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Photocatalytic Oxidative Dehydrogenation of 2-Propanol with Niobium Oxide Supported on Porous Vycor Glass

Yuji Wada* and Akira Morikawa
Department of Chemical Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152

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2-Propanol was catalytically converted to acetone on niobium oxide supported on porous Vycor glass in the presence of oxygen or nitrogen monoxide under UV irradiation. The light of wavelength shorter than 300 nm was effective for the reaction. The VIS-UV absorption measurements showed that niobium oxide was reduced by 2-propanol under the irradiation and Nb^{4+} formed by the photoreduction was reoxidized by oxygen. The kinetics of the reoxidation was investigated by means of spectroscopic measurements. The redox mechanism is proposed for the photocatalytic oxidation of 2-propanol.

In the periodic table, niobium belongs to 5A group and is located closely to Ti, Mo, and V. The catalytic activity of these oxides effective for chemical processes assisted by visible or ultraviolet irradiation has been well-investigated.[1] Similarity of niobium oxide in chemical and physical properties, such as crystal structure[2] and a semiconducting property,[3] to the oxides of the elements mentioned above suggests that the oxide can be a candidate of a catalyst for photoassisted chemical processes.

Photoactivation of niobium oxide catalyst has been reported.[4] Niobium oxide, which is catalytically inactive for ethylene dimerization, becomes active for the reaction by irradiation with ultraviolet light in the presence of ethylene. The catalyst once activated by the irradiation maintains its activity after the irradiation is ceased. This phenomenon has been attributed to the formation of Nb^{4+} ions, which are active sites for the reaction, by the reduction of Nb^{5+} ions with ethylene under the irradiation. If Nb^{4+} ions are readily oxidized by a proper oxidant, this photo-system can be designed as a photo-redox cycle.

The authors have found that 2-propanol is continuously converted to acetone in the presence of oxygen gas on niobium oxide supported on porous Vycor glass under irradiation with ultraviolet light. This paper deals with kinetic and spectroscopic investigations of this photocatalysis system to clarify the role of the niobium species in the photo-redox cycle.

Experimental

Materials. Porous Vycor glass was purchased from Corning Glass Works. Niobium pentachloride was kindly supplied from Professor M. Nangyo at Tohoku University. Its purity of 99.96% has been guaranteed. 2-Propanol purchased from Wako Chemical Co. was dried with molecular sieve 5A and thoroughly degassed before use.

Preparation of Catalyst. Porous Vycor glass of ca. 1 mm thickness was calcined at 550 °C in oxygen gas and then soaked at room temperature into a solution of niobium pentachloride in concentrated hydrochloric acid (0.5 mol-Nb l^{-}HClaq^{-1}). After 12 h, the glass was washed with deionized water and stored in the water for 12 h to ensure hydrolysis of niobium chloride in the pore system of the Vycor glass. The amount of supported Nb, determined by radioactivation analysis, was 3 wt%-Nb_2O_5. The weights of the catalyst used were 0.356 and 0.482 g for the reaction experiments and the spectroscopic measurements, respectively. The catalyst is denoted by Nb_2O_5/PVG hereafter.

Apparatus. The reaction was carried out in a conventional gas-circulating system with a reaction volume of 149 ml, connected to a vacuum system. A reactor (Fig. 1-a) was made of quartz glass whose bottom was a flat, transparent quartz plate. The catalyst was laid on the bottom, through which the catalyst was irradiated by the light of a medium-pressure mercury lamp. The reaction temperature was controlled by an electric furnace whose bottom was open for the irradiation.

For measurements of visible and ultraviolet absorption spectra, a quartz-made rectangular cell was used, where the catalyst could be treated in the same way as in the reaction experiments. A small room is attached at the top of the cell for admitting oxygen gas onto the catalyst during the measurements. The catalyst was placed as shown in Fig. 1-b. A spectrometer, Shimadzu UV-200, was employed for light absorption measurements.

