

Selective Production of Hydrazine by a Catalytic Oxidation Process over Ti-, V-, Ti-V- and Ti-B-Silicalites

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A simple catalytic process to obtain hydrazine by oxidation of ketone-NH₃ system by H₂O₂ is reported; Ti-, V-, Ti-V- and Ti-B-silicalites of MFI structure are found to be active as catalysts in this oxidation reaction.

Hydrazine is one of the most important and versatile chemicals due to its wide application in a variety of fields of science and technology such as rocket fuel, fuel cells and electroless plating. So far several processes have been discovered and patented for hydrazine production. The chemistry of hypochlorite oxidation of ammonia to hydrazine was first established by Raschig¹ in 1907. The reaction still provides the scientific basis for the commercial production of hydrazine. In the modern age, there is an urgent need to replace wasteful and toxic stoichiometric oxidants with more ecologically friendly technologies. The use of clean oxygen donors such as H₂O₂ in the area of oxidation of organic compounds based on catalytic oxygen transfer, is certainly one of the best solutions to environmental problems. Earlier an industrial process for hydrazine synthesis was disclosed by Schrimann (UGINE-KUHLMANN), which involves the hydrogen peroxide oxidation of the ketone-NH₃ system in the presence of a nitrile.² In another catalytic oxidation process,^{3,4} the same reaction was performed at 200 °C, and 1–8 atm using benzophenone and ammonia in the presence of zinc chloride and copper(I) chloride as catalysts. Recently Hayashi⁵ made a detailed literature survey concerning hydrazine synthesis.

We report here, for the first time, the novel catalytic oxidation process for hydrazine synthesis from heptan-4-one, NH₃ (in solution) and oxygen from H₂O₂, via azine formation with recovery of heptan-4-one. The proposed process is advantageous from an environmental point of view and runs at 55 °C and 1 atm. It is based on a catalytic oxygen transfer process using titanium, vanadium and boron silicalite molecular sieves with substituted Ti and/or V, B in the framework, which are catalytically active in the selective oxidation of a number of organic substrates with H₂O₂.^{6–9}

The catalysts TS-1 (Ti/Si = 0.026), VS-1 (V/Si = 0.023), TVS-1 (Ti/Si = 0.014, V/Si = 0.025) and TBS-1 (Ti/Si = 0.014, B/Si = 0.027) silicalites used in this study were synthesised hydrothermally. In order to have a high probability for Ti and/or V ions to be located inside the siliceous domains, samples were synthesised with a relatively high Si fraction in the precursor gel. The XRD patterns for the crystalline phase identification of as-synthesised samples are characteristic of the highly crystalline pure MFI type structure, with an orthorhombic symmetry. Diffuse reflectance (DR) spectra of TS-1 and TVS-1 samples in the UV-VIS region showed a single strong transition band centred at *ca.* 213 nm which is undoubtedly associated with an electronic transition localized on a structure containing most of the Ti in essentially tetrahedral coordination. The two transition bands observed with the VS-1 sample are due to different coordinations of V in the molecular sieve.

The catalytic runs for hydrazine synthesis were carried out in a reactor system described earlier.⁹ The reaction conditions were: catalyst = 0.2 (g), heptan-4-one:NH₃:H₂O₂ (mol ratio) = 1:17.09:0.51, reaction temperature 328 K and reaction time ≤ 24 h. At different times samples from both the organic and aqueous phases were collected through the sampling port. Analysis of the reaction products was performed by gas chromatography using a packed Porapak column and a TCD detector. The volume of collected O₂ gas was recorded as a function of reaction time and decomposition of H₂O₂ during the reaction was calculated to be complete.

Table 1 lists the result of the catalytic oxidation of a mixture of ketone (heptan-4-one), NH₃ (introduced as a 28% aqueous solution) over Ti-, V-, Ti-V- and Ti-B-silicalites of MFI structure using H₂O₂ (30% aqueous solution) as the oxidant. An increase in the production of hydrazine was observed with the reaction time. It was found that TS-1, VS-1, TVS-1 and TBS-1 are effective catalysts but VS-1 was the most selective catalyst for the production of hydrazine (Fig. 1). The maximum conversion of heptan-4-one is observed over TVS-1. A decrease of ketone conversion after 5 h is shown in Fig. 2. This decrease is consistent with the higher hydrazine production which

Table 1 Hydrazine synthesis by catalytic oxidation over Ti-, V-, Ti-V- and Ti-B-silicalites of MFI structure

Catalyst ^a	<i>t</i> /h	Ketone conv. (mol %)	Product distribution (mol %)			H ₂ O ₂ decomp. (mol %)
			Imine	Oxime	Hydrazine	
VS-1	1	38.9	9.2	73.6	17.2	6.8
	3	43.2	8.6	65.4	26.0	12.4
	5	56.2	8.8	65.0	26.2	16.4
	24	31.5	4.4	33.5	62.1	—
TVS-1	1	37.2	9.9	76.3	13.8	4.3
	3	48.6	8.4	70.1	21.5	8.9
	5	59.5	8.9	67.0	24.1	13.7
	24	34.6	4.5	37.2	58.3	—
TS-1	1	20.9	11.0	75.2	13.8	6.5
	3	38.2	9.8	71.0	19.2	9.7
	5	51.0	4.5	73.2	22.3	12.7
	24	22.3	5.2	39.2	55.6	—
TBS-1	1	25.6	10.0	84.7	5.3	9.8
	3	33.9	8.7	83.1	8.2	14.2
	5	49.4	7.6	83.6	8.8	17.3
	24	34.5	5.0	60.7	34.3	—

^a No reaction without catalyst.

