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Catalysis Today 96 (2004) 205–209

www.elsevier.com/locate/cattod

Selective photo-oxidation of various hydrocarbons in the liquid phase over V_2O_5/Al_2O_3

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Abstract

More than 0.22 mmol of isolated VO_4 species of V_2O_5/Al_2O_3 exhibited the highest evolution of the partial oxidation products (alcohol and ketone) in the oxidation of cyclohexane and cyclopentane. The conversion of cyclohexane and the selectivity of the partial oxidation products were achieved to be 0.49% and 85% over 0.8 g of 3.5 wt.% V_2O_5/Al_2O_3, respectively, where the K/A ratio was 6.2. In addition, V_2O_5/Al_2O_3 can selectively oxidize various hydrocarbons in the liquid phase by the one-step oxygen atom insertion to C–H bond. The order of priority was tertiary carbon > secondary carbon > primary carbon > benzene ring.

Keywords: Cyclohexane; Cyclohexanone; Selective oxidation; V_2O_5/Al_2O_3; Photocatalyst

1. Introduction

The oxidation of cyclohexane is an essential process to produce 6-nylon and 6,6-nylon. ε-caprolactam or adipic acid which is a raw material for 6-nylon or 6,6-nylon synthesis is obtained by the cyclohexanone oximation with hydroxylammonium sulfate or the oxidation of the K/A (cyclohexanone/cyclohexanol) oil by means of HNO_3, respectively[1–3]. The K/A oil is produced by auto-oxidation process of cyclohexane over cobalt-base homogeneous catalyst above 423 K under about 8 kPa pressure[4,5]. It is very difficult to control the conversion of cyclohexane and the K/A ratio because of auto-oxidation. The conventional cyclohexane oxidation is operated at 4% conversion to inhibit the formation of by-product and the complete oxidation to CO_2. Recently, some authors found new catalysts which make the oxidation of cyclohexane proceed under mild condition (at room temperature and atmosphere pressure) [6–20]. We investigated the oxidation of cyclohexane over photocatalysts to achieve high conversion and K/A ratio under mild condition. In our laboratory, it has been reported that the selective oxidations of light alkanes [21–26] and alkenes [27–29] in the gas phase proceed over highly dispersed silica-supported vanadium oxide catalyst (V_2O_5/SiO_2). It has been concluded that active sites are the isolated VO_4 species on silica. Many groups also investigated the photoactivity of highly dispersed vanadium oxide on supports [30–35]. On the other hand, in the liquid phase, it was found that 2.5 wt.% V_2O_5/Al_2O_3 exhibits the highest conversion and selectivity in the oxidation of cyclohexane under photoirradiation in four supports (SiO_2, Al_2O_3, TiO_2, ZrO_2) [36]. It was first reported that the highly dispersed vanadium species on alumina shows high photoactivity as compared with that on silica. In addition, we clarified two important factors in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 photocatalyst in the quasi-flowing system [37]. The factors are described as follows

(1) The O_2 concentration should be kept above 30% to achieve the high K/A ratio.
(2) The irradiated wavelength should be cut off $\lambda <$ 300 nm to inhibit the formation of CO_2 and the ester compound as a by-product.

The K/A ratio depended on the O_2 concentration. In the closed system, the lower the O_2 concentration in the reactor

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0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.06.144

was, the smaller the K/A ratio was. We obtained the factor (1) in carrying out the photo-oxidation of cyclohexane under various O_2 concentrations in the quasi-flowing system. Moreover, cyclohexyl hexanoate as a by-product was formed by elongation of the photoirradiation time. It is well-known that ketene is generated by photoexcitation of ketone irradiated by UV-ray, $\lambda < 300$ nm (Norrish Type I reaction) [38]. Unstable ketene reacts with alcohol to ester readily. Therefore, cyclohexyl hexanoate is generated from photoexcited cyclohexanone (ketene) and cyclohexanol which are formed in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3. The formation of by-product was remarkably suppressed under photoirradiation $\lambda > 330$ nm because Norrish Type I reaction occurs by UV-ray, $\lambda < 300$ nm. In addition, the formation of CO_2 was likewise inhibited under photoirradiation $\lambda > 330$ nm. We acquired the factor (2) in carrying out the photo-oxidation of cyclohexane with various cut-filters. When various ketones were added to cyclohexane substrate, the evolutions of cyclohexane and CO_2 increased in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3. It has been clarified that the formations of cyclohexane and CO_2 relate to the photodecomposition of ketone (Norrish Type I reaction) closely. In this study, we performed the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 with various amounts of catalyst and V_2O_5 loading to optimize the reaction in the quasi-flowing system. Moreover, V_2O_5/Al_2O_3 was applied to selective photo-oxidations of various hydrocarbons.

