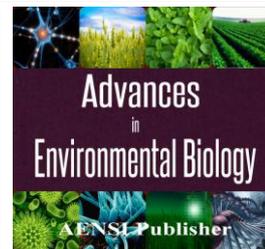




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Catalytic Activity of Nano-Sized γ -Alumina Supported Vanadium Oxide Toward the Oxidation of Cyclohexane using *tert*-butylhydroperoxide and Hydrogen Peroxide

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ABSTRACT

Vanadium oxides supported on nano γ -alumina were synthesized and were well characterized. Catalytic activities of the supported vanadium oxides for oxidation of cyclohexane to cyclohexanol and cyclohexanone with *tert*-butylhydroperoxide (TBHP) and H₂O₂ as the oxidant in the liquid phase were considered. For the V₂O₅/nano- γ -alumina catalysts, acetonitrile as the solvent was employed. The products of the catalysis are cyclohexanone and cyclohexanol. The conversion percent of cyclohexane depended on oxidant and the catalyst. TBHP was found to be better oxidant than H₂O₂ since minimal destruction of the catalyst and higher conversion of cyclohexane were observed when this oxidant was employed. Under these reaction conditions, the order of catalytic activities is as follows: 5%V₂O₅/ γ -alumina > 7.5%V₂O₅/ γ -alumina > 2.5%V₂O₅/ γ -alumina. With 5%V₂O₅ supported on γ -alumina and under our experimental conditions, the conversion percent of cyclohexane is 13.98%.

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INTRODUCTION

The partial selective oxidation of hydrocarbons is a major goal of today's research in catalysis as selectively oxidized hydrocarbons can be used as feedstock for the preparation of fine chemicals [1,2]. Among various alkanes oxidation, partial oxidation of cyclohexane to cyclohexanol and cyclohexanone, the intermediates in manufacturing nylon-6 or nylon-6, 6, have attracted commercial interest [3]. The present industrial process for cyclohexane oxidation is carried out around 150 °C and 1-2 MPa pressure under homogeneous reaction condition that results in the conversion of less than 6% and selectivity of cyclohexanol and cyclohexanone of around 80% over metal cobalt salt or metal-boric acid. Because of the relatively harsh condition and limited conversion, scientists have been trying to improve conversion of cyclohexane to desired products since the 1960s [4-12].

Supported vanadium oxide catalysts are frequently used as catalysts in partial oxidation reactions [13-15]. In these catalysts, Al₂O₃, TiO₂, SiO₂ and ZrO₂ are commonly used as the supports. Bulk oxides in general cannot be used in industrial processes as they impart poor thermal stability that lead to fast deactivation of the catalyst. Furthermore, it is also known that bulk V₂O₅ leads to high combustion of organic molecules to carbon oxides [16]. Makgwane *et al.* [17] have studied the oxidation of cyclohexane with H₂O₂ in the presence of hetero-mixed tungsten – vanadia (WO₃/V₂O₅) as catalyst. In another report Baoshan Li and coworkers have employed V-MCM-41 with high content of vanadium in the framework for selective oxidation of cyclohexane with H₂O₂ as oxidant. The V-MCM-41 samples exhibited excellent catalytic performance of up to 22.57% cyclohexane conversion and 99.53% selectivity for cyclohexanone and cyclohexanol in the cyclohexane oxidation [18]. However, to the best of our knowledge, there is no report for application of V₂O₅ supported on γ -alumina for partial oxidation of cyclohexane with H₂O₂ and TBHP. In this work we report V₂O₅ supported on γ -alumina as catalysts for partial oxidation of cyclohexane to cyclohexanol and cyclohexanone in the liquid phase.

*Experimental:**Instrument and reagents:*

FT-IR spectra were performed on a Bomem MB102 model in KBr plates. Powder X-ray diffractions were performed by a Siemens D 5000. Specific surface area was measured by BET techniques in liquid N₂ temperature by a Strohlien. The surface morphology of the samples was obtained using a Jeol-JSM-5610 LV scanning electron microscopes (SEM). Products were analyzed by a GC, Shimadzu 8A, using authentic samples equipped with a TCD detector using OV-17, Propak-N, packed (2 m) columns and He as the carrier gas. GC-MS analysis of the products was performed with GC-MS model of Thermoquest-Finnigan Trace, equipped with a DB-1 fused silica column (with a length of 60 m and internal diameter of 0.25 mm and film thickness of 0.25 μm) with Helium as the carrier gas. All the reagents were commercial grade obtained from Merck. None of the oxidation products were found in the cyclohexane before the oxidation reaction.

