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# Highly selective and direct oxidation of cyclohexane to cyclohexanone over vanadium exchanged NaY at room temperature under solvent-free conditions

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## ABSTRACT

Vanadium exchanged zeolite Y has been synthesized by simple ion-exchange on NaY and resulting V–Y material has been employed as a heterogeneous catalyst for highly selective and direct one-pot liquid phase oxidation of cyclohexane to cyclohexanone under solvent-free conditions at room temperature. The catalyst (V–Y) has been thoroughly characterized by powder X-ray diffraction (PXRD), $N_2$ sorption, transmission electron microscopic (TEM), Fourier transform infrared (FT IR), UV–visible, X-ray photoelectron spectroscopic (XPS) and atomic absorption spectroscopic (AAS) analyses. The selective oxidation reaction proceeds smoothly over this V-containing heterogeneous catalyst in the presence of *tert*-butylhydroperoxide (TBHP) as oxidant and the progress of the reaction has been monitored thoroughly by gas chromatographic (GC) and gas chromatography coupled with mass spectrometric (GC–MS) analyses. The recycling efficiency of the V–Y catalyst has been tested by conducting the catalytic reaction repeatedly with the recovered catalyst, where almost retention of the original catalytic activity and selectivity after five reaction cycles has been observed. The effect of oxidant amounts on the catalytic reaction has been studied. Mechanistic pathway for the catalytic reaction over this inexpensive, non-air sensitive, eco-friendly and reusable vanadium exchanged zeolite has been proposed, suggesting future potential of V–Y in solvent-free liquid phase selective oxidation reactions under very mild conditions.

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## 1. Introduction

Saturated hydrocarbons like *n*-hexane, cyclohexane etc. can be catalytically converted to a mixture of aliphatic and aromatic fine chemicals through a wide variety of chemical reactions [1], but it's very challenging to oxidize them selectively into a value added chemicals in a controlled fashion under mild reaction conditions [2–4]. Selective liquid phase oxidation of cyclohexane to cyclohexanone via activation of relatively inert C—H bond is a very important reaction in chemical industry. Because, a great majority of cyclohexanone combined with cyclohexanol (a mixture called 'KA oil', K = ketone, A = alcohol) is consumed for synthesis of ε-caprolactam and the remaining portion is supplied for the preparation of adipic acid, both of which are employed as important precursors for the manufacturing nylon 6 and nylon 6,6 polymers [5]. Conventionally, cyclohexanone is produced in homogeneous medium from the aerobic oxidation of cyclohexane at elevated temperature (423–433 K) and high pressure (1–2 MPa) using cobalt or metal–boric acid catalysts [6]. But this process suffers from the disadvantages like low conversion, poor selectivity toward main products, catalyst separation and environmental hazards [7]. Reactions carried out in heterogeneous media in the presence of Co, Fe-based catalysts give lower yield of the main products or require involvement of toxic solvents [8], which are environmentally not acceptable.

In recent times a wide range of catalytic processes have been developed globally for the environment benign green synthesis of cyclohexanone over different heterogeneous catalysts [9,10]. A solvent-free high temperature oxidation of cyclohexane using 1.0 MPa $O_2$ pressure over transition metal containing ZSM-5 catalyst has been reported by Yuan et al., where the total conversion does not exceed 10 mol% even after using *tert*-butylhydroperoxide

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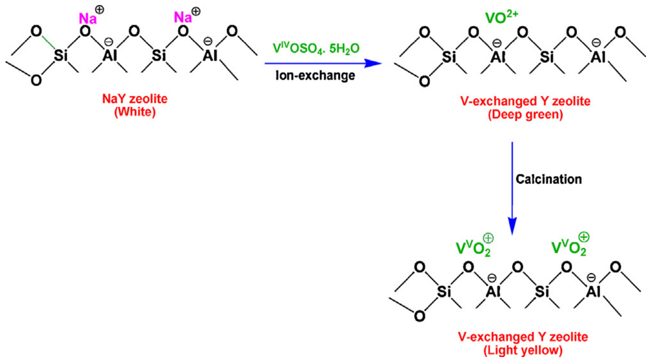
(TBHP) as initiator [11]. Similar attempts have also been made using Au/MgO [12], Cu-supported SBA-15 [13], gold C-scorpionate complexes [14], Au nanoparticle supported silica [15], Ce/AlPO-5 [16], Bi-SBA-15 [17], etc. in the presence of peroxides or under $O_2$ pressure for selective oxidation of cyclohexane. Hattori et al. have reported a green pathway for cyclohexane oxidation via photo-induced reaction over reactive Fe/$TiO_2$ catalyst [10]. Similarly, Shiraishi et al. have reported the photocatalytic oxidation of cyclohexane with molecular oxygen over $WO_3$ loaded with Pt nanoparticles under irradiation of visible light, which leads to mixture of cyclohexananol and cyclohexanone [18]. However, most of these methods neither require high temperature nor bear a significantly low conversion level of cyclohexane. In this context, remarkably high catalytic conversion (>80%) of cyclohexane together with high selectivity for ketone product has been observed by Sarkar et al. who have performed the reaction at room temperature using Cu nanocluster supported over $Cr_2O_3$ [19]. But they could not avoid considerable amount of cyclohexanol along with the main ketone product and involvement of organic solvent in this partial oxidation reaction. On the other hand, we have observed high selectivity for cyclohexanol in the catalytic oxidation of cyclohexane over Cr-MCM-41 under liquid phase reaction conditions using TBHP as oxidant [20]. Hence, a suitable environment friendly microporous/mesoporous catalyst is very demanding, which can work efficiently under solvent-free conditions in the selective catalytic transformation of cyclohexane to cyclohexanone at room temperature.

