Selective photo-oxidation of neat cyclohexane in the liquid phase over V_2O_5/Al_2O_3

Kentaro Teramura, Tsunehiro Tanaka*, Masaya Kani,
Tomohiro Hosokawa, Takuzo Funabiki

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

Abstract

V_2O_5/Al_2O_3 exhibits the high selectivity to partial oxidation compounds (cyclohexanol and cyclohexanone) as compared with TiO_2 in the photo-oxidation of cyclohexane in the liquid phase. This reaction is an environmentally friendly reaction since it proceeds at ambient temperature and atmospheric pressure without a solvent. The features of the reaction are a high selectivity to partial oxidation products and a reasonable ketone/alcohol ratio (K/A ratio). However, by elongation of the photoirradiation time, cyclohexyl hexanoate as a by-product was generated and the K/A ratio decreased gradually. Retention of the high O_2 concentration in the gas phase and irradiation of light $\lambda > 330$ nm are keys to the selective formation of the partial oxidation compounds with a reasonable K/A ratio in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3. In the present study, a selectivity of 87% to the partial oxidation compounds was achieved with the K/A ratio of 3.8.
© 2003 Elsevier B.V. All rights reserved.

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

1. Introduction

Nowadays, much attention is paid to the one-step oxygen atom insertion to hydrocarbons, what is called "selective or partial oxidation process," in the presence of O_2 as an oxidant in the viewpoint of the Green Sustainable Chemistry [1,2]. In particular, the application of photocatalyst to the selective oxidation in the presence of O_2 has been investigated for a long time since the reaction can be operated under mild conditions (at room temperature and ambient pressure). From 1970s to 1980s, there were many reports related to the selective oxidation over TiO_2 photocatalyst. Pichat [3] summarized the studies of the selective oxidation of a variety of organic compounds in the liquid phase over TiO_2 and concluded that TiO_2 photocatalyst can selectively oxidize a variety of organic compounds in the liquid phase. However, he also mentioned that oxidations by heterogeneous photocatalysis are limited to a small number of cases at the present state of knowledge. It is well-known that TiO_2 photocatalyst is applied to the com-

plete oxidation of harmful organic compounds (i.e. dioxin compounds, endocrine disrupters and volatile organic compounds (VOCs)) [4,5]. A series of reports clarified that it is difficult to inhibit the complete oxidation of hydrocarbons over TiO_2 photocatalyst. Therefore, since then, the study of the selective photo-oxidation has been scarcely reported.

Recently, some research groups revive the study of the selective photocatalytic oxidation of hydrocarbons with new concepts [6]. Ohno et al. reported that the epoxidation of olefins [7–9] and the dihydroxylation of naphthalene [10,11] proceeded over irradiated TiO_2. They clarified the relationship between the crystal phase of TiO_2 and the photocatalytic activity [12–14]. On the other hand, Yoshida et al. [15,16] reported the epoxidation of propene in the gas phase over TiO_2/SiO_2 and Shimizu et al. [17] researched the selective oxidation of benzene and cyclohexane over Ti–mica under irradiation in the liquid phase. These studies have shown that highly dispersed titanium oxide exhibits the appreciable activity in the selective photo-oxidation. Maldotti et al. also reported the selective photo-oxidation of cyclohexane over Fe–porphyrin modified TiO_2 [18,19], polyoxotungstate modified SiO_2 [20,21] and MCM-41 [22]. We have reported a series of works on the selective

* Corresponding author. Tel.: +81-75-383-2559;
fax: +81-75-383-2561.
  E-mail address: tanaka@dcc.mbox.media.kyoto-u.ac.jp (T. Tanaka).

photo-oxidation of gaseous light alkenes [23–25] and alkanes [26–31] over silica-supported vanadium oxide in the presence of O_2. It has been clarified that the active sites of the selective photo-oxidation are the isolated tetrahedral VO_4 species, which are highly dispersed on a support. Many groups also investigated the photo-activity of highly dispersed vanadium oxide on supports [32–37]. Recently, we have performed the photo-oxidation of cyclohexane in the liquid phase in the presence of O_2 over various oxide supported vanadium oxide catalysts and have found out that the most active catalyst is alumina-supported vanadium oxide (V_2O_5/Al_2O_3) [38]. It is the first report that the highly dispersed vanadium species on alumina exhibits photo-activity although vanadium oxide and alumina are photo-inactive.