2. Experimental

Alumina-supported vanadium oxide catalyst (V_2O_5/Al_2O_3) was prepared by impregnation of alumina powder with an aqueous solution of ammonium metavanadate (NH_4VO_3) at 353 K, followed by evaporation, drying and calcination at 773 K in a stream of dry air for 5 h [36,37]. Alumina used as a support in the study is JRC-ALO-8 supplied from the Japan Catalysis Society.

The photocatalytic reaction was carried out in a quasi-flowing batch system at atmospheric pressure. The reactor is similar to a Schrenck flask and is made of Pyrex glass with a flat glass in the bottom. V_2O_5/Al_2O_3 as a catalyst sample (0.1 g) and cyclohexane as a substance (30 ml: Wako GR, 99.5%) were introduced to the reactor. In this study, no solvent was used. The catalyst was not evacuated nor pretreated in the presence of O_2. In addition, cyclohexane was used without further purification. The suspension stirred by a magnetic stirrer at 323 K was irradiated from the flat bottom of the reactor through a reflection by a cold mirror with a 500 W ultrahigh-pressure Hg lamp supplied by USHIO Denki Co. Oxygen was flowed to the reactor at 2 cm^3 mim^{-1}through cyclohexane saturators. Organic products were analyzed by FID GC and GC mass spectrometry. The O_2 concentration was monitored by TCD GC and was determined with regard to the N_2 concentration and vapor pressure of cyclohexane. Further, at the down stream of the flow reactor, a trap with barium hydroxide solution ($Ba(OH)_2$) was equipped to determine the quantity of carbon dioxide (CO_2) as barium carbonate

3. Results and discussion

Cyclohexanol, cyclohexanone and CO_2 were produced in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3. Other probable compounds were not detected during the whole reaction time. Cyclohexanediol and cyclohexanedione were not generated in this reaction. The production of cyclohexanehydroperoxide was not identified by iodometry although some authors proposed this product as an intermediate of the cyclohexane oxidation. In addition, dicyclohexyl was not obtained in the liquid suspension. Therefore, the radical species do not relate to the formation of cyclohexanol and cyclohexanone in the photo-oxidation of cyclohexane. No product was detected in the dark at all. The evolution of cyclohexanol and cyclohexanone responded to illumination dominantly. The reaction did not proceed under photoirradiation without a catalyst. Photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 is not a photochemical reaction but a photocatalytic reaction.

We investigated the effect of V_2O_5 loading on the reaction activity and selectivity. Fig. 1 shows the evolution of cyclohexanone in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 with various amounts of V_2O_5 loading after 24 h photoirradiation. The increase in V_2O_5 loading caused the enhancement of cyclohexanone evolution until 3.5 wt.% loading. After that, the activity fell down in increasing in loading amount more. In addition, V_2O_5 itself was inactive in the photo-oxidation of cyclohexane. It is well-known that supported vanadium oxide aggregates into V_2O_5 at higher loadings while it disperses as isolated VO_4 species on alumina at very low loadings [39–41].