Microporous zeolites, which bear cation exchange sites in the crystalline alumnosilicate frameworks can be the ideal host to carry out liquid phase catalytic reactions under environment friendly conditions [21–24]. Thus, keeping all these developments in mind we have synthesized vanadium exchanged NaY zeolite material, which could act as an efficient catalyst for the liquid phase oxidation reactions under very mild conditions. There are number of successful reports on liquid phase oxidation of cyclohexane over V-based catalysts, which require relatively severe reaction conditions [25]. Due to high oxidizing property of 3*d* transition elements, when they are loaded in the aluminosilicate framework of NaY zeolites they can often employed in the liquid phase oxidation reaction [26]. V-containing materials especially showed excellent catalytic properties for various critical oxidation reactions, like hydroxylation of benzene to phenol [27], functionalization of *n*-butane to maleic anhydride [28], etc. Zeolitic framework being highly stable, inexpensive, non-corrosive, environment friendly and have inherent ability for high product selectivity could be employed as good support for different heteroelements [29,30]. Thus, when the vanadyl cation has been exchanged for Na in NaY the resulting material can serve as efficient heterogeneous catalyst for hydrocarbon oxidation with very high K/A ratio. Herein, we report a very simple, environment friendly, highly selective and one-pot route for the oxidation of cyclohexane to cyclohexanone over V–Y zeolite. In addition, investigations have been carried out to understand the role of oxidant, catalyst amounts and porous solid supports for this highly selective conversion of cyclohexane to cyclohexanone. Further attempts are also made to test the recyclability of the catalyst and to check the probability of the leaching of $VO_2{}^+$-species from the catalyst surface.

## 2. Experimental

### 2.1. Materials used

NaY zeolite and $VO SO_4{\cdot}5H_2O$ used for preparation of the catalyst were purchased from Sigma-Aldrich and Loba Chemie (India), respectively. Cyclohexane (Sigma-Aldrich) and TBHP (5.0–6.0 M in decane, Sigma-Aldrich) were used as substrate and oxidizing agent, respectively. All the chemicals were used without further purification.



**Scheme 1.** Schematic representation depicting the formation of V-exchanged Y zeolite (V–Y).

### 2.2. Catalyst synthesis

$VO_2{}^+$-exchanged NaY zeolite (designated as V–Y) was prepared exchanging the $Na^+$ ions of NaY by V(IV) ions via aqueous ion-exchange method followed by calcination in air. First, NaY was activated by heating at 773 K in air for 6 h. In a typical synthesis, 10.0 mmol of $VOSO_4{\cdot}5H_2O$ was dissolved in 30 ml of distilled water followed by addition of 1.0 g activated NaY. Then this mixture was stirred at 363 K for 24 h during which the color of the mixture changed from blue to deep green. Then the reaction mixture was cooled to room temperature, filtered and washed thoroughly with hot distilled water till the filtrate became colorless. This ion-exchange process was repeated twice more to get higher loading of vanadium into zeolite Y. The material thus obtained was dried at 373 K in air for overnight and finally heated at 773 K for about 4 h to get yellow vanadium-exchanged material V–Y. A simple schematic representation of formation of V–Y catalyst is shown in Scheme 1.

### 2.3. Physicochemical characterizations

Powder X-ray diffraction (PXRD) patterns of the vanadium exchanged NaY zeolite as well as NaY were recorded by a Bruker AXS D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current, calibrated with a standard silicon sample using Ni-filtered Cu-*K*α ($\lambda = 0.15406$ nm) radiation. The diffraction data was collected in a $2\theta$ range of 5–60° with scan rate and step size of $0.1^\circ\,s^{-1}$ and $0.02^\circ$ $step^{-1}$, respectively. BET surface areas of the parent zeolite and V-exchanged samples were measured from nitrogen adsorption/desorption isotherms obtained by using a Quantachrome Autosorb 1C instrument at 77 K temperature. Prior to gas adsorption, the sample was degassed for 5 h at 413 K. Total pore volume was estimated from the $N_2$ uptake at the relative pressure of $P/P_0 = 0.99$. UV–visible diffuse reflectance spectra (DRS) were obtained by using a Shimadzu UV 2401PC spectrophotometer with an integrating sphere attachment; a $BaSO_4$ pellet was used as background standard and analysis was done with solid sample in the wavelength range of 200–800 nm at room temperature (303 K). A Perkin-Elmer 3100 atomic absorption spectrometer was used to measure the percentage of vanadium in our catalyst. For this chemical analysis the material was digested with $H_2SO_4$, HF and few drops of $H_2O_2$ and then dissolved in water to prepare an aqueous solution of V–Y. Fourier transform infrared (FT IR) spectra of the samples were recorded at room temperature on KBr pellets by using a Perkin Elmer Spectrum BX FT IR spectrophotometer. X-ray photoelectron spectroscopic (XPS) analysis of V–Y was performed on an Omicron nanotech system operated at 15 kV and 20 mA with

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