The selective photo-oxidation of cyclohexane is an attractive reaction since ε-caprolactam and adipic acid, which are key intermediates for nylon synthesis, are produced from cyclohexanone [39–41]. The main manufacturing process of cyclohexanol and cyclohexanone synthesis is the direct oxidation of cyclohexane in the air although there are alternative routes, the hydrogenation of phenol and the hydration of cyclohexene [40,41]. The reaction in the conventional process is fundamentally auto-oxidation. Accordingly, it is difficult to control the ratio of cyclohexanone to cyclohexanol (K/A ratio). Cyclohexanol produced as a by-product is dehydrogenated to cyclohexanone using Zn or Cu catalyst. It is one of the most important issues to enhance the K/A ratio in the cyclohexane oxidation system. In 1989, Mu et al. [42] reported the selective photo-oxidation of cyclohexane in the liquid phase in the presence of O_2 over TiO_2 for the first time; 0.3% conversion of cyclohexane and 88% selectivity to the partial oxidation products were observed and the K/A ratio was 16.6. Lu et al. [43] have confirmed the reproducibility of their report and have found that the conversion of cyclohexane is high over the mixture of TiO_2 and TS-1 in comparison with that over TiO_2 only. In addition, Boarini et al. [44] have reported that the selectivity to CO_2 is 5.2% after 90 min for the photo-oxidation of neat cyclohexane over TiO_2. The feature of their report is that the selectivity to CO_2 is very low. However, Shimizu et al. [17] recently reported that the selectivity to CO_2 is 78.7% over irradiated TiO_2 for 12 h. They defined the selectivity to CO_2 as $(CO_2/(C_6\text{-ol}+C_6\text{-one}+CO_2))$. We evaluated the selectivity on the basis of cyclohexane conversion $((1/6)\,CO_2/(C_6\text{-ol}+C_6\text{-one}+(1/6)\,CO_2))$ and concluded that the selectivity to CO_2 was 39%. In the case of the cyclohexane oxidation process, it is important to keep the high K/A ratio and inhibit the formation of by-products and CO_2. In the present work, we have carried out the photo-oxidation of neat cyclohexane over V_2O_5/Al_2O_3 and TiO_2 as an archetypal example. We have investigated the method for controlling the K/A ratio and the selectivity to CO_2 with the formation of by-products suppressed and have found that the O_2 concentration and the wavelength of the irradiated light are the key factors.

2. Experimental

2.1. Materials

Alumina-supported vanadium oxide catalyst (V_2O_5/Al_2O_3) was prepared conventionally by impregnating alumina with an aqueous solution of ammonium metavanadate (NH_4VO_3) at 353 K for 2 h. Alumina used as a support in this study is JRC-ALO-8 supplied from the Japan Catalysis Society. After the impregnation, the suspension was evaporated to dryness at 373 K gradually. The sample was kept at 383 K for 24 h in an oven, followed by calcining in air at 773 K for 5 h. The sample was ground to powder under 100 mesh after calcination. The loading amount of vanadium atom is 2.5 wt.% as V_2O_5. Specific surface area is estimated to be 170 m^2/g by the BET method. No crystalline vanadium compounds were identified by XRD analysis. It has been confirmed by XAFS spectroscopy that vanadium species are highly dispersed on alumina.

2.2. Reaction

The reaction was carried out in a closed batch system or a quasi-flowing system at atmospheric pressure. The reactor used in this study is similar to a Schrenck flask and is made of Pylex 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 substrate (30 ml: Wako GR, 99.5%) were introduced to the reactor. In this study, no solvents were used. The catalyst was neither evacuated nor pretreated in the presence of O_2. 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 reflection by a cold mirror with a 500 W ultrahigh-pressure Hg lamp supplied by USHIO Denki Co. Oxygen was kept at 1 atm with a rubber balloon in the case of the closed batch system. On the other hand, oxygen was flowed to the reactor at 2 cm^3/min through cyclohexane saturators in the case of the quasi-flowing system. 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 the vapor pressure of cyclohexane. Further, at the downstream 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 ($BaCO_3$).

3. Results and discussion

The products were cyclohexanol, cyclohexanone and CO_2 over V_2O_5/Al_2O_3. Other possible products like diols and diones were not detected during the whole reaction time. This is very likely judging from the product distribution dealing in the gas phase photocatalytic oxidation of light alkanes [30,31]. Fundamentally, the oxygenation is initiated with the interaction between hydrogen atom of the hydrocarbon and

oxygen atom of the surface vanadate species and therefore ketone is formed primarily [29]. If the diol or dione was formed, they would be produced by consecutive oxidation of the ketone. But when the photo-oxidation was carried out with cyclohexanone as a reactant, only carbon dioxide was obtained. When the sole reactant was changed to cyclohexanol, cyclohexanone and carbon dioxide were produced. These results show that the dione and diol are formed as neither a primary product nor a consecutive product in the present system. No hydroperoxides (for example, hydrogen peroxide and cyclohexanehydroperoxide) was detected by iodometry. In addition, dicyclohexyl was not found out in the liquid suspension. Some groups confirmed that dicyclohexyl was produced for the photo-oxidation of cyclohexane over TiO_2 and proposed that the formation of the cyclohexyl radical, namely, the photon abstraction, is a primary reaction [44,45]. However, it is expected that a free radical is not concerned with the oxidation of cyclohexane over V_2O_5/Al_2O_3 because neither the hydroperoxides nor the dicyclohexyl was detected in the present reaction. It is known that V_2O_5 itself is photo-inert [46,47]. We confirmed that neither of V_2O_5 nor Al_2O_3 was photo-active for this reaction. No product was observed at 353 K in the dark at all. The increase in the products stopped when the light-irradiation was turned off, and the amount of cyclohexanol and cyclohexanone increased when the light-irradiation was turned on again. This indicates the good response to photoirradiation. In addition, the reaction did not proceed under irradiation without a catalyst at all. Evidently, it is not a photochemical reaction but a photocatalytic reaction. The catalyst was not deactivated after 600 h. Table 1 shows the conversion of cyclohexane, the selectivities to cyclohexanol, cyclohexanone and CO_2, and the K/A ratio for the oxidation of cyclohexane over irradiated V_2O_5/Al_2O_3 or TiO_2 and the relevant reported results [17,42,43] are shown for comparison. The conversion and the selectivity were estimated with the following formulae