Accordingly, the highly-dispersed species is an isolated VO_4 species and the aggregated species is like V_2O_5. Gao and

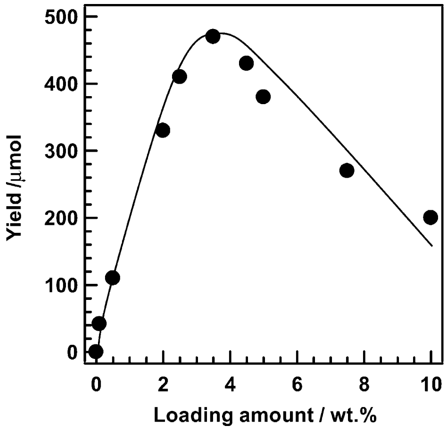


Fig. 1. The evolution of cyclohexanone in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 (0.1 g) with various amounts of V_2O_5 loading after 24 h photoirradiation.

Wachs [41] confirmed by UV–vis–NIR diffuse reflectance spectroscopy that the polymerized VO_4 species appeared at 6.92 wt.% loading on alumina (2.2 V atom/nm^2). It was proposed that the vanadium species changes from the isolated VO_4 species to the polymerized VO_5/VO_6 species via the polymerized VO_4 species. Therefore, the isolated VO_4 species build the 2D-network each other and change to the polymerized VO4 species in increasing in loading amount. The polymerized VO_5/VO_6 species like V_2O_5 (3D-network) are generated at higher loading over monolayer coverage. In our case, it is inferred that the isolated VO_4 species is active and the polymerized VO_4 and VO_5/VO_6 species are inactive. The specific surface area of alumina used in this study was 140 m^{2}g^{-1}. The surface density of 3.5 wt.% V_2O_5/Al_2O_3 was 1.7 V atom/nm^2. In conclusion, the vanadium species aggregates over 1.7 V atom/nm^2 and the polymerized VO_4 species were formed on alumina although Gao and Wachs [41] observed the polymerized VO_4 species at 2.2 V atom/nm^2. This result was reconfirmed by the photo-oxidation of cyclopentane over V_2O_5/Al_2O_3. Cyclopentanol, cyclopentanone and CO_2 were produced in this reaction. Fig. 2 shows that the evolution of cyclopentanone in photo-oxidation of cyclopentane over V_2O_5/Al_2O_3 with various amounts of V_2O_5 loading after 5 h photoirradiation. In the case of the photo-oxidation of cyclopentane, 3.5 wt.% V_2O_5/Al_2O_3 also exhibited the highest activity.

Fig. 3 or Fig. 4 shows the effect of the quantity of 2.5 wt.% V_2O_5/Al_2O_3 on the photo-oxidation of cyclohexane and cyclopentane to cyclohexanone and cyclopentanone, respectively, after 24 h of photoirradiation. The evolution of cyclohexanone increased until 0.8 g of catalyst. After that, the activity was constant. Because of the photoirradiation to the steady dimension, the amount of vanadium species which are activated under photoirradiation was saturated above 0.8 g. Past 0.22 mmol isolated V atoms are ineffectual in our system due to saturation. We have uncovered two important factors for the photo-oxidation of cyclohexane to obtain cyclohexanone preferentially as follows [37]. (1) The O_2 concentration should be kept above 30% to achieve the high K/A ratio. (2) The irradiated wavelength should be cut off $\lambda < 300$ nm to inhibit the formation of CO_2 and the ester compound as a by-product. We performed optimization in the selective photo-oxidation of cyclohexane over 0.8 g of 3.5 wt.% V_2O_5/Al_2O_3 (0.31 mmol of V atom) keeping the O_2 concentration at 80% and cutting off the wavelength below 300 nm as shown in Fig. 5. 990 μmol cyclohexanone, 160 μmol cyclohexanol and 1260 μmol CO_2 were evolved efficiently for 24 h photoirradiation. Accordingly, the conversion of cyclohexane and the selectivity of the partial oxidation products were achieved to be 0.49% and 85%, respectively, where the K/A ratio was 6.2. In addition, 1000 μmol cyclohexanone, 210 μmol cyclohexanol and 1190 μmol CO_2 were evolved efficiently over 0.8 g of 2.5 wt.% V_2O_5/Al_2O_3 (0.22 mmol of V atom). The activity in using 0.8 g of 2.5 wt.% V_2O_5/Al_2O_3 was similar to that in using 0.8 g of 3.5 wt.% V_2O_5/Al_2O_3. This implies the following. The surface vanadium species of 3.5 wt.% V_2O_5/Al_2O_3 are highly dispersed on alumina. When more than 0.22 mmol of isolated VO_4 species are admitted, the charge transfer from O atom to V atom is the time-determine step in the photo-oxidation of hydrocarbons in the liquid phase. Some isolated VO_4 species can not be activated because the irradiated facet area is limited. Therefore, it is possible to enhance the evolution of