Procedures. The catalyst, Nb_2O_5/PVG, was treated with oxygen in the reactor at 500 °C for 1 h and degassed at the same temperature for 1 h before the reaction. The reaction was initiated by the irradiation after 2-propanol and oxygen gas were introduced into the reaction system. A portion of a

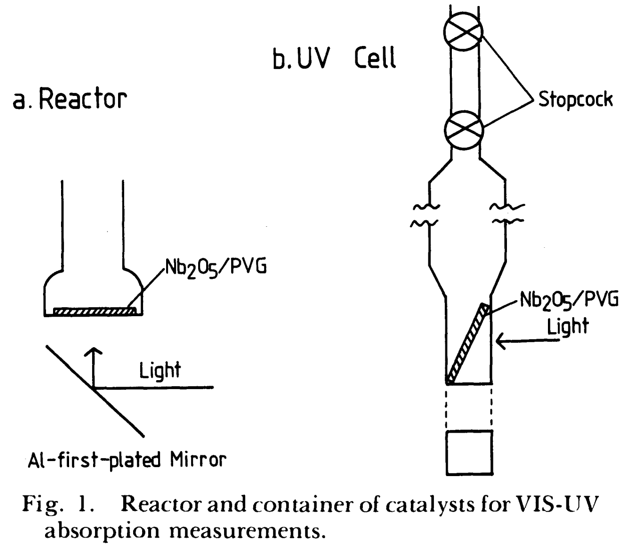

Fig. 1. Reactor and container of catalysts for VIS-UV absorption measurements.

reaction mixture was taken at appropriate time interval and analyzed by gas chromatography. A column (2 m) with packing, PEG 20M on Chromosorb W/AW, was used at 80 °C for the chromatography.

Results

It has been found that acetone was produced from the mixture of 2-propanol and oxygen gas on niobium oxide supported on porous Vycor glass under the irradiation at room temperature. No acetone was detected without the irradiation even at 100 °C. Propene, acetaldehyde, and CO_2 were observed beside acetone. They were less than 1% in yield even after the reaction was performed for 3 h. Figure 2 shows the formation of acetone along the irradiation time on Nb_2O_5/PVG, at room temperature (23—26 °C). Acetone was produced proportionally to the duration of the irradiation.

When no oxygen was present in the reaction system, the formation of only a small amount of acetone was observed within 60 min of the reaction time and its amount was not increased further (see Fig. 2). The acetone formation started again by the addition of oxygen and its rate was the same as that in the presence of oxygen gas. The catalyst was turned to black in color with a bluish cast after the reaction without oxygen gas, suggesting that niobium ion (IV) was produced during the reaction. The catalyst returned to transparent immediately by the addition of oxygen gas.

Figure 3 is a dependence of the rate of the acetone formation on a pressure of oxygen gas. A curve fits to the Langmuir-Hinshelwood type rate equation where the rate follows the first order of the amount of adsorbed oxygen (Eq. 1).

$$r = \mathrm{d(acetone)}/\mathrm{d}t = kKP(O_2)/\{1+KP(O_2)\} \quad (1)$$

where k and K are constants and $P(O_2)$ denotes a pressure of oxygen gas.

The effect of the reaction temperature was examined in the range of the temperature, 75—150 °C. Rather large amount of propene was produced at these temperatures. This type of dehydration of 2-propanol took place in a dark in the same rate as in the irradiation. Figure 4 shows an Arrhenius type plot of the acetone formation rate. The apparent activation energy of 23 kJ mol^{-1} was estimated from the linear line of the plot.

In order to reveal an effective region of the wavelength to the dehydrogenation, light filters were inserted in between the reactor and the light source. Figure 5 shows that the light of wavelength shorter than 300 nm was effective for the reaction.

Oxidants other than oxygen, such as NO and N_2O, were tested. NO acted as an oxidant, but, the reaction rate was slower by a factor of 3 than when oxygen gas was used. When N_2O was used, the amount of acetone and its change along the irradiation time were the same as those observed in the absence of any oxidant as mentioned above.