Preparation of the catalysts:

Aluminum nitrate {Al(NO₃)₃.9H₂O}, aqueous ammonia {NH₃.H₂O} and deionized water were used as starting chemicals. Two hundred milliliters of deionized water was taken in a 2 l capacity round-bottom flask and stirred well using magnetic stirrer. Then, aluminum nitrate (1.5 M) solution and (12 M) solution of aqueous ammonia were added to 200 ml of deionized water drop by drop to precipitate Al cations in the form of hydroxides. The temperature was maintained ~50 °C during precipitation/digestion experiment. The pH after precipitation was found to be in the range of 6-6.5. The precipitates were further digested at 50 °C for 1 h. After the alumina gel was formed, it was filtered and washed by distilled water. Then aqueous solution of ammonium metavanadate was added to the alumina-gel. This gel was stirred and homogenized and was placed in an oven under temperature of 100 °C for 24 h. The mixture was then heated 2 °C/min till the temperature reached 500 °C and the mixture was kept at this temperature for 4 h.

Experimental procedure:

In a typical procedure, a mixture of 1.0 g catalyst, 25 ml solvent and 10 mmol cyclohexane was stirred under nitrogen in a 50 ml round bottom flask equipped with a condenser and a dropping funnel at room temperature for 30 min. Then 16 mmol of TBHP (solution 80% in di-*tert*-butylperoxide) or H₂O₂ (30% in H₂O) was added as oxidizing reagents. The resulting mixture was then refluxed for 8 h under N₂ atmosphere. After filtration, the solid was washed with solvent and then the reaction mixture was analyzed by GC. Products identification was done with GC-MS and confirmed by comparison of their retention times with authentic commercial samples of these compounds.

RESULTS AND DISCUSSIONS

Characterization of the catalysts:

The IR spectrum of pure V₂O₅ gives sharp bands at 1020 and 831 cm⁻¹, which are due to the V=O stretching and V-O-V deformation modes of vanadium oxide, respectively. IR spectra of catalysts supported V₂O₅ reveal a very weak band at 1020 cm⁻¹, which is associated with V₂O₅ species on the alumina surface. Therefore, these spectra confirm formation of V₂O₅ in the alumina matrix. The peak observed at 3400 to 3500 cm⁻¹ can be related to Al-OH stretching vibrations.

The XRD pattern presented in Figure 1 indicates that γ-alumina is formed. There is no significant change in the XRD pattern with 5 wt.% V₂O₅ supported on γ-alumina which confirms that V₂O₅ dispersed through pores does not change the γ-alumina structure.

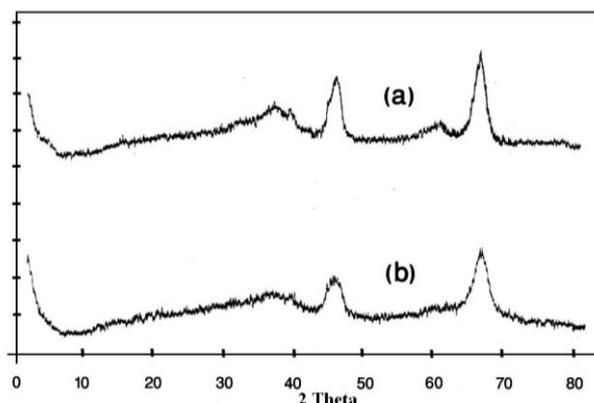


Fig. 1: XRD patterns of (a) γ-alumina, and (b) 5 wt.% V₂O₅/γ-alumina.

Scanning electron micrograph (SEM) of a typical sample of 5 wt.% V_2O_5 supported on γ -alumina is shown in Figure 2. It is clarified that the sizes of the particles are in the ranges of 30-45 nm. This result was coincident with the particle sizes calculated from the Scherrer equation.

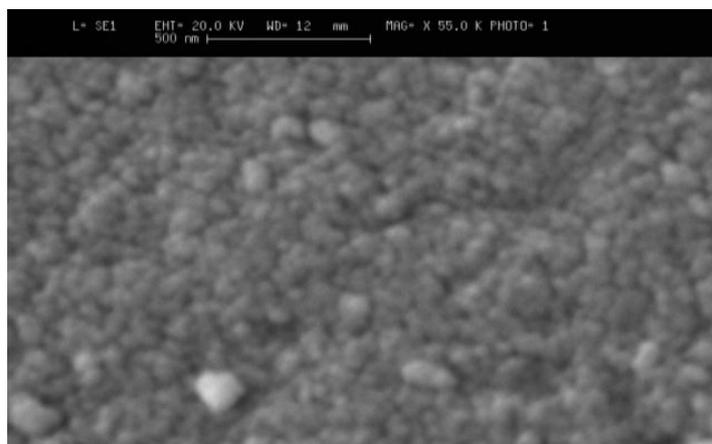


Fig. 2: SEM photograph of 5 wt.% V_2O_5/γ -alumina.