$$\text{Conversion (\%)} = \frac{(\text{C}_6\text{-ol} + \text{C}_6\text{-one} + (1/6)\,\text{CO}_2)}{\text{C}_6\text{H}_{12}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{C}_6\text{-ol or C}_6\text{-one or }(1/6)\,\text{CO}_2}{(\text{C}_6\text{-ol} + \text{C}_6\text{-one} + (1/6)\,\text{CO}_2)} \times 100$$

In our case, the conversion of cyclohexane and the K/A ratio on TiO_2 were very high; however, the selectivity to CO_2 was also extremely high (33%) though the selectivity to CO_2 was very low (12%) in Mu et al. [42] and Lu et al. [43] reports listed in entries 1–3. In addition, Boarini et al. [44] also reported very low CO_2 selectivity (5.2%) after 90 min for the photo-oxidation of neat cyclohexane over TiO_2, although we could not estimate the precise amount of cyclohexane and TiO_2 because the unit of concentration (mol/dm^3) was used. On the other hand, Shimizu et al. [17] reported that the selectivity to CO_2 was 39% (entries 4 and 5) and these results were reproduced by us as shown in entry 6. It is very crucial to inhibit the consecutive oxidation over irradiated TiO_2 because the evolution of CO_2 increased with the irradiation time. In the case of V_2O_5/Al_2O_3, the selectivity to the partial oxidation compounds (cyclohexanol and cyclohexanone) was 91% and the K/A ratio was 1.7 after photoirradiation for 24 h. In the present study, the high selectivity and the reasonable K/A ratio are attained for the first time except for Ti modified catalysts [17,42–44].

However, when we used a closed batch reactor, by elongation of the photoirradiation time, a by-product was generated and the evolution rate of cyclohexanol increased gradually in contrast to that of cyclohexanone as shown in Fig. 1(a). The by-product was assigned to an ester compound, cyclohexyl hexanoate, by GC-Mass spectrometry. We confirmed that this compound was formed by the reaction of ketene and cyclohexanol as shown in Scheme 1 [48]. The former compound is formed by photoexcitation of cyclohexanone irradiated by UV-ray, $\lambda < 300$ nm. The produced ketene reacts with H_2O to convert to n-hexanoic acid readily because ketene is very unstable. Finally, cyclohexyl hexanoate is generated from n-hexanoic acid and cyclohexanol. The evolution rate of cyclohexanol increased gradually, and conversely, that of cyclohexanone decreased. The yield of cyclohexanol reached the same level as that of cyclohexanone at 120 h irradiation time. Then, the evolution rate of cyclohexanol increased. Then, the O_2 concentration in the gas phase remarkably decreased. The K/A ratio decreased, corresponding to lowering of the O_2 concentration as shown in Fig. 1(b). This suggests that the evolution rates of cyclohexanol and cyclohexanone are related to the O_2 concentration.

Table 1
The selected results of the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 and TiO_2

