



Vanadium resin as an efficient catalyst for the liquid phase ammoximation of cyclic ketones

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ABSTRACT

A new vanadium resin catalyst has been prepared through ion exchange at the cationic sites of Amberlite IR 120 resin. This vanadium-loaded resin is characterized by using AAS, UV-vis, FTIR and EPR spectroscopic tools. Ammoximation of cyclic ketones e.g. cyclohexanone, cyclooctanone and cyclododecanone in the presence of aqueous hydrogen peroxide and ammonia have been carried out under eco-friendly liquid phase conditions over this vanadium resin at 333 K. Interestingly, for ammoximation of cyclohexanone the progress of the reaction could be visually monitored from the change in color of the catalyst during the reactions; after the consumption of H_2O_2 the orange catalyst returns back to its original green color. For all the cyclic ketones corresponding oximes are obtained as major products with moderately high yields. The new catalytic system described herein is an efficient and eco-friendly method for the ammoximation of bulky cyclic ketones, with the advantages of good conversion and selectivity, devoid of hazardous solvents and byproducts.

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1. Introduction

Transition metal-containing heterogeneous catalysts have been studied extensively by academia and industry over many decades because of their versatile potential in a wide range of eco-friendly clean partial oxidation reactions, e.g. oxidation of C–H, N–H, S–H, etc. [1], epoxidation of olefins [1–3], hydroxylation of aromatics [4], ammoximation of ketones [5–14], etc. These partial oxidation reactions have replaced the large-scale use of hazardous organic peracids and disposable metal complexes, which are harmful to the environment. Among these selective partial oxidation reactions, ammoximation reaction is of particular interest [5–19]. Because ϵ -caprolactam, essential component of the versatile polymer nylon-66, is largely produced by the acid catalyzed Beckman rearrangement of the cyclohexanone oxime [20,21], which can be very efficiently and selectively produced by ammoximation of cyclohexanone over microporous titanium silicate TS-1 [1–4] using dilute aqueous hydrogen peroxide and liquid ammonia. Although there are many reports on microporous vanadium silicates and other vanadium-containing molecular sieves and their high catalytic activity in liquid phase selective oxidation reactions [22,23], vanadium-containing catalysts have rarely been employed in the ammoximation of ketones.

Amberlite is a “Gel”-type ion-exchange resin having styrene-divinylbenzene (DVB) framework composition [24]. We have prepared a vanadium resin catalyst by exchanging Na^+ sites of Amberlite IR 120 resin with VO^{2+} from aqueous $VOSO_4$ solution. Herein, we report this new and simple catalytic system for liquid phase ammoximation of cyclic ketones like cyclohexanone, cyclooctanone and cyclododecanone to their respective oximes. To the best of our knowledge this is the first report of ammoximation reaction of ketones using a vanadium-containing resin as catalyst. Resin catalysts are usually deactivated in repeated reactions, mainly owing to the decomposition of the organic (styrene-DVB) framework at higher temperature [25]. Efforts were thus made in order to develop regeneration method to enhance the catalyst life. By decreasing the reaction temperature we could suppress the decomposition of V-resin and H_2O_2 . Hence the reaction temperature was kept relatively mild (333 K). Amberlite IR 120 resin does not have a specific or true porosity, but intermolecular distances representing an apparent porosity of 4 nm or less is a sufficient dimension for the ions/molecules that can migrate through the gel structure to exchange sites [26] could be responsible for high catalytic activity.

2. Experimental

Strongly acidic cation exchange resin Amberlite IR 120 (hydrogen form, 16–50 mesh, Sigma–Aldrich), was soaked in a brine solution for 24 h, washed thoroughly with double distilled water

