



Influence of surface and acid properties of vanadia supported on ceria promoted with rice husk silica on cyclohexanol decomposition

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Abstract

Cyclohexanol decomposition activity of supported vanadia catalysts is ascribed to the high surface area, total acidity and interaction between supported vanadia and the amorphous support. Among the supported catalysts, the effect of vanadia over various wt% V_2O_5 (2–10) loading indicates that the catalyst comprising of 6 wt% V_2O_5 exhibits higher acidity and decomposition activity. Structural characterization of the catalysts has been done by techniques like energy dispersive X-ray analysis, X-ray diffraction and BET surface area. Acidity of the catalysts has been measured by temperature programmed desorption using ammonia as a probe molecule and the results have been correlated with the activity of catalysts.

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1. Introduction

Decomposition of cyclohexanol is an important industrial process since the products obtained are used as raw materials for the manufacture of fine chemicals in chemical industry [1,2]. Besides, this reaction is considered as a test reaction for acid–base properties of solid catalysts as well as a model reaction to determine the catalytic activity of metal oxides [3–6]. It is generally accepted that the dehydration of cyclohexanol to cyclohexene occurs on acid sites, while dehydrogenation to cyclohexanone is associated with both acid/base and redox sites [7]. However, recent reports indicated that both acid and basic sites were responsible for the dehydration processes in the vapour phase conversion of alcohols [8,9]. Dehydrogenation activity over spinel type catalysts was suggested by the presence of both basic and redox properties [10]. Cyclohexanol decomposition on ceria catalysts has been reported [11]. Acid–base properties of metal oxides were dependent on number of variables such as metal salt, method of prep-

aration, precipitation agent, calcination temperature and the effect of promoters. Effect of a promoter in any reaction is to enhance the reaction rate with better product selectivity at lower temperatures [12]. Several metal oxides have been tested towards cyclohexanol decomposition reaction [13]. Stronger acid sites are found to be responsible for the formation of methylcyclopentenes through the secondary reaction of cyclohexene and aromatization of cyclohexanol produced phenol in small quantities [14].

Vanadia containing catalysts probably constitute the family of catalysts often used for partial and selective oxidation of organic compounds [15]. Ceria is best known for its redox property and oxygen storage capacity [16]. Silica is a well-known support and the application of silica as a catalyst support has been extensively studied to meet the demand for high melting point, high metal dispersion, higher thermal stability and surface area and consequently high activity [17]. The presence of silica in rice husk has been known since 1938. Instead of commonly used silica gel (SiO_2), rice husk ash has been first adopted as a catalyst support by Chang et al. and found to exhibit a very high activity for the rice husk ash supported nickel catalysts in CO_2 hydrogenation [18]. In this context, the preparation

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of catalysts utilizing rice husk silica, which is composed of extremely pure amorphous silica, is very relevant.

In the present work, we report the influence of acidity of vanadia supported on ceria promoted with rice husk silica during vapour phase decomposition of cyclohexanol. The effect of vanadia loading, reaction temperature and flow rate on the decomposition has also been investigated. Catalysts were characterized by various physico-chemical techniques. Acidity was measured by temperature programmed desorption using ammonia.

2. Experimental

Silica (RS) was prepared by burning acid treated (10% conc. HCl for 2 h at 100 °C) rice husk at 600 °C in a muffle furnace for 6 h. Rice husk silica promoted ceria (CRS, 1:1 mole ratio based on oxides) prepared by deposition precipitation in which, requisite quantities of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (IRE, Udyogamandal, Kerala) and silica were mixed together and precipitated by 1:1 NH_3 solution. To impregnate vanadia with loadings of various wt% V_2O_5 , the requisite quantity of ammonium metavanadate (CDH, LR) was dissolved (0.001 M) in aqueous oxalic acid solution (0.1 M) and to this, dried support was added and mechanically stirred for 6 h. After keeping overnight, the excess water was evaporated on a water bath. The resulting hydroxides were filtered, dried for 12 h at 110 °C and sieved to mesh size below 100 μm . All the systems were calcined at 500 °C for 5 h in a closed muffle furnace in flowing air prior to use. Supported catalysts are denoted as $x\text{VCRS}$ where $x = 2, 4, 6, 8$ and 10 wt% V_2O_5 and VCRS for $\text{V}_2\text{O}_5/\text{CeO}_2$ -rice husk silica.