| Entry	Catalyst	C_6H_{12} (ml)	Solvent	Time (h)	Conversion (%)	$C_6H_{11}OH$	Selectivity (%) $C_6H_{10}O$	CO_2	K/A	Reference
1	TiO_2/70 mg	10	–	3	0.3	5	83	12	17	[42]
2	TiO_2/30 mg	10	–	3	0.055	5.0	82.5	12.5	17	[43]
3	TiO_2 + TS-1	10	CH_2Cl_2/10 ml	3	0.27	30.9	67.6	1.5	2.2	[43]
4	TiO_2/20 mg	10	H_2O/10 ml	12	0.25	0	61	39	–	[17]
5	Ti–mica	10	H_2O/10 ml	12	0.084	26	68	6	2.6	[17]
6	TiO_2/100 mg	30	–	24	0.76	1	66	33	66	This study
7	V_2O_5/Al_2O_3/100 mg	30	–	5	0.11	24	64	12	2.7	This study
8	V_2O_5/Al_2O_3/100 mg	30	–	24	0.35	34	57	9	1.7	This study
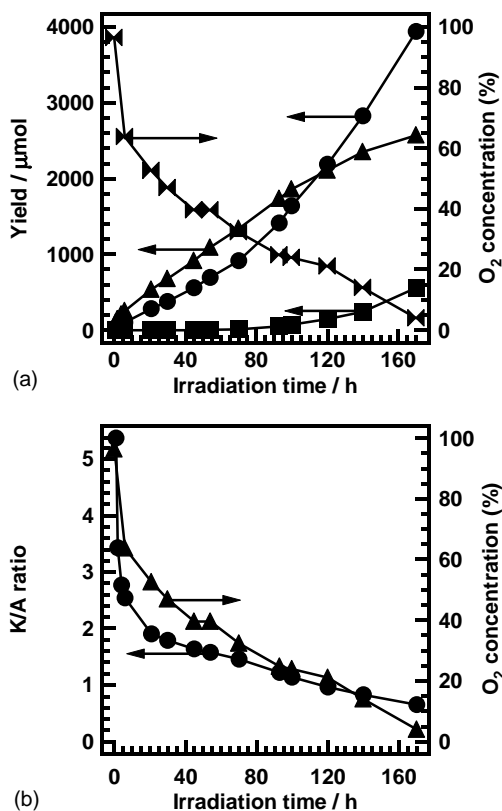
Fig. 1. (a) The evolutions of cyclohexanol (circle), cyclohexanone (triangle) and by-product (square), and the consumption of the O_2 concentration (butterfly). (b) The time course of the K/A ratio (circle) and the O_2 concentration (triangle) in the gas phase over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g).
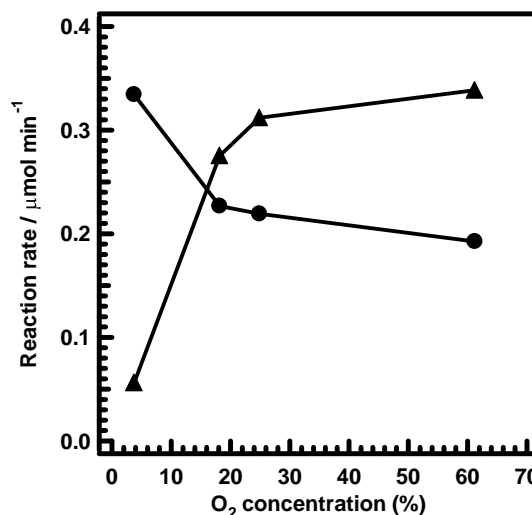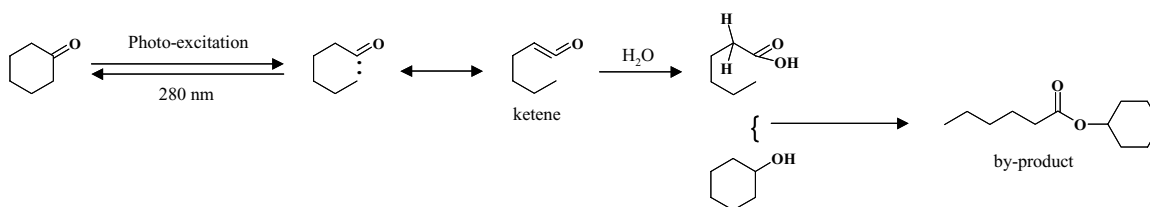

Fig. 2. The steady-state rates of cyclohexanol (circle) and cyclohexanone evolution (triangle) under different O_2 concentrations over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g).

Fig. 2 shows the evolution rates of cyclohexanol and cyclohexanone under different O_2 concentrations. The O_2 concentration was kept constant by using the quasi-flowing batch system. The reaction rate was monitored 5 h after photoirradiation started where the products yield increased linearly with the irradiation time. The production rates of cyclohexanol and cyclohexanone show different dependency upon the O_2 concentration, respectively. The evolution rate of cyclohexanol is reduced and that of cyclohexanone enhanced with an increase in the O_2 concentration. Above 30% O_2 concentration, both rates leveled off. This result shows that high K/A ratio can be achieved at the O_2 concentration higher than 30%.

It is important to investigate initial evolution rates of cyclohexanol and cyclohexanone in order to elucidate the role of the O_2 concentration for the photo-oxidation of cyclohexane. Fig. 3(a) shows the initial evolution rates of the selective oxidation compounds under different O_2 concentrations. The initial evolution rate of cyclohexanone is always kept high as compared with that of cyclohexanol and both rates were constant above 10% O_2 concentration. Fig. 3(b) shows the Langmuir-plot converted from Fig. 3(a). It was determined that the initial evolution rate of cyclohexanol is first order against the O_2 pressure, while that of cyclohexanone is zeroth order. Boarini et al. [44] investigated the effect of the O_2 partial pressure on the formation of cyclohexanol and cyclohexanone in suspensions of TiO_2 in a 1:1 C_6H_{12}/CH_2Cl_2 medium. They proposed that cyclohexanol and cyclohexanone are formed by the different radical reaction mechanisms. From the Langmuir-plot of their data, we confirmed that both the evolution rates of cyclohexanol and cyclohexanone over TiO_2 were first order against the O_2 pressure. Then, we agree with the mechanism they proposed for the photo-oxidation of cyclohexane over TiO_2. On the other hand, in our case, the evolution rate of cyclohexanol is first order against the O_2 pressure, while that of cyclohexanone was zeroth order. In addition, the initial rate

