include carbonyl compounds from the corresponding oximes, nitroso dimers, nitroalkanes and secondary oxidized products. As seen in table 1, conversion of amines over VS-1 is lower than over TS-1; however, this is mainly due to the lower vanadium content in VS-1 as compared to the Ti content in TS-1. Comparison on the basis of turnover numbers shows that both catalysts have similar activities.

As in the case of TS-1 [11], the oxidation of aromatic primary amines (with no α-hydrogen) over VS-1 leads mainly to their azoxy derivatives. For example, the oxidation of aniline gave azoxybenzene with 90% selectivity. The azoxy derivatives are obtained by reaction between the nitroso and hydroxylamine, which are generated by successive oxidation of the amine substrate [11].

The influence of three different solvents at different hydrogen peroxide concentrations is reported in table 2. Very similar product distributions were obtained in the presence of both methanol and ethanol. However, in the bi-phasic oxidation using chloroform as solvent, significant quantities of nitroalkanes were formed at the expense of oximes. Literature data indicate that oxidation of amine by peroxotungstophosphate (PCWP) in the presence of chloroform leads to lower oxime selectivities than in the presence of *t*-butanol [13]. Similarly, Gilbert and Borden [14] reported very high selectivities towards nitroalkanes during peracid oxidation of aliphatic amines in the presence of chlorinated hydrocarbons including chloroform at 60–80°C.

Table 2
Influence of various solvents on the oxidation of primary amines over VS-1 [a]

Amine	FR [b]	Solvent	Conv. (%)	Product distribution (wt%)		
				oxime	nitro	imine
n-propylamine	1	chloroform	20	25	20	42
n-propylamine	1	methanol	28	33	–	31
n-propylamine	1	ethanol	34	34	4	52
n-propylamine	2	chloroform	9	30	18	49
n-propylamine	2	methanol	10	35	–	53
n-butylamine	2	chloroform	9	25	16	50
n-butylamine	2	methanol	8	42	–	42

[a] Reaction conditions: catalyst weight (g) = 2; temperature (K) = 338; 25 ml solvent; reaction time (h) = 2.

[b] FR = molar feed ratio, amine/H_2O_2.

Table 2 also reports the effect of hydrogen peroxide concentration on the *n*-propylamine conversion as well as the product selectivities. The increase in hydrogen peroxide concentration brings about an increase in the overall conversion and a decrease in selectivity towards both oxime and imine. When a molar *n*-propylamine to hydrogen peroxide ratio of 0.5 is used a large number of secondary oxidized products were obtained (54%).

In conclusion, vanadium silicalite molecular sieves catalyze the selective oxidation of aliphatic and aromatic amines. Compared to titanium silicalites, they are less selective towards oxime, but exhibit good selectivities towards imine formation. These imines are formed by the condensation of the amine substrate and the carbonyl compound, formed by further oxidation of the oxime. Chloroform favors the formation of nitroalkanes. The increase in hydrogen peroxide concentration increases the conversion of amine, but leads to a complex product mixture with lower selectivities toward imine and oxime. VS-1 also catalyzes the oxidation of aniline to azoxybenzene with a very high selectivity.

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