The chemical composition of catalysts were obtained from Stereoscan 440 Cambridge, UK energy dispersive X-ray analyzer used in conjunction with SEM. Powder X-ray diffraction pattern collected on Rigaku D-Max Ni filtered with $\text{Cu K}\alpha$ radiation. BET surface area and total pore volume was determined by N_2 adsorption at 77 K on Micromeritics Flow Prep-060 Gemini 2360 instrument. Acidity measurements were performed by temperature programmed desorption (TPD) of ammonia using a conventional flow apparatus. In a typical experiment, about 500 mg of catalyst was activated at 500 °C for 1 h and kept in a tube. The sample was degassed by passage of nitrogen at 300 °C for 1 h. Subsequently, catalyst was saturated with pure anhydrous ammonia gas and the system was allowed to attain equilibrium. After 30 min, the excess and physisorbed ammonia was subsequently flushed with flowing nitrogen. TPD analysis was then carried out by desorption of ammonia from room temperature (RT) to 600 (°C) at a heating rate of 20 °C /minute in the nitrogen atmosphere and trapped in H_2SO_4 (0.025 N). The amount of ammonia desorbed is calculated by titrating against NaOH (0.025 N).

Vapour phase decomposition of cyclohexanol was carried out in a conventional fixed-bed, vertical, down-flow, silica reactor placed inside a double-zone furnace at atmospheric pressure. The temperature was controlled by an

externally wrapped heating wire. Cyclohexanol was introduced through a syringe after dilution with dried nitrogen (50 cm^3/min). About 500 mg of the catalyst was used for each run. The liquid products were collected after passing through a condenser with traps cooled with ice at different time intervals. Products collected after 2 h were analyzed on Chemito 1000 GC equipped with FID detector using a BP-1 capillary column. Analysis was done using a linear temperature programme (from 80 to 230 °C at 10 °C/ min), with injection and detection pot temperatures as 200 °C. The products obtained were identified by comparison with standards. The catalytic activity was expressed as the percentage conversion (wt%) of cyclohexanol and the selectivity for a product is expressed as the amount of the particular product divided by total amount of product, multiplied by 100.

3. Results and discussion

The chemical composition, BET surface area and pore volume and the crystallite size calculated by Scherrer formula from XRD data is presented in Table 1. Rice husk silica shows surface area of 224 $\text{m}^2 \text{g}^{-1}$. Silica contains 98.81 atom% Si from EDX analysis. The composition of Si in supported catalysts was found to be lowered as wt% of V_2O_5 loading increased. Upon silica promotion surface area and pore volume of ceria was increased. Incorporation of vanadia leads to a noticeable decrease in the specific surface area of the catalysts; such a decrease is more pronounced as the vanadia content is increased. This is mainly due to penetration of the dispersed vanadium oxide into the pores of the support and solid-state reactions between the dispersed vanadium oxide and the support may also contribute to the observed decrease in surface area [19]. However, the extent of decrease in surface area is lower in supported catalysts, suggesting that the degree of sintering can be reduced with high surface area support in amorphous form as evidenced from XRD pattern [20]. The X-ray reflections of ceria (Fig. 1(a)) were observed at $2\theta/^\circ \sim 28.32, 32.86, 47.34$ and 56.12 corresponding to a typical cubic crystal structure of fluorite type [21]. Silica obtained from rice husk is found to be X-ray amorphous with a broad diffraction peak around $2\theta/^\circ \sim 22$ [22]. Silica promoted ceria exhibits poor crystallinity with the diffraction lines due to ceria only is visible. For supported catalysts (Fig. 1(b)) intensity of diffraction peaks is found to be low due to the amorphous nature of support with appreciable changes in the shape and position of the peaks. Thus the presence of silica could maintain the amorphous character at high calcination temperature, which in turn can minimize the sintering of oxides, which is most responsible for the lowering of surface areas [23]. Crystallite size of silica promoted ceria is lowered and a small increase in crystallite size of ceria (Table 1) is observed as the weight percentage of vanadia loading increases. The result shows that vanadia can be fairly easily dispersed on the high surface area support for 2–10 wt% loading.