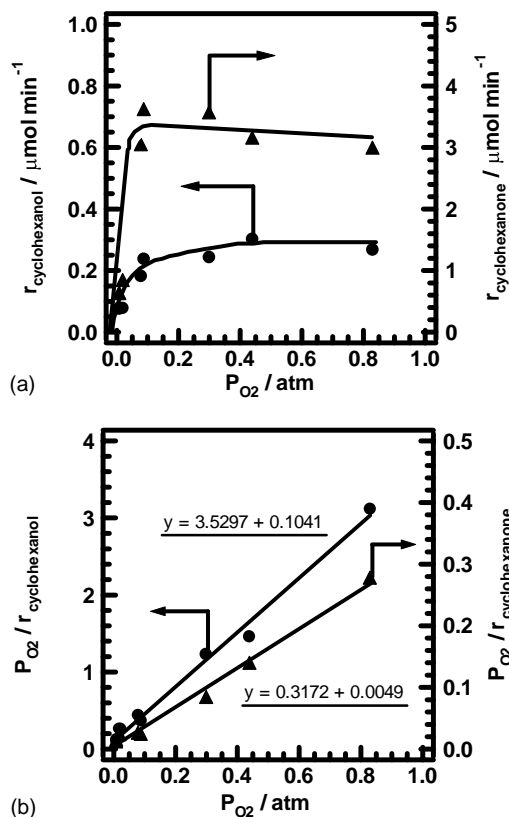Scheme 1. The formation process of the by-product in the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3.

(a)

(b)

Fig. 3. (a) The initial rates of cyclohexanol (circle) and cyclohexanone (triangle) evolution under different O_2 concentrations over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g). (b) The Langmuir-plot of (a).

of cyclohexanone was 12 times as fast as that of cyclohexanol. Therefore, the evolution processes of cyclohexanol and cyclohexanone over V_2O_5/Al_2O_3 are also independent; however, the O_2 radical species in the liquid phase would not be concerned with the evolution of cyclohexanone.

We performed the photo-oxidation of cyclohexane in the presence of cyclohexanol or cyclohexanone in the liquid phase to investigate the reaction mechanism. Fig. 4 shows the time course of the photo-oxidation of cyclohexane substrate in the presence of 3100 μmol cyclohexanol over V_2O_5/Al_2O_3. The amount of cyclohexanol decreased gradually and the evolution of cyclohexanone and CO_2 increased over the case without additives. This indicates that cyclohexanol is oxidized to cyclohexanone over irradiated V_2O_5/Al_2O_3. 2-Pentanone was generated and the initial evolution rates of cyclohexanol and cyclohexanone were suppressed when 2-pentanol as an additive was used instead of cyclohexanol. Accordingly, alcohol is preferentially adsorbed on V_2O_5/Al_2O_3 as compared with cyclohexane and oxidized to ketone or CO_2. Actually, the higher the concentration of cyclohexanol was, the slower the evolution rate of cyclohexanone was. The evolution of 2-propanone and the consumption of 2-propanol were not compatible in the presence of 2-propanol. Most produced alcohols would be adsorbed on alumina support of V_2O_5/Al_2O_3. The oxi-
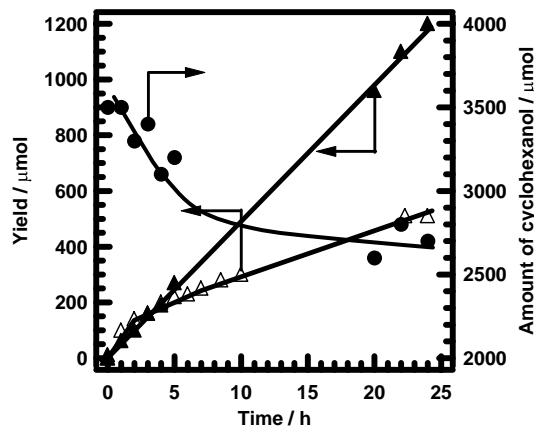

Fig. 4. The time course of cyclohexanone (closed triangle) and cyclohexanol (closed circle) for the photo-oxidation of cyclohexane in the presence of 3100 μmol cyclohexanol over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g) as compared with that of cyclohexanone (opened triangle) in the absence of additives.

dation process of cyclohexanol should be also conceivable as one of the evolution process of cyclohexanone but this contribution would be small.