UV-Absorption Analysis. As described in the previous section, the color of the catalyst turned to black

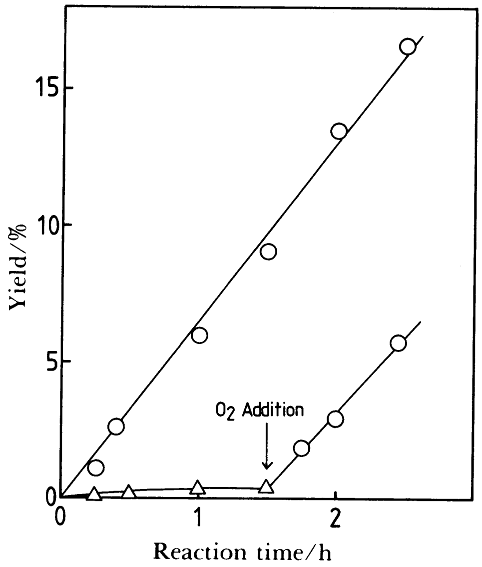

Fig. 2. Acetone formation along the irradiation time. Reaction temperature, 25 °C. 2-Propanol, 3.1× 10^{-4} mol. Pressure of oxygen, 40 Torr (1 Torr= 1.33×10^2 Pa). (○) In the presence of O_2, and (△) in the absence of O_2.

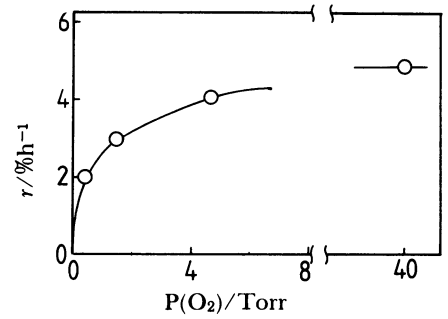

Fig. 3. Dependence of the reaction rate on oxygen pressure. Reaction temperature, 25 °C. 2-Propanol, 3.1×10^{-4} mol.

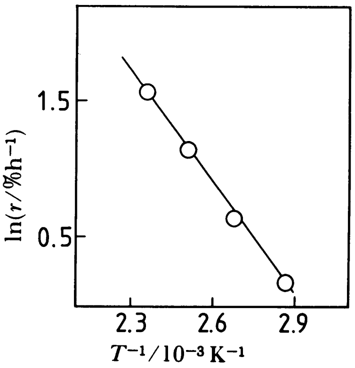

Fig. 4. Dependence of the rate of acetone formation on the reaction temperature. 2-Propanol, 3.4×10^{-4} mol. Pressure of oxygen, 40 Torr.

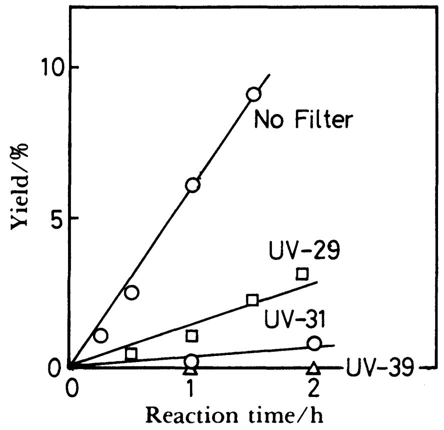

Fig. 5. Effect of the light filters on the reaction. Reaction temperature, 25 °C. 2-Propanol, 3.4× 10^{-4} mol. Pressure of oxygen, 40 Torr. The notation of the filters is after Toshiba Co. The number of filter denotes one tenth of the wavelength at 50% reduction of light intensity transmitted.

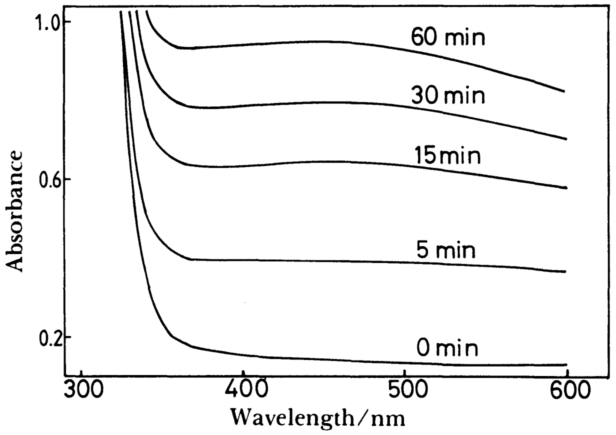

Fig. 6. VIS-UV absorption spectra of Nb_2O_5/PVG photoreduced by 2-propanol. The numbers shown are the irradiation times.