Table 1
Chemical composition and physical properties of catalysts

Catalyst	Composition (atom%)			BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Crystallite size (nm)
	Ce	Si	V			
Ce	100.00	–	–	67	0.11	12
RS	–	98.81	–	224	0.28	–
CS	55.18	44.82	–	102	0.27	10
2VCRS	39.06	54.88	6.09	94	0.26	8
4VCRS	41.32	52.34	6.34	90	0.25	9
6VCRS	38.29	53.43	8.28	76	0.18	11
8VCRS	43.67	44.79	11.25	66	0.14	12
10VCRS	43.02	40.29	16.70	52	0.15	10

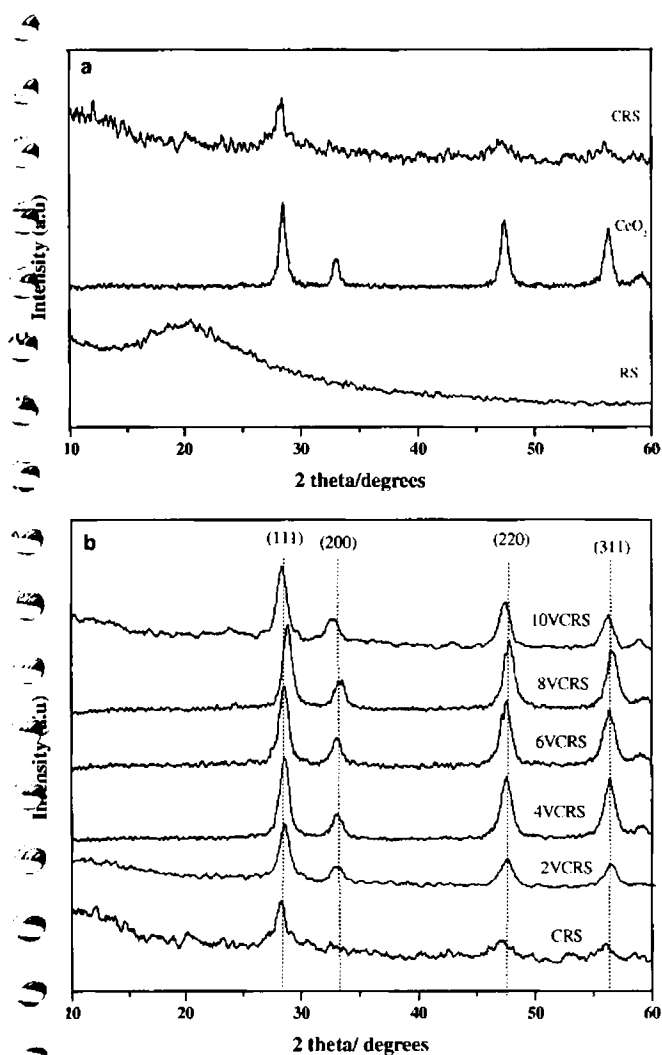


Fig. 1. X-ray diffraction pattern of: (a) supports and (b) supported vanadia catalysts.