Specific surface area measured with BET method was $210 \text{ m}^2/\text{g}$ for γ -alumina and $175 \text{ m}^2/\text{g}$ for 5 wt.% V_2O_5/γ -alumina. This reduction in specific surface area for the supported V_2O_5 may be an indication of encapsulation of V_2O_5 in the γ -alumina pores.

Catalytic oxidation of cyclohexane:

The use of TBHP as an oxidant was based on the earlier studies on the oxidation of cyclohexane [19], this oxidant was found to cause minimal destruction of the vanadium oxide catalyst, and to give better selectivity of the products. For comparative purposes, H_2O_2 was also employed as an oxidant. The solvent of acetonitrile was employed for the catalysis, since all the reagents dissolved and gave the highest yields of the products.

The performance of the set of samples prepared as heterogeneous catalysts for the oxidation of cyclohexane was tested using hydrogen peroxide and *tert*-butylhydroperoxide as oxidizing reagents (Table 1). In all the cases the only products observed were cyclohexanol and cyclohexanone. In the presence of 5 wt.% V_2O_5/γ -alumina, conversion percentage of cyclohexane was 13.98% with TBHP as an oxidant. Contrastive experiment result show that cyclohexane oxidation with TBHP and H_2O_2 did not occur in the absence of the catalyst under the same reaction condition. This indicated that vanadium oxide supported on γ -alumina acted catalysis during cyclohexane oxidation.

To investigate the catalytic power of reused vanadium oxides supported on γ -alumina, the catalyst used in each catalytic oxidation was isolated from the reaction mixture for reuse later. The experimental results showed that vanadium oxides supported on γ -alumina could be reused several times. These results proved that vanadium oxides supported on γ -alumina possessed good reusable catalysis.

Table 1: Results of the cyclohexane oxidation using $V_2O_5/\text{nano-}\gamma$ -alumina as catalysts

Product selectivity (%)		Conversion C_6H_{12} (%)	Oxidant	Catalyst
Cyclohexanone	Cyclohexanol			
57	43	9.37	TBHP	2.5% V_2O_5/γ -alumina
39	61	7.18	H_2O_2	2.5% V_2O_5/γ -alumina
56	44	13.98	TBHP	5% V_2O_5/γ -alumina
41	59	10.54	H_2O_2	5% V_2O_5/γ -alumina
55	45	11.93	TBHP	7.5% V_2O_5/γ -alumina
38	62	8.98	H_2O_2	7.5% V_2O_5/γ -alumina
63	37	1.22	TBHP	γ -alumina
46	54	0.83	H_2O_2	γ -alumina

Reaction condition: 1.0 g catalyst, cyclohexane 10 mmol, oxidant 16 mmol, solvent of acetonitrile, reflux temperature, reaction time 8 h, $\text{Conver.} = (\text{mole of cyclohexane reacted}/\text{moles of cyclohexane in the feed}) \times 100$. $\text{Selec.}i = (\text{moles of cyclohexane converted to } i/\text{moles of cyclohexane reacted}) \times 100$.

Influences of reaction time on cyclohexane oxidation reaction:

In this experiment, the change in conversion (%) of cyclohexane in the presence of TBHP oxidant and 5% $V_2O_5/\text{nano-}\gamma$ -alumina catalyst was monitored and plotted with respect to time (Figure 3). The reaction was carried out at reflux temperature for 8 h with 1.0 g catalyst and 10 mmol cyclohexane and 16 mmol TBHP in a

round bottom flask and some samples was drawn out at regular intervals and analyzed by GC. Figure 3 shows that the conversion of cyclohexane increases continuously until 13.9% as time increases and then remains constant after 7 h, therefore duration about 7-8 h is proper reaction time.

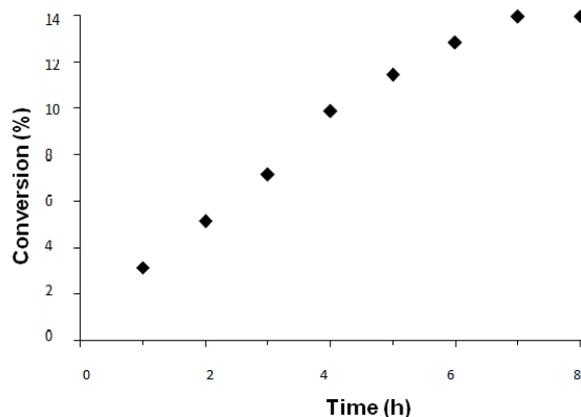


Fig. 3: The effect of reaction time on cyclohexane conversion. Reaction condition: 1.0 g 5% V_2O_5 /nano- γ -alumina catalyst, cyclohexane 10 mmol, TBHP 16 mmol, reflux temperature.