The steady-state rate of cyclohexanone was significantly low compared with the initial rate although that of cyclohexanol was almost constant. This indicates that cyclohexanone is decomposed to other compounds. The photo-oxidation of cyclohexane in the presence of small amount of various ketones was carried out to clarify the effect of decomposition of cyclohexanone. Table 2 shows enhancement of amount of cyclohexanol, cyclohexanone and CO_2 when cyclohexanone, cyclopentanone or 2-pentanone was added into the cyclohexane substrate. It is surprising that the amount of cyclohexanol increased by a large margin by addition of these ketones. It was found that cyclopentanone and 2-pentanone decreased under irradiation. Table 3 shows the evolution of cyclohexanol for the photo-oxidation of cyclohexane in the presence of small amount of cyclohexanone. The evolution of cyclohexanol became negligible when the UV-33 cut filter was used. The formation of cyclohexanol and CO_2 were also confirmed under irradiation without a catalyst, but were inhibited under irradiation $\lambda > 300$ nm. The absorption band of the ketones lies at around 300 nm. It is speculated that

Table 2
The photo-oxidation of cyclohexane in the presence of the additives over V_2O_5/Al_2O_3 under irradiation for 24 h

Additive compound	Additive amount (μmol)	Cyclohexanol (μmol)	Cyclohexanone (μmol)	CO_2 (μmol)
None	–	340	560	510
Cyclohexanone	3600	700	–	990
Cyclopentanone	3400	620	540	920
2-Pentanone	3600	640	940	880

Reaction time: 24 h; catalyst (2.5 wt.% V_2O_5/Al_2O_3): 0.1 g; substrate (cyclohexane): 30 ml.

Table 3
The evolution of cyclohexanol and CO_2 in the photo-oxidation of cyclohexane in the presence of small amount of cyclohexanone

Entry	Catalyst	Cut filter	Cyclohexanol (μmol)	CO_2 (μmol)
1	None	None	460	250
2	None	UV-35	30	110
3	2.5 wt.% V_2O_5/Al_2O_3 (0.1 g)	UV-35	130	260

Reaction time: 24 h; substrate (cyclohexane): 30 ml; additive (cyclohexanone): 3000 μmol.

photo-decomposition of ketone (Norrish Type I reaction) as shown in Scheme 1 contributes to the evolution of cyclohexanol. However, the evolution of cyclohexanol could not be suppressed in the presence of V_2O_5/Al_2O_3 despite of using the cut filter. Therefore, the ketone molecules adsorbed on V_2O_5/Al_2O_3 can be activated under irradiation $\lambda > 300$ nm. It was confirmed by Raman spectroscopy that ketone molecules interact with V=O species of V_2O_5/Al_2O_3.

Fig. 5 shows the evolutions of cyclohexanol, cyclohexanone and CO_2 under irradiation of the different wavelength light for 24 h. The wavelength was selected with cut filters (TOSHIBA Co.). UV-*x* and Y-*x* denote the filter which cuts off half light intensity with the wavelengths $\lambda = 10x$ nm and light intensity with the wavelength $\lambda = (10x - 30)$ nm absolutely, respectively. All compounds yield decreased according to cutting wavelength with each cut filter. However, it is worthy of special mention that the oxidation can proceed under irradiation with the Y-43 or 45 filter, namely between visible light area. It is well-known that a fluorescent lamp emits light with 417 nm wavelength strongly. We carried out the oxidation of cyclohexane over irradiated V_2O_5/Al_2O_3 with a fluorescent lamp (Panasonic, 27 W). The reaction proceeded gradually, and 50 μmol cyclohexanone and 4 μmol cyclohexanol were produced for 100 h. In the present case, CO_2 was not detected. From the practical standpoint, it is highly important that the photo-oxidation of cyclohexane proceeds under fluorescent lamp irradiation. To investigate the effect of the irradiated wavelength upon product selec-
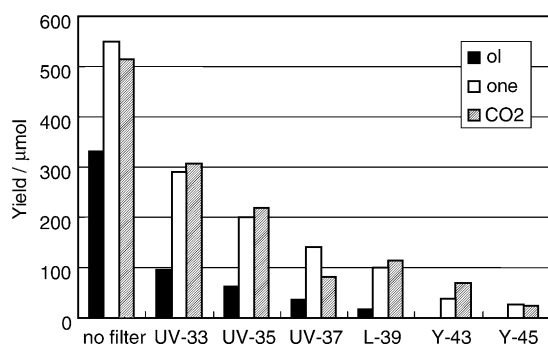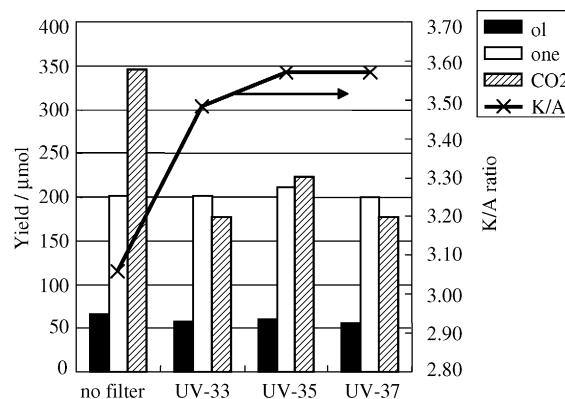

Fig. 6. The amounts of cyclohexanol, cyclohexanone and CO_2, and the K/A ratio under photoirradiation of various wavelengths at 0.1% conversion of cyclohexane over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g).

tivity, the amounts of three products (cyclohexanol, cyclohexanone and CO_2) at 0.1% conversion of cyclohexane were compared under photoirradiation of various wavelengths, as shown in Fig. 6. The generation of CO_2 was remarkably suppressed under photoirradiation $\lambda > 330$ nm. However, the K/A ratio scarcely depends on the wavelength of irradiation. (It is important to irradiate the light $\lambda > 330$ nm in order to accomplish the high selectivity to the partial oxidation compounds.) Therefore, the effective wavelength for the selective oxidation is different from that for the complete oxidation.