Temperature programmed desorption (TPD) of probe molecules like ammonia or pyridine is a well-known method for the determination of acidity of solid heterogeneous catalysts as well as acid strength since it is easy and reproducible. Ammonia is used frequently as a probe molecule because of its small molecular size, stability and strong basic strength. Ammonia can be adsorbed on an oxide surface through hydrogen bonds or through

dipolar interaction yielding the total acidity of the system [24]. The acid strength distribution is classified depending on desorption temperature region. The total acidity measurements carried out by step-wise temperature programmed desorption of ammonia for all catalysts are summarized in Table 2. The acidity measurement indicates that ceria possesses less acidity since it is a basic oxide and acidity enhanced upon silica promotion and vanadia loading [25]. Amorphous silica obtained from rice husk exhibits high total acidity. Acidity of supported catalysts is found to be more in comparison with ceria. In the case of ceria, silica and silica promoted ceria, the increased BET surface area is accompanied by a parallel increase in total acidity values. For supported catalysts, higher number of acid sites than ceria can be attributed to the presence of acidic oxides SiO_2 and V_2O_5 . The total acidity increased up to 6 wt% V_2O_5 loading and then decreased with further increase in V_2O_5 content to 10 wt%. It could be due to masking of acidic sites by highly dispersed vanadium oxide phase on the surface of the support. Decrease in acidity may also be correlated to the formation of an orthovanadate (CeVO_4) type phase on the support [26]. Formation of orthovanadate structure was observed from $^{51}\text{VMASNMR}$ spectra for supported catalysts above 8 wt% V_2O_5 loading (data not shown). From EDX measurements, the at% of Si was found to be lower for 8 and 10 wt% V_2O_5 loading than 6 wt%. This can also cause reduction in total acidity values since the presence of amorphous silica helps to increase the acidic sites.

Table 2
Acidity distribution of catalysts from TPD- NH_3

Catalyst	Acidity distribution (mmol g^{-1})			
	Weak RT–200 ($^\circ\text{C}$)	Medium 201–400 ($^\circ\text{C}$)	Strong 401–600 ($^\circ\text{C}$)	Total 100–600 ($^\circ\text{C}$)
Ce	0.34	0.12	0.05	0.51
RS	1.13	0.17	0.09	1.39
CRS	0.58	0.13	0.07	0.79
2VCRS	0.59	0.19	0.11	0.89
4VCRS	0.79	0.21	0.13	1.13
6VCRS	0.92	0.24	0.12	1.28
8VCRS	0.73	0.28	0.09	1.11
10VCRS	0.67	0.29	0.09	1.06

The characterized catalysts were tested in the vapour phase cyclohexanol decomposition reaction. In order to optimize the standard conditions, influence of reaction parameters such as temperature and flow rate of reactant on the reaction has been carried out with selected catalysts. The effect of temperature on cyclohexanol conversion carried out in vapour phase over 6VCRS is depicted in Fig. 2. The overall conversion of cyclohexanol showed an increasing trend with an increase in reaction temperature. A maximum of 98.3 wt% conversion was obtained at temperature of 350 °C with cyclohexene as the only product, suggesting that active sites are not deactivated due to coke deposition. The reaction with various cyclohexanol feed rate was carried out from 4 to 7 ml h⁻¹ at 250 °C. It can be seen from Fig. 3 that the cyclohexanol conversion decreased with an increase in flow rate. Cyclohexene selectivity also showed some dependence on flow rate, it decreases upon increase in flow rate. In general, a decrease in the conversion is observed at higher space velocities due to lesser contact time and thus kinetics get affected [27]. For further reaction, flow rate of 5 ml h⁻¹ was selected. The conversion and selectivity remains constant for the supported catalysts

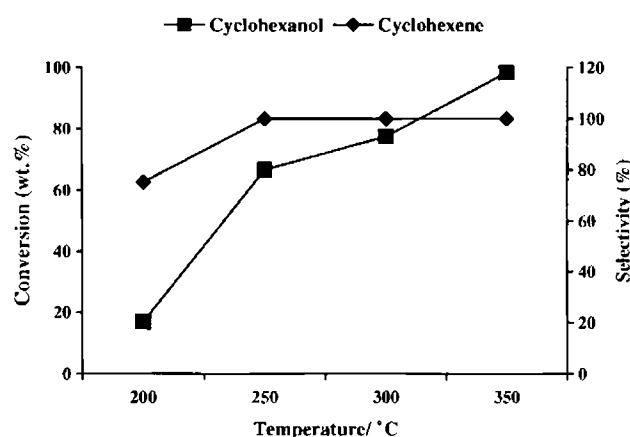


Fig. 2. Influence of temperature on decomposition (reaction conditions: 6VCRS, 500 mg; flow rate, 5 ml h⁻¹; and time on stream, 2 h).