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and air dried. This has converted the H-form of the resin into Na-form, which was necessary to protect the acid catalyzed over oxidation of the substrates. One gram of this Na-form of the resin was then stirred with 10 millimolar aqueous solution of vanadium (IV) oxide sulphate hydrate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) for 12 h and then washed repeatedly with distilled water till the washings were free of vanadium. The vanadium-loaded resin thus obtained was air dried (hereafter designated as V-IR-120) and characterized thoroughly before carrying out the catalytic reactions. For the Fourier transform infrared (FTIR) measurement a Nicolet Magna IR 750 spectrometer Series II was used. UV–vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu 2401PC UV–vis spectrophotometer with an integrating sphere attachment using BaSO_4 as background standard. EPR spectra were acquired using a Varian EPR spectrophotometer equipped with manual data acquisition. Typical EPR spectral parameters were: X-band frequency = 9.45 GHz, modulation amplitude = 3.2×10 G and modulation frequency = 100 kHz. A Shimadzu AA-6300 double beam atomic absorption spectrophotometer (AAS) was used for wet chemical analysis. Liquid phase ammoxidation reactions were carried out in a two-necked round bottom flask fitted with a water condenser and stirred at 333 K. Hydrogen peroxide (30% w/v) and ammonia (25% aqueous) were added immediately after the substrate and catalyst were taken in *t*-butanol. To keep the reaction mixture saturated with peroxide and ammonia during the entire period of reaction and also to assure H_2O_2 economy and considering the fact that ammonia is highly volatile, H_2O_2 and NH_3 were added periodically and during this addition the visible color change of the reaction was pragmatic. During the periodic addition of H_2O_2 in the reaction mixture the color of the catalyst changed from green to orange and after the consumption of H_2O_2 the catalyst regained its original green color. At the start of the reaction 20% each of the total H_2O_2 and NH_3 used for the reaction was added. Thereafter 10% H_2O_2 and NH_3 was added at one hour intervals. Thus the addition of H_2O_2 and NH_3 was continued until 9 h. Aliquots of the reaction mixture were withdrawn at various time intervals and the products were analyzed by using Agilent 6890A gas chromatograph fitted with HP-1 (polar) capillary column and FID. GC analysis conditions were: initial temperature 353 K, initial time 4 min, program rate $5^\circ/\text{min}$, final temperature 493 K and final time 10 min.

3. Results and discussion

In Fig. 1, UV–vis DRS spectrum of the pure Amberlite IR 120 resin (Fig. 1a), V-IR-120 (Fig. 1b) and vanadium-loaded resin in the presence of H_2O_2 (V-IR-120- H_2O_2 , Fig. 1c) are shown. The broad absorbance in the region of 700–800 nm may be assigned to the overlapping of d_{xy} to d_{xz} and d_{xy} to $d_{x^2-y^2}$ transitions of the vanadium species [27]. Strong bands observed in the UV region at 236, 265 and 340 nm for all the samples are characterized as π – π^* charge transfer transitions originating from styrene-DVB moieties present in the resin. After the addition of H_2O_2 the dark green vanadium-loaded resin change its color to orange, which is also evidenced in its UV–vis spectra (Fig. 1b and c), showing two new bands in the region near 390 and 450 nm and this may be attributed to the formation of hydroperoxo vanadium species and corresponding LMCT transition after the addition of H_2O_2 [28,29]. However,

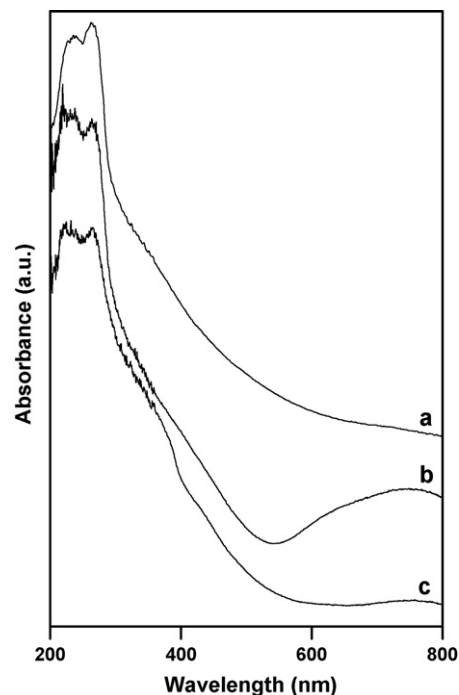


Fig. 1. UV–vis diffuse reflectance spectra of IR-120 (a), V-IR-120 (b) and V-IR-120- H_2O_2 (c).