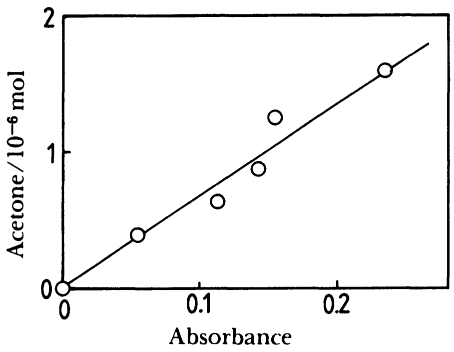

Fig. 7. Relation between the absorbance at 450 nm of the photoreduced Nb_2O_5/PVG and the amount of acetone formed.

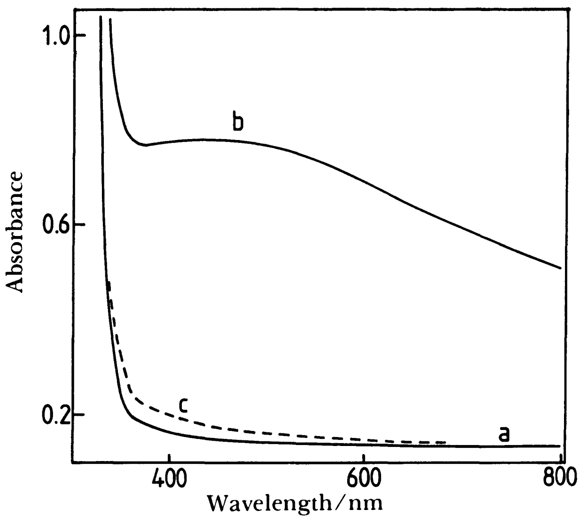

Fig. 8. Change in the VIS-UV absorption spectrum of photoreduced Nb_2O_5/PVG by the admission of oxygen. (a) Before the photoreduction, (b) photoreduced, (c) after O_2 admission to the sample of (b).

with bluish cast by UV irradiation in the presence of 2-propanol alone. This change in color suggests the formation of Nb^{4+} ion.

Figure 6 shows VIS-UV absorption spectra of the catalyst observed before and after the irradiation. The sample strongly absorbed UV light of wavelength shorter than 300 nm. After the irradiation in the presence of only 2-propanol, a broad absorption band appeared in the region from UV to visible light, corresponding to the color change of the catalyst observed when the reaction was carried out without oxygen gas.

An absorption maximum is distinguished at 450 nm in the spectra shown in Fig. 6. It has been reported that Nb^{4+} in an aqueous oxalic-acid solution has an absorption maximum at around 450 nm.[5] Compared to the latter absorption spectrum, the absorption band observed for the oxide supported on the glass was very broad. The broadening of absorption bands observed for a condensed phase is rather general phenomenon in the observation of electronic spectra. Therefore, the absorption band of the Nb_2O_5/PVG observed after the irradiation in the presence of only 2-propanol is attributed to Nb^{4+} ion which is situated on the surface of the porous glass in its rather strong interaction with either the silica network of the glass or the niobia framework supported on the glass. It is suggested that the Nb^{4+} ion must be produced through reduction of Nb_2O_5 by 2-propanol, being converted to acetone at the same time. Figure 7 represents a relation between the amount of acetone formed during the various irradiation times and the absorbance at 450 nm of the catalyst measured after the irradiation. Acetone was collected by degassing the catalyst after a certain irradiation time of the catalyst with UV light in the presence of only 2-propanol. A proportional relationship between the two values rationalized the above suggestion for the path of the Nb^{4+} ion production.

Transient Analysis of Reoxidation of Catalyst. Figure 8 shows a change in the spectrum of the photoreduced catalyst by its exposure to oxygen gas. The

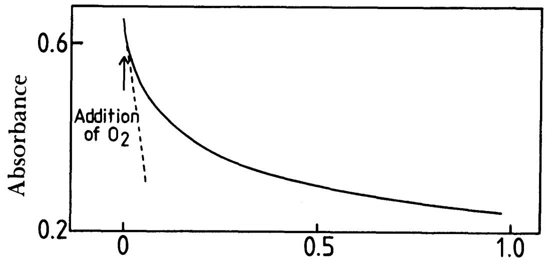

Fig. 9. Decrease of the absorbance at 450 nm by the admission of oxygen.