In the present study, we investigated the superiority of V_2O_5/Al_2O_3 for the selective oxidation as compared with TiO_2. It is clarified that the K/A ratio and the selectivity to the partial oxidation compounds can be controlled by the O_2 concentration and the irradiated wavelength, respectively. The most important factors are

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

We performed optimization for the selective photo-oxidation of cyclohexane over V_2O_5/Al_2O_3. To maintain the high K/A ratio, we carried out the photo-oxidation of cyclohexane over V_2O_5/Al_2O_3 with keeping the O_2 concentration at 80%, and to avoid the formation of ketene and CO_2, we cut off light with the wavelengths $\lambda < 330$ nm as shown in Fig. 7. The wavelength below 300 nm can be cut off absolutely with the UV-33 cut filter. No ester by-product was produced under this condition. Further, the evolution of cyclohexanone became dominant and the high K/A ratio was achieved. The evolution rates of cyclohexanol and cyclohexanone became constant after 5 h. 640 μmol cyclohexanone, 170 μmol cyclohexanol and 704 μmol CO_2 were produced efficiently for 100 h irradiation. As a consequence, a conversion of 0.33% and a selectivity of 87% were achieved with the K/A ratio of 3.8.
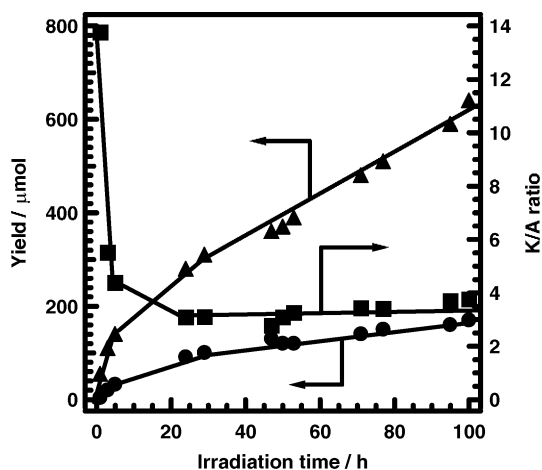

Fig. 5. The amounts of cyclohexanol, cyclohexanone and CO_2 under irradiation with cut filter for 24 h over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g). UV-*x* or Y-*x* denotes the filter which cuts off half light intensity with the wavelengths $\lambda = 10x$ nm and light intensity with the wavelength $\lambda = (10x - 30)$ nm absolutely, respectively.

Fig. 7. The evolutions of cyclohexanol (circle) and cyclohexanone (triangle), and the K/A ratio (square) at 80% O_2 concentration under irradiation of the wavelength $\lambda > 300$ nm over 2.5 wt.% V_2O_5/Al_2O_3 (0.1 g).

4. Conclusion

V_2O_5/Al_2O_3 catalyst is active for the selective oxidation of cyclohexane in the presence of molecular oxygen under photoirradiation. The important factors are (1) the O_2 concentration should be kept above 30% to achieve the high K/A ratio and (2) the irradiated wavelength $\lambda < 300$ nm should be cut off to inhibit the formation of CO_2 and by-product. This reaction proceeds at ambient temperature and atmospheric pressure without a solvent. Because of photocatalytic reaction, the reaction exhibits high response to the light-irradiation. The features of the reaction are the high selectivity to the partial oxidation compounds and the reasonable K/A ratio. In addition, for V_2O_5/Al_2O_3, the effective wavelength for the photo-decomposition of cyclohexanone shifts to longer wavelengths. Mechanistic study and development of more active catalysts are now in progress.