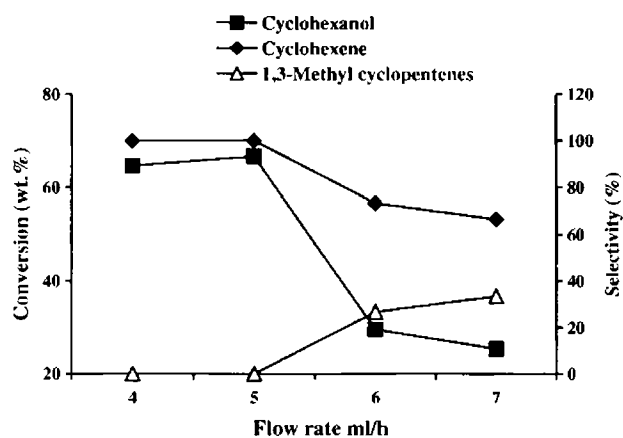


Fig. 3. Influence of flow rate on decomposition (reaction conditions: 6VCRS, 500 mg; temperature, 250 °C; and time on stream, 2 h).

upto 4 h. After this time period, a decrease in conversion observed which may be due to catalyst deactivation that has occurred by the coke deposition.

The results of cyclohexanol decomposition obtained over all catalysts are presented in Table 3. Product analysis shows cyclohexene as the main reaction product along with small amounts of cyclopentenes. No cyclohexanone was formed over any catalysts under the reaction conditions studied. In accordance with Brandao et al., the presence of nitrogen atmosphere throughout the reaction period can be a reason [28] since the dehydrogenation of cyclohexanol occurs on basic/redox sites and vanadia–ceria combination catalysts are best known for its redox property [29]. Amorphous silica from rice husk produced cyclohexene with small amount of cyclopentenes as secondary oxidative products on strong acid sites. For silica promoted ceria, conversion rate and cyclohexene selectivity increased compared to ceria. To determine the role of physical properties on catalytic behaviour of these catalysts, a correlation diagram developed is seen in Fig. 4(a) and (b). A good correlation between decomposition activity and total acidity values obtained by TPD-ammonia is observed. Cyclohexanol conversion rate is in accordance with its total acidity obtained by ammonia desorption method for all the catalysts studied. For silica promoted ceria, activity and selectivity are lowered than silica due to the lowering of surface area and total acidity since ceria is well known as a basic oxide. Thus in this case, the dehydration of cyclohexanol to cyclohexene is exclusively related to the total acidity of the oxides in accordance with several reports [26]. The formation of methyl cyclopentenes over these catalysts suggest that the isomerization activity must be associated with the presence of all acid sites in agreement with the result Bautista et al. [30].

For supported vanadia catalysts, conversion rate increases up to 6 wt% V₂O₅ loading exclusively giving cyclohexene as the product and for higher loadings activity is reduced. In general, the greatest activity in the dehydration to cyclohexene is associated with acid sites, while dehydrogenation to cyclohexanone is generally with basic/redox sites [31,32]. In the present case, supported vanadia on rice husk silica promoted ceria produced only cyclohexene. The dehydration activity observed under

Table 3
Results of cyclohexanol decomposition reaction over catalysts

Catalyst	Conversion (wt%)	Selectivity (%)	
		Cyclohexene	(1,3)-Methyl cyclopentenes
Ce	12.5	72.5	27.5
RS	49.2	99.4	0.6
CRS	22.1	76.6	23.4
2VCRS	23.2	100	–
4VCRS	38.1	100	–
6VCRS	68.6	100	–
8VCRS	47.8	100	–
10VCRS	46.4	100	–

Reaction conditions: catalyst 500 mg, flow rate 5 ml h⁻¹, temperature 250 °C, time on stream 2 h.