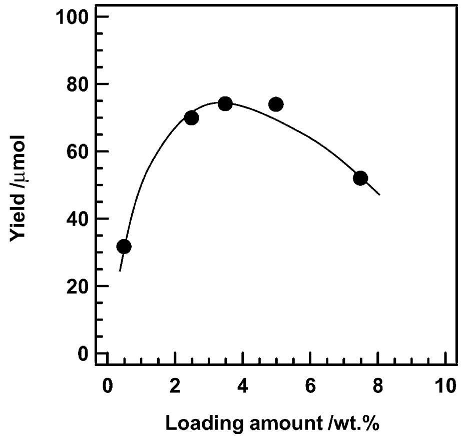


Fig. 2. The evolution of cyclopentanone in the photo-oxidation of cyclopentane over V_2O_5/Al_2O_3 (0.1 g) with various amounts of V_2O_5 loading after 24 h photoirradiation.

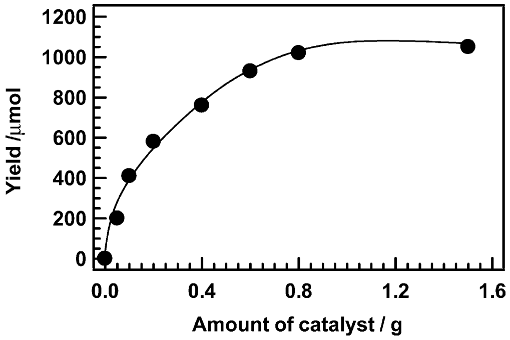


Fig. 3. The evolution of cyclohexanone in the photo-oxidation of cyclohexane in increasing in quantity of 2.5 wt.% V_2O_5/Al_2O_3 after 24 h photoirradiation.

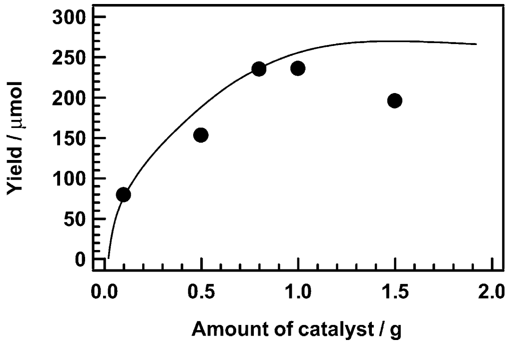


Fig. 4. The evolution of cyclopentanone in the photo-oxidation of cyclopentane in increasing in quantity of 2.5 wt.% V_2O_5/Al_2O_3 after 24 h photoirradiation.

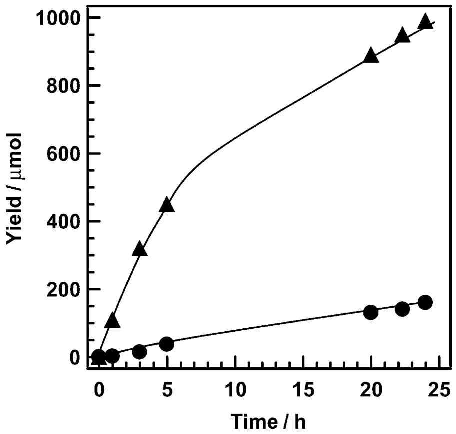
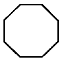
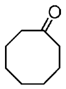
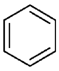
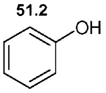
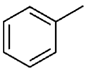
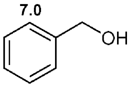
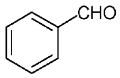
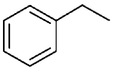
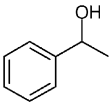
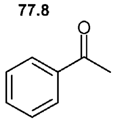
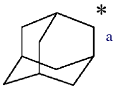
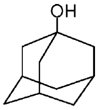
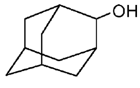
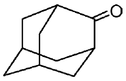
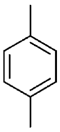
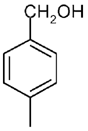
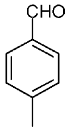