because of overlap of this band by the adsorption of the resin itself in the range of 200–400 nm, it is hard to assign the adsorption of the species developed by the addition of H_2O_2 (Fig. 1b and c). In general orange red colored oxoperoxovanadates (V) are synthesized by reacting vanadyl salts (IV) with H_2O_2 [30]. V-IR-120 and V-IR-120- H_2O_2 absorbs red and blue light, respectively, and thus they are green and orange in color (complementary to the absorption). This oxoperoxo vanadium (V) species oxidizes the substrates and itself reverts back to vanadium (IV) and thus after the consumption of H_2O_2 the catalyst became dark green again. In this process the substrates consume H_2O_2 to get converted into their respective oximes. Atomic absorption spectroscopic (AAS) method was employed for the chemical analysis of V-IR-120. The solution for AAS analysis was prepared by eluting the vanadium-loaded resin with 30% HCl (general method of resin regeneration). The AAS data indicated 1.13 wt% vanadium loading over this Amberlite IR 120 resin. The ion-exchange capacity of the resin (due to ionic $-\text{SO}_3\text{Na}$ groups) was $1.9 \text{ mequiv g}^{-1}$. Thus most of the exchange sites at the resin surface have been occupied by the VO^{2+} centers (two $-\text{SO}_3^-$ centers are balanced by one VO^{2+} center), which can be effective for the liquid phase catalytic reactions. The FTIR spectrum of both the vanadium-loaded green colored resin and the hydrogen peroxide reacted orange colored resin shows the $\nu \text{ V=O}$ at 1004 cm^{-1} indicating the presence of oxovanadyl species in both the form [31].

EPR spectral data on V-IR-120 samples before and after the catalytic reaction is shown in Table 1, which again confirms the loading of the vanadium over the resin. The representative spectra are shown in Fig. 2. The EPR spectra of fresh catalyst and the oxidant treated catalyst display axial EPR spectra at room temperature

Table 1
EPR parameters (g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp}) obtained for the fresh and used V-IR-120.^a

Catalyst	g_{\parallel}	g_{\perp}	$A_{\parallel}/10^{-4} \text{ cm}^{-1}$	$A_{\perp}/10^{-4} \text{ cm}^{-1}$	g_{av}	A_{av}
Before H_2O_2 addition	1.977	1.952	102.5	24.5	1.96	50.5
After H_2O_2 addition	1.962	1.431	130	22.3	1.61	58.2

^a Experimental errors are: $\Delta g \pm 0.002$, $\Delta A \pm 3 \times 10^{-4} \text{ cm}^{-1}$, $g_{\text{av}} = 1/3[2g_{\perp} + g_{\parallel}]$, $A_{\text{av}} = 1/3[2A_{\perp} + A_{\parallel}]$.

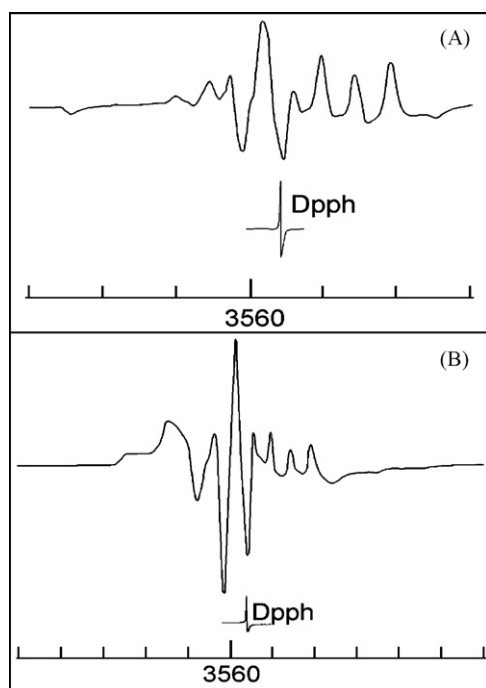


Fig. 2. Room temperature EPR spectra of V-IR-120 (a) and V-IR-120-H₂O₂ (b).

with well-resolved eight ⁵¹V ($I=7/2$) hyperfine lines [32–35]. This result indicates the presence of V⁴⁺ species in V-IR-120 and V-IR-120-H₂O₂ samples. In Table 1 various EPR signal parameters are shown. The $g_{\parallel} > g_{\perp}$ and $A_{\parallel} > A_{\perp}$ relationships suggest the presence of axially compressed d_{xy} configuration.