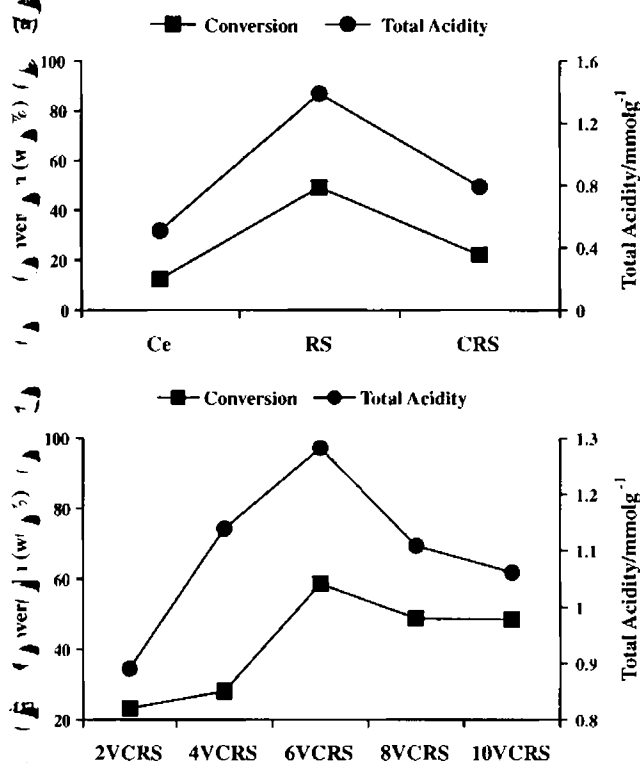


Fig. 4. Correlation of activity with total acidity (reaction conditions: catalyst, 500 mg; temperature, 250 °C and time on stream, 2 h).

hydrogen stream is a typical acid-catalyzed reaction and it indicates that the catalyst possesses some surface acidity [32]. The influence of BET surface area of supported vanadia catalysts on catalytic activity is found negligible since segregation of active phase over a support always reduces the surface area [34]. The cyclohexanol conversion rate and total acidity values obtained from TPD measurements show good correlation for supported vanadia catalysts. Thus, in this case the dehydration of cyclohexanol to cyclohexene takes place on acid sites. Fig. 5 shows the effect of vanadium (atom%) loading on the cyclohexanol conversion over these catalysts. With increase in vanadium content, the conversion of cyclohexanol gradually increases, reaching a maximum of 68.6 wt% at 8.28 atom% and there-

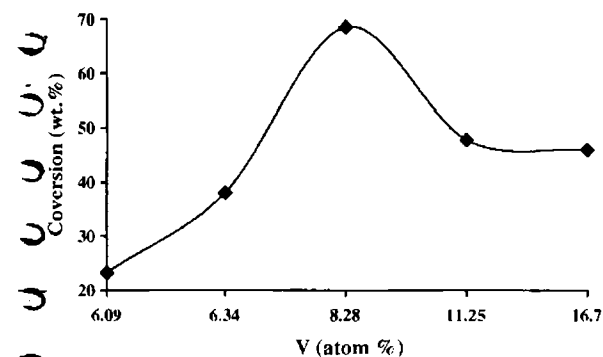


Fig. 5. Activity against atom% of vanadium (reaction conditions: catalyst, 500 mg; temperature, 250 °C and time on stream, 2 h).

after, the conversion decreased with further increase in vanadium content. The high conversion rate for low loading may be due to highly dispersed smaller crystallites of vanadia over the support surface.

4. Conclusions

Supported vanadia catalysts have been prepared using rice husk silica promoted ceria as support and were characterized with various instrumental techniques. Promotion of ceria support by rice husk silica produced amorphous catalysts at calcination temperature of 500 °C, which presents high number of active acid sites. Total acidity of the catalysts were measured by temperature programmed desorption using ammonia as a probe molecule. All the catalysts were found highly active towards vapour phase cyclohexanol dehydration to produce cyclohexene under the studied conditions. A correlation between total acidity and conversion of cyclohexanol has been observed for the catalysts.

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