References

[1] G. Centi, M. Misono, Catal. Today 41 (1998) 287.
[2] I. Arends, R.A. Sheldon, Appl. Catal. A: Gen. 212 (2001) 175.
[3] P. Pichat, Catal. Today 19 (1994) 313.
[4] A. Mills, R.H. Davies, D. Worsley, Chem. Soc. Rev. 22 (1993) 417.
[5] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[6] A. Maldotti, A. Molinari, R. Amadelli, Chem. Rev. 102 (2002) 3811.
[7] T. Ohno, T. Kigoshi, K. Nakabeya, M. Matsumura, Chem. Lett. (1998) 877.
[8] T. Ohno, K. Nakabeya, M. Matsumura, J. Catal. 176 (1998) 76.
[9] T. Ohno, Y. Masaki, S. Hirayama, M. Matsumura, J. Catal. 204 (2001) 163.
[10] J.G. Jia, T. Ohno, Y. Masaki, M. Matsumura, Chem. Lett. (1999) 963.
[11] J.G. Jia, T. Ohno, M. Matsumura, Chem. Lett. (2000) 908.
[12] T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, J. Catal. 203 (2001) 82.
[13] T. Ohno, K. Sarukawa, M. Matsumura, J. Phys. Chem. B 105 (2001) 2417.
[14] T. Ohno, K. Sarukawa, M. Matsumura, N. J. Chem. 26 (2002) 1167.
[15] H. Yoshida, C. Murata, T. Hattori, Chem. Commun. (1999) 1551.
[16] H. Yoshida, C. Murata, T. Hattori, J. Catal. 194 (2000) 364.
[17] K.I. Shimizu, T. Kaneko, T. Fujishima, T. Kodama, H. Yoshida, Y. Kitayama, Appl. Catal. A: Gen. 225 (2002) 185.
[18] R. Amadelli, M. Bregola, E. Polo, V. Carassiti, A. Maldotti, J. Chem. Soc., Chem. Commun. (1992) 1355.
[19] A. Molinari, R. Amadelli, L. Antolini, A. Maldotti, P. Battioni, D. Mansuy, J. Mol. Catal. A: Chem. 158 (2000) 521.
[20] A. Molinari, R. Amadelli, L. Andreotti, A. Maldotti, J. Chem. Soc., Dalton Trans. (1999) 1203.
[21] A. Molinari, R. Amadelli, A. Mazzacani, G. Sartori, A. Maldotti, Langmuir 18 (2002) 5400.
[22] A. Maldotti, A. Molinari, G. Varani, M. Lenarda, L. Storaro, F. Bigi, R. Maggi, A. Mazzacani, G. Sartori, J. Catal. 209 (2002) 210.
[23] S. Yoshida, T. Tanaka, M. Okada, T. Funabiki, J. Chem. Soc., Faraday Trans. 1 80 (1984) 119.
[24] T. Tanaka, M. Ooe, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 1 82 (1986) 35.
[25] T. Tanaka, Y. Nishimura, S. Kawasaki, M. Ooe, T. Funabiki, S. Yoshida, J. Catal. 118 (1989) 327.
[26] T. Tanaka, S. Takenaka, T. Funabiki, S. Yoshida, Chem. Lett. (1994) 1585.
[27] S. Takenaka, T. Kuriyama, T. Tanaka, T. Funabiki, S. Yoshida, J. Catal. 155 (1995) 196.
[28] T. Tanaka, S. Takenaka, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 92 (1996) 1975.
[29] S. Takenaka, T. Tanaka, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. 93 (1997) 4151.
[30] T. Tanaka, T. Ito, T. Funabiki, S. Yoshida, Stud. Surf. Sci. Catal. 130 (2000) 1961.
[31] T. Tanaka, T. Ito, S. Takenaka, T. Funabiki, S. Yoshida, Catal. Today 61 (2000) 109.
[32] A.M. Gritscov, V.A. Shvets, V.B. Kazansky, Kinet. Katal. 15 (1974) 1257.
[33] A.M. Gritscov, V.A. Shvets, V.B. Kazansky, Chem. Phys. Lett. 35 (1975) 511.
[34] M. Anpo, I. Tanahashi, Y. Kubokawa, J. Phys. Chem. 84 (1980) 3440.
[35] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, J. Chem. Soc., Faraday Trans. I 84 (1988) 2987.
[36] S. Yoshida, T. Tanaka, T. Hanada, T. Hiraiwa, H. Kanai, T. Funabiki, Catal. Lett. 12 (1992) 277.
[37] T. Tanaka, Y. Nishimura, S. I. Kawasaki, T. Funabiki, S. Yoshida, J. Chem. Soc., Chem. Commun. (1987) 506.
[38] K. Teramura, T. Tanaka, T. Yamamoto, T. Funabiki, J. Mol. Catal. A: Chem. 165 (2001) 299.
[39] A. Castellan, J.C.J. Bart, S. Cavallaro, Catal. Today 9 (1991) 237.
[40] G. Bellussi, C. Perego, Cattech 4 (2000) 4.
[41] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. de Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinace, E.L. Pires, Appl. Catal. A: Gen. 211 (2001) 1.
[42] W. Mu, J.M. Herrmann, P. Pichat, Catal. Lett. 3 (1989) 73.
[43] G. X. Lu, H. X. Gao, J. H. Suo, S. B. Li, J. Chem. Soc., Chem. Commun. (1994) 2423.
[44] P. Boarini, V. Carassiti, A. Maldotti, R. Amadelli, Langmuir 14 (1998) 2080.
[45] M.A. Gonzalez, S.G. Howell, S.K. Sikdar, J. Catal. 183 (1999) 159.
[46] P. Pichat, J.M. Herrmann, J. Disdler, M.N. Mozzanega, J. Phy. Chem. 83 (1979) 3122.
[47] S. Yoshida, Y. Matsumura, S. Noda, T. Funabiki, J. Chem. Soc., Faraday Trans. 1 77 (1981) 2237.
[48] G.O. Schenck, S. Frank, Chem. Ber. 98 (1965) 2056.