Table 2 presents the data of the results on liquid phase ammoximation of cyclohexanone, cyclooctanone and cyclododecanone over the V-IR-120 catalyst. As seen from this table that cyclohexanone oxime, cyclooctanone oxime and cyclododecanone oxime, respectively were obtained as major products (selectivity 75–82%). In Fig. 3 conversions of various ketones to their respective oximes are plotted at different reaction times. Among these substrates cyclohexanone showed maximum reactivity. The reactivity of these ketones follows the order cyclohexanone > cyclooctanone > cyclododecanone. Titanium-containing organic–inorganic hybrid mesoporous silica also followed the same order [6]. The color of the reaction products in all the cases were dark red to brown

Table 2
Ammoximation of cyclic ketones.^a

Entry	Substrate	Conversion (%)	Product selectivity (%)		TOF ^c
			Oxime	Other products ^b	
1	Cyclohexanone	81.3	79.4	20.6	18.7
2	Cyclooctanone	56.1	75.3	24.7	10.0
3	Cyclododecanone	42.1	81.6	18.4	5.2
4	Cyclohexanone ^d	1.2	47.4	52.6	–
5	Cyclohexanone ^e	77.1	77.5	22.5	17.3
6	Cyclooctanone ^e	55.2	75.2	24.8	9.8
7	Cyclododecanone ^e	41.3	81.4	18.6	5.1
8	Cyclohexanone ^f	86.5	86.8	13.2	7.4

^a Catalyst = 0.1 g (1.13 wt% V), substrate = 0.5 g (q moles), H₂O₂ = $q \times 1.2$ moles, NH₃ = $q \times 2.5$ moles, solvent (t -butanol) = 6 ml, temperature = 333 K, reaction time = 10 h.

^b Cyclic amides mostly obtained as byproduct.

^c TOF = moles of ketone converted per mole of V per h.

^d Blank reaction in absence of any catalyst.

^e After the second catalytic reaction, the catalyst was filtered, washed thoroughly with t -butanol and then dried under vacuum and then reused for the third cycle.

^f TS-1 (2.86 wt% Ti) was used as catalyst.

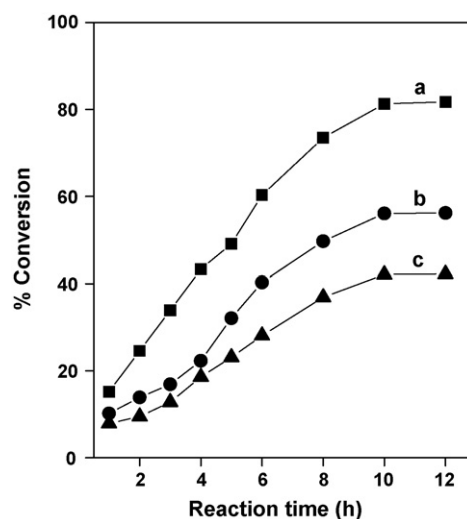


Fig. 3. Conversions of cyclohexanone (a), cyclooctanone (b) and cyclododecanone (c) at different reaction time.

suggesting the possibility of the formation of large molecular conjugated byproducts [36–38]. V⁴⁺ heterogenized over the resin surface [26,39–42] can generate Lewis acid sites, which may be responsible for this further rearrangement reaction of oxime. A blank reaction in absence of any catalyst in the ammoximation of cyclohexanone resulted almost no reaction (Table 2, entry 4). V-IR-120 catalyst after the ammoximation of cyclohexanone was filtered washed with t -butanol and dried under vacuum. This catalyst was used in a repeated run (Table 2, entries 5–7) and we observed very little loss in catalytic activity for these recycled catalyst (Fig. 4). This result suggested that our V-resin could be an efficient catalyst for repeated reaction cycles. A reference TS-1 (Si/Ti = 27.2, Ti = 2.85 wt%) was used in the ammoximation of cyclohexanone under identical reaction condition and we observed 86.5% ketone conversion and 86.8% oxime selectivity after 10 h reaction time. Observed TOF for TS-1 was much lower than that for V-IR-120 (Table 2, entry 8). Resin does not have true porosity and thus it is presumed that here the reactivity of V-resin catalyst is due to surface activity. Although the selectivity for oximes in this case is little lower than that of the TS-1 but the TOF is appreciatively high. The TOF values for the ammoximation of all three cyclic ketones were very high, suggesting high efficiency of V-IR-120 under liquid phase conditions.