Influences of the loading amount of vanadium oxide on cyclohexane oxidation reaction:

For investigation of the loading effect V_2O_5 on the conversion and selectivity of the products three catalysts were tested. In Table 1, details of the conversion and selectivity of the products for each catalyst are shown. It is observed that maximum conversion and selectivity for cyclohexanol and cyclohexanone occurs with the catalyst of 5 wt.% V_2O_5 . It is known that vanadium oxide can be highly dispersed on γ -alumina at low loading (5 wt.%) and stabilized as isolated VO_4 species [20, 21]. Gao and Wachs [20] reported that polymerized VO_4 species appeared at 7.0 wt.% loading and increased with an increase in V_2O_5 loading. A drop of conversion and selectivity for cyclohexanol and cyclohexanone of the catalyst with higher loadings than 5 wt.% would be attributed to the polymerization of VO_4 species. In the present reaction with the catalyst of 5 wt.% V_2O_5 , we conclude that highly dispersed VO_4 species over γ -alumina is the active species.

Under these reaction conditions, the order of catalytic activities is as follows: 5% V_2O_5 / γ -alumina > 7.5% V_2O_5 / γ -alumina > 2.5% V_2O_5 / γ -alumina.

Influences of oxidant type on cyclohexane oxidation reaction:

Figure 4 shows that the reactivity of the cyclohexane toward oxidation with TBHP and H_2O_2 on vanadium oxides supported on nano- γ -alumina catalysts depend on type of oxidant. *tert*-Butylhydroperoxide was found to be a more convenient oxidizing reagent due to weaker O-O bond than hydrogen peroxide. In this regard, it is worth noting that using H_2O_2 as reactant the complexes (both encapsulated and unsupported V_2O_5) lose their characteristic color during the course of the reaction. IR spectroscopy of the recovered catalysts evidenced the degradation of the vanadium oxides. This behavior contrasts with that of TBHP which does not produce decomposition of the vanadium oxides as assessed by IR spectra at the end of the reaction.

Similar IR spectra were obtained for the catalyst before and after the reaction test with TBHP and the result confirms that the catalyst is stable, decomposition of V_2O_5 was negligible and its reactivity was preserved.

Comparison of catalytic power of γ -alumina-supported V_2O_5 with that unsupported V_2O_5 :

The experimental data of cyclohexane oxidation catalyzed by the γ -alumina-supported vanadium oxide or unsupported vanadium oxide in the presence of TBHP oxidant shows that the partial oxidation of cyclohexane catalyzed by vanadium oxide supported on γ -alumina had better conversion than that of unsupported vanadium oxide. When V_2O_5 supported on γ -alumina was used as catalyst, the cyclohexane conversion was 13.98%. However, when the unsupported V_2O_5 was used as the catalyst, the cyclohexane conversion was 8.37%. The result confirms the high stability of the vanadium oxide on the alumina surface or in the alumina cavities.

Conclusions:

The nano- γ -alumina encapsulated vanadium oxides, V_2O_5 /nano- γ -alumina, have been prepared and characterized. Catalytic activities of these catalysts have been tested for the partial oxidation of cyclohexane to cyclohexanone and cyclohexanol using TBHP as the oxidant, in the presence of acetonitrile solvent. A maximum of 13.98% conversion of cyclohexane has been achieved with 5 wt.% V_2O_5 /nano- γ -alumina using TBHP as the oxidant, where selectivity of cyclohexanone and cyclohexanol are 56% and 44% , respectively.

They are stable, reusable and can be easily separated after the reaction, which endow vanadium oxides supported on nano- γ -alumina with a bright future in industrial applications.

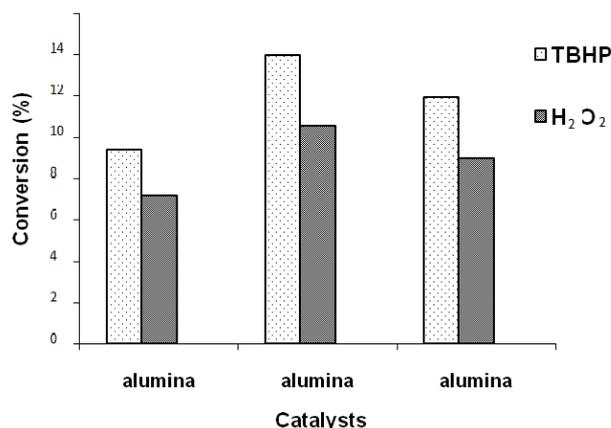


Fig. 4: The effect of oxidant type on cyclohexane conversion in the presence of various catalysts. Reaction condition: 1.0 g 5% V₂O₅/nano- γ -alumina catalyst, cyclohexane 10 mmol, oxidant 16 mmol, reflux temperature.

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