Fig. 5. Time course of the cyclohexanone (circle) and cyclohexanol (triangle) evolutions in the selective photo-oxidation of cyclohexane over 0.8 g of 3.5 wt.% V_2O_5/Al_2O_3.

cyclohexanone more if the irradiated facet area increased simply.

We performed the photo-oxidation of various hydrocarbons to apply V_2O_5/Al_2O_3 in other selective oxidation systems as shown in Table 1. V_2O_5/Al_2O_3 could oxidize various hydrocarbons selectively. Only cyclooctanone was formed in the photo-oxidation of cyclooctane. It was confirmed that the formation scheme of ketone do not correspond to that of alcohol because ketone was generated preferentially as compared with alcohol in the photo-oxidation of cyclopentane, cyclohexane and cyclooctane. Therefore, the isolated VO_4 species play an important role in the formation of ketones from hydrocarbons. In addition, benzene and benzene derivatives were also oxidized selectivity over V_2O_5/Al_2O_3 under photoirradiation. It is significant to produce phenol from benzene by one-step oxidation. In the case of the photo-oxidation of toluene, ethyl benzene or adamantane the major product is benzaldehyde, acetophenone or 1-adamantanol, respectively. Especially, benzoic acid was not generated from toluene. We also performed the photo-oxidation of o-xylene and obtained 4-methyl-benzaldehyde as a major product and 4-methyl-benzylalcohol as a minor product. In conclusion, the oxidation ability of V_2O_5/Al_2O_3 is the insertion of one oxygen atom to C–H bond and the order of priority was tertiary carbon > secondary carbon > primary carbon > benzene ring. This result was similar to the photo-oxidation of various hydrocarbons over V_2O_5/SiO_2 in the gas phase [21–26]. Therefore, the isolated VO_4 species on supports achieves the selective photo-oxidation of hydrocarbons (one oxygen atom insertion to C–H bond).

Table 1
The evolutions of selective oxidation products in the photo-oxidation of various hydrocarbons over V_2O_5/Al_2O_3 under photoirradiation

Substrate	Time (h)	Yield/μmol		
	24	 51.2		
	5	 7.0		
	24	 3.6	 77.8	
	24	 12.2	 51.7	
 * [a]	24	 5.7	 0.3	 1.6
	24	 18.6	 245.2	

Catalyst, 2.5 wt.% V_2O_5/Al_2O_3, 0.1 g. Substrate, 1 ml. Solvent, acetonitrile, 3 ml.

[a] Adamantane, 150 μmol; acetonitrile, 4 ml.

4. Conclusion

In our cyclohexane photo-oxidation system, the evolutions of cyclohexanone and cyclohexanol indicated maximum when 0.22 mmol of isolated VO_4 species were included on the surface of V_2O_5/Al_2O_3 photocatalyst. The conversion of cyclohexane and the selectivity of the partial oxidation products were achieved to be 0.49% and 85% over 0.8 g of 3.5 wt.% V_2O_5/Al_2O_3, respectively, where the K/A ratio was 6.2. In addition, V_2O_5/Al_2O_3 exhibited the ability of selective oxidation of various hydrocarbons in the liquid phase. Especially, it is attracted attention that benzene was oxidized to phenol by one-step oxidation. The oxidation ability of V_2O_5/Al_2O_3 is the insertion of one oxygen atom to C–H bond and the order of priority was tertiary carbon > secondary carbon > primary carbon > benzene ring.

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