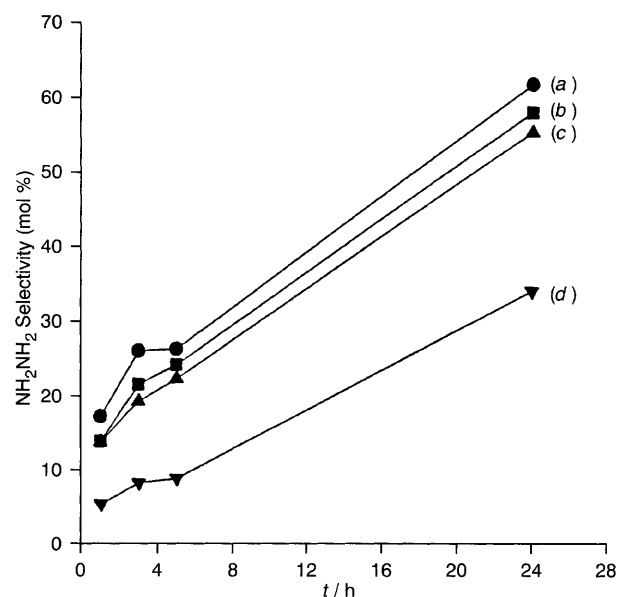


Fig. 1 Hydrazine selectivity as a function of reaction time: (a) VS-1, (b) TVS-1, (c) TS-1 and (d) TBS-1

according to the proposed reaction pathway (Scheme 1) must be associated with the reformation of the ketone.[†] The excess of NH_3 may accelerate the azine formation by increasing the rate of imine production and the rate of imine desorption. No

reaction was observed in the absence of the catalyst or H_2O_2 . It was also noticed that most of the hydrazine remains in the aqueous phase, while the organic phase contains only a small fraction of the total hydrazine produced.

Therefore, this new catalytic ammoxidation process proposed for the production of hydrazine involves the condensation of heptan-4-one with ammonia to the corresponding imine in the presence of Ti-, V-, Ti-V- and Ti-B-silicalites, followed by oxidative coupling of the imine to azine, and hydrolysis of azine into hydrazine with recovery of heptan-4-one.[‡] Another direct pathway for the production of the oxime through NH_3 oxidation to hydroxylamine and condensation with the ketone is also possible. This was, however, not indicated in Scheme 1 as no hydroxylamine was observed in the products. The azine intermediate was not detected either and may react very quickly to yield hydrazine. Kinetic studies are in progress which should provide stimulating suggestions for the practical modification of the process.

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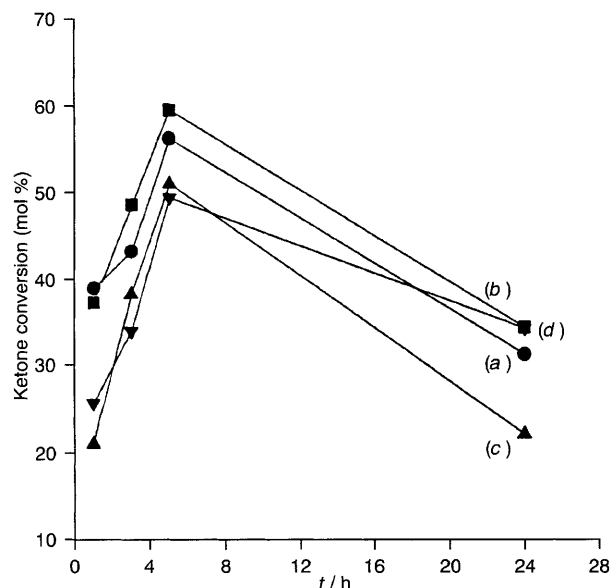
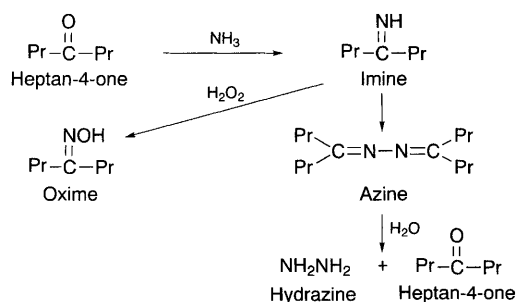


Fig. 2 Ketone conversion as a function of reaction time: (a) VS-1, (b) TVS-1, (c) TS-1 and (d) TBS-1



Scheme 1 Proposed reaction scheme for hydrazine synthesis

Footnotes

[†] This decrease may be regarded as reflecting the comparative rates of azine and oxime formation.

[‡] Heptan-4-one could be regarded as acting as a homogeneous co-catalyst.

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