In the presence of H₂O₂ and ammonia, V-IR-120 either catalyzes the formation of hydroxylamine from ammonia through N–H bond

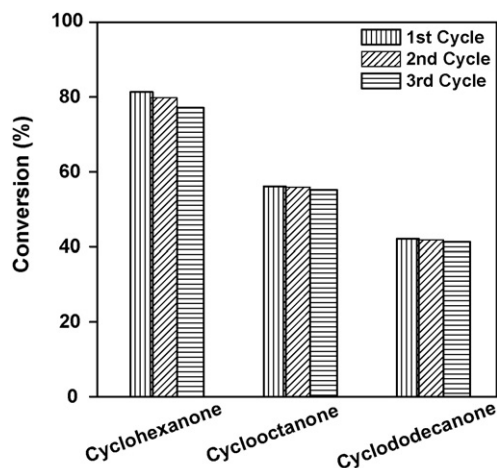


Fig. 4. Recyclability chart of V-IR-120 over different substrates.

oxidation, which could react with the ketones to give respective oximes. Otherwise it oxidizes the imine formed between the reaction of ketone and ammonia to its respective oxime. In either case one molecule each of H_2O_2 and NH_3 are necessary for the conversion of a molecule of the ketone to its corresponding oxime. It is pertinent to mention here that high cation exchange site of the resin matrix plays crucial role for the catalyst support. High cation exchange capacity of Amberlite IR 120 helps to immobilize large amount of active V^{4+} species and provide a favorable environment to stabilize the hydroperoxo species in V-IR-120- H_2O_2 . After the completion of the cyclohexanone ammoximation, we have measured the amount of H_2O_2 left after the reactions through titration and could not find any undecomposed H_2O_2 in the reaction mixture. Since we have used little excess of H_2O_2 in the reaction mixture, disappearance of H_2O_2 could be due to its decomposition of the unreacted H_2O_2 molecules at the elevated reaction temperature. However, for the ammoximation of cyclooctanone and cyclododecanone their were some undecomposed H_2O_2 in the reaction mixture after the reaction and the catalyst remained orange after reaching maximum conversion levels for the respective reactions. We have carried out the ammoximation of cyclohexanone, cyclooctanone and cyclododecanone for three repeating cycles and results are shown as bar diagram in Fig. 4. As seen from this diagram that V-IR-120 catalyst has retained its initial activity for three repeating cycles during ammoximation of these cyclic ketones. Thus our experimental results suggested that vanadium exchanged resin is a very efficient environment friendly catalyst for the ammoximation of cyclic ketones to their respective oximes.

4. Conclusion

In conclusion, we describe herein a new and very efficient catalytic system, V-resin through simple cation exchange by VO^{2+} on Amberlite IR 120 resin. Spectroscopic results suggested the immobilization of V(IV) in the resin matrix and generation of the active centers for the catalytic reaction. This V-resin showed excellent catalytic activity and selectivity in the ammoximation of cyclic ketones, e.g. cyclohexanone, cyclooctanone and cyclododecanone to their respective oximes under green and mild liquid phase condition in the presence of H_2O_2 and NH_3 as oxidant and reagent, respectively. Simply by observing the change in the color of the V-resin catalyst during reaction, the consumption of H_2O_2 in the reactions can be monitored. Catalyst can be easily separated from the reaction mixture and reused without much loss in catalytic activity. This simple and versatile method for the preparation of this very active ammoximation catalyst and eco-friendly liquid phase oxidation reaction conditions may be widely applicable for the synthesis of value added fine chemicals.

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