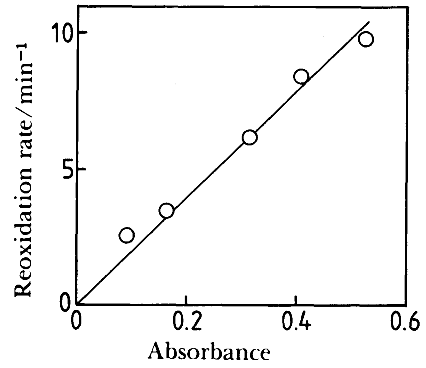

Fig. 10. Dependence of the Nb^{4+} reoxidation rate on the absorbance at 450 nm.

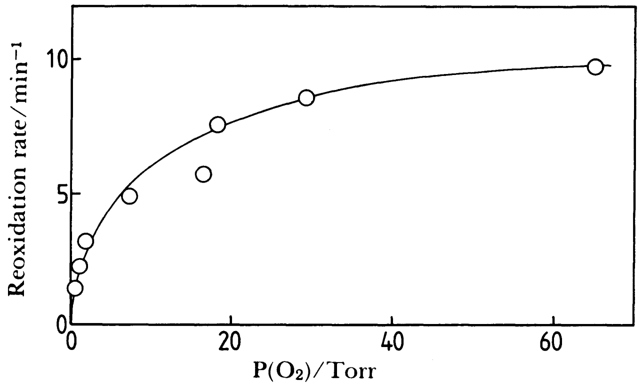

Fig. 11. Dependence of the Nb^{4+} reoxidation rate on the pressure of oxygen.

absorption band disappeared immediately by the exposure, indicating that Nb^{4+} was reoxidized easily by oxygen gas. The spectrum measured after the exposure was almost coincident with that observed before the reduction. The change of the absorbance at 450 nm could be recorded continuously by admitting oxygen gas onto the photoreduced catalyst (Fig. 9). Since the absorbance corresponds to the concentration of Nb^{4+} species, the result in Fig. 9 shows that the rate of the oxidation of the Nb^{4+} species decreases with increasing the exposure time, but the oxidation completed 80% within 1 min. This method allowed kinetic investigation of the reoxidation of the catalyst. The initial rate of the oxidation was evaluated from the slope of the dotted line drawn in Fig. 9 at the contact time, 0 min. Figures 10 and 11 show the dependencies of the initial rate on the initial absorbance of Nb^{4+} species and on the pressure of oxygen admitted on the catalyst showing a constant, initial absorbance of Nb^{4+} species, respectively. It is concluded from the two figures that the oxidation rate follows the first order kinetics on the concentration of Nb^{4+} on the surface and depends upon the concentration of oxygen molecules in a Langmuir-Hinshelwood type of equation as follows.

$$r = k[Nb^{4+}]KP(O_2)/\{1 + KP(O_2)\} \tag{2}$$

Discussion

Photoreduction. The present spectroscopic investigation has shown that the irradiation causes photoreduction of Nb^{5+} in the oxide to Nb^{4+} in the presence of 2-propanol. Visible and ultraviolet absorption spectrum of thin film of niobium oxide has shown the light absorption below 400 nm,[6] which overlaps to the same region (<300 nm) effective for the reaction of 2-propanol photooxidation. The linear relationship between the amount of formed acetone and the absorbance of Nb^{4+} on the catalyst (Fig. 7) shows that alcohol reacts with Nb^{5+} to produce acetone and Nb^{4+} according to the stoichiometry described in the Reaction i.

$$\begin{aligned} &Nb^{5+}\text{-}O^{2-}\text{-}Nb^{5+} + CH_3CH(OH)CH_3 \rightarrow \\ &\qquad 2Nb^{4+} + CH_3COCH_3 + H_2O \end{aligned} \tag{i}$$

As far as the homogeneous character of Nb^{4+} species formed in the Reaction i is supposed, its absorption coefficient at 450 nm was evaluated to be 1.5×10^6 mol^{-1} g-cat. cm^{-1} from the slope of the line in Fig. 7 and the thickness of the catalyst, 1 mm. Nb^{4+} formed by photoreduction must be present only on the surface and cannot migrate into the bulk of the niobium oxide, since the reduction occurs at room temperature. The amount of Nb^{4+} estimated from the stoichiometry of the Reaction i is 3.4×10^{-6} mol g-cat.$^{-1}$ for the catalyst photoreduced for 15 min. This amount corresponds to 1.3% of the total Nb^{5+} ions supported on the glass.

When titanium oxide was irradiated in the presence of alcohol, the color of the oxide turned to purple, showing that the photoreduction occurred.[7] This is essentially the same phenomenon as was observed for the present Nb_2O_5/PVG system.

Photoactivation of niobium oxide observed for the dimerization of ethylene has been explained by the photoreduction of the niobium oxide, which results in the formation of Nb^{4+} species by the photoreduction, which acts as an active site for ethylene dimerization.[4] Thus the niobium oxide is generally photoreduced in the presence of an organic reductant such as alcohols or olefins to give Nb^{4+} species.

Reoxidation. Nb^{4+} formed by the photoreduction is readily reoxidized by oxygen gas at room temperature as shown in Fig. 8. The oxidation curve in Fig. 9 fits to Elovich equation, suggesting that Nb^{4+} ions are heterogeneous in their reactivity for oxygen.

The rate equation for the reoxidation, obtained as shown by Eq. 2, indicates that Nb^{4+} species disappears through a reaction of adsorbed molecular oxygen, O_2(a), with Nb^{4+}, as follows.

$$O_2 \rightleftarrows O_2(a) \qquad \text{(ii)}$$

$$Nb^{4+} + O_2(a) \rightarrow Nb^{5+} - O_2^- \qquad \text{(iii)}$$

It is plausible that O_2^- oxygen species must be formed at the first step of the reoxidation as shown in the Reaction iii. This is supported by the ESR observation that O_2^- is formed by oxygen admission on the silica-niobia which has been preliminarily reduced by hydrogen gas.[8] The O_2^- must be successively oxidized and finally converted to lattice oxygen (O^{2-}).

Catalytic Oxidation of 2-Propanol. The photooxidation of 2-propanol on Nb_2O_5/PVG proceeds via a redox mechanism of the oxide. The whole reaction steps are in the following.

$$Nb^{5+}\text{-}O^{2-}\text{-}Nb^{5+} + h\nu \rightarrow (Nb^{4+}\ O^-\text{-}Nb^{5+})^* \qquad \text{(iv)}$$

$$(Nb^{4+}\ O^-\text{-}Nb^{5+})^* + \text{2-PrOH} \rightarrow 2Nb^{4+} + CH_3COCH_3 + H_2O \qquad \text{(v)}$$

$$2Nb^{4+} + O_2 \rightarrow (Nb^{5+}\text{-}O_2^-\ Nb^{4+}) \qquad \text{(vi)}$$

$$(Nb^{5+}\text{-}O_2^-\ Nb^{4+}) + 2Nb^{4+} \rightarrow 2(Nb^{5+}\text{-}O^{2-}\text{-}Nb^{5+}) \qquad \text{(vii)}$$

This redox mechanism contains the photoreduction and the reoxidation discussed in the previous sections.

Yoshida et al. have proposed a redox mechanism for the photooxidation of CO and propene on V_2O_5 supported on silica.[9,10] The lattice oxygen of the oxide is responsible for the oxidation reaction in this mechanism.

Formenti et al. have proposed a mechanism of photooxidation of paraffin on TiO_2, where alcohols are formed from paraffins at first, and then the alcohols are converted to olefins, which are oxidized to ketones finally.[11] Since a small amount of propene was detected for the Nb_2O_5/PVG system, olefin can be an intermediate in the Reaction v.

A similarity of the rate equations of the acetone formation, Eq. 1, and of the reoxidation of the catalyst, Eq. 2, leads us to assume that the reoxidation, either of the reactions, vi or vii, is rate determining. In the mechanism of photodehydrogenation of alcohol on metal-supported titania proposed by Pichat et al.[7] and Herrmann et al.,[12] the abstraction of α-hydrogen from alcohol is rate determining. However the abstraction of hydrogen does not seem to be rate determining for the Nb_2O_5 system, because no isotope effect was observed when $CD_3CD(OD)CD_3$ was used as a reactant.

To get a general idea of 2-propanol photooxidation on metal oxides, literature data were compared as follows. The rate of the acetone formation in the present system was 4.0×10^{-7} mol s^{-1} for 1g of Nb_2O_5 at room temperature. Cunningham et al. have reported that the rates of the same reaction on irradiated TiO_2 and ZnO were 3×10^{-8} and 8×10^{-9} mol s^{-1} g^{-1}, respectively.[13] The rate calculated from the data for TiO_2 in the report by Bickley et al. was 1.2×10^{-10} mol s^{-1} g^{-1}.[14] The formation of acetaldehyde on TiO_2 has been 10 times slower than that of acetone.[13] On ZnO the two products were formed almost at the same rate.[13] The amount of acetaldehyde formed during the reaction on niobium oxide supported on porous Vycor glass was less than 1/50 of acetone. Although comparison in experimental procedures and conditions, i.e., a shape of a reactor, intensity and energy distribution of light, and a form of a catalyst, must be taken into account among these photocatalytic systems, the difference between the photocatalytic performances of TiO_2 or ZnO and that of niobium oxide is so large that it can be mentioned that niobium oxide is more active than TiO_2 and ZnO in the photooxidation of 2-propanol and far more selective for the formation of acetone.

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References

1) Ti: P. Pichat "Photoelectrochemistry, Photocatalysis, and Photoreactors," ed by M. Schiavello, D. Reidel Publishing Company, 1985, p. 425. S. J. Teichner and M. Formenti, in the same book, p. 457. Mo: M. Anpo, I. Tanahashi, and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. 1*, **78**, 2121 (1982). V: M. Anpo, I. Tanahashi, and Y. Kubokawa, *J. Phys. Chem.*, **84**, 3440 (1980). S. Yoshida, Y. Matsumura, S. Noda, and T. Funabiki, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2237 (1981).

2) H. Shaefer, R. Gruehn, and F. Shule, *Angew. Chem.*, **78**, 28 (1966).

3) P. Clechet, J. R. Martin, R. Olier, and C. Vollny, *C. R. Acad. Sci. Paris*, **282C**, 887 (1976).

4) A. Morikawa, T. Nakajima, I. Nishiyama, and K. Otsuka, *Nippon Kagaku Kaishi*, **1984**, 239; A. Morikawa, T. Nakajima, I. Nishiyama, and K. Otsuka, Proc. 8th Intern. Congr. Catal., **4**, 815 (1984).

5) R. E. Elson, *J. Phys. Chem.*, **75**, 4193 (1953).

6) D. C. Conlon and W. P. Doyle, *J. Chem. Phys.*, **35**, 752 (1961).

7) P. Pichat, J.-M. Herrmann, J. Disdier, H. Courbon, and M.-N. Mozzanega, *Nouv. J. Chim.*, **5**, 627 (1981).

8) Unpublished data.

9) S. Yoshida, Y. Matsumura, S. Noda, and T. Funabiki, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2237 (1981).

10) S. Yoshida, T. Tanaka, M. Okada, and T. Funabiki, *J. Chem. Soc., Faraday Trans. 1*, **80**, 119 (1984).

11) M. Formenti, F. Juillet, and S. J. Teichner, *Bull. Soc. Chim. France*, **1976**, 1031, 1315.

12) J. M. Herrmann and P. Pichat, "Spillover of adsorbed species," Studies in Sur. Sci. Catal., **17**, ed by G. M. Pajonk, S. J. Teichner, and J. E. Germain, Elsevier (1983), pp. 77—87.

13) J. Cunningham and B. K. Hodnett, *J. Chem. Soc., Faraday Trans. 1*, **77**, 2777 (1981).

14) R. I. Bickley, G. Munuera, and F. S. Stone, *J. Catal.*, **31**, 398 (1973).