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Selective Formation of Acetal by Photooxidation of Ethanol over Silica-supported Niobium Oxide Catalysts

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UV-irradiation of silica-supported niobium oxide suspended in liquid ethanol under atmospheric oxygen led to the selective production of 1,1-diethoxyethane. The absence of oxygen or UV-irradiation with wavelengths of λ>320 nm remarkably suppressed the reaction. The activity normalized to the number of niobium ions suggests that the active site is highly dispersed niobate species. Ethanal is the primary product of the photooxidation and 1,1-diethoxyethane is formed by acid catalysis.

Photoenergy conversion using heterogeneous catalysts is of current interest. From the view of chemical synthesis, the reactions on photocatalysts are intriguing for the selective formation of target compounds because photocatalytic reactions usually take place under mild conditions and they can be controlled easily by light irradiation. However, in the case of photooxidation of hydrocarbons and alcohols,[1] the selectivity to partial oxidation is often low because of excess photoactivation of target products to lead to total oxidation. For example, the formation of diethyl acetal on a $TiSe_2$ photocatalyst was recently reported by Iseda *et al.*,[2] but the selectivity was low. In the present paper, we report that a combination of an acid catalyzed reaction with photocatalytic oxidation can suppress the further oxidation of primary products. Thus, the highly selective formation of diethyl acetal (1,1-diethoxyethane) has been achieved over silica-supported niobium oxide (Nb_2O_5/SiO_2) which has dual functions of acid catalysis and photocatalysis.

The catalyst samples Nb_2O_5/SiO_2 were prepared by impregnating silica (specific surface area : 550 m^2g^{-1}) with an aqueous solution of niobium oxalate, followed by calcination in a dried air stream for 5 h.[3] Prior to the reactions, the catalysts were evacuated for 1 h at 673 K and treated with 60 kPa of oxygen at 673 K for 2 h. Ethanol (1 cm^3) and the catalyst (0.2 g) were put in a quartz test tube of 16 mm diameter filled with atmospheric oxygen. The reaction was carried out with stirring the reaction liquid under photoirradiation from a 500 W super high pressure Hg lamp. The products were analyzed by *g. l. c.*

Table 1 lists the product distribution after 7 h irradiation. Ethene of less than 1 μmol was detected in the gas phase for each run except entries 7,8,10,11. The formation of diethyl ether was not observed for any runs. The results show that dehydration of ethanol proceeds quite slowly. Niobium oxide of a single phase is almost inactive referring to the result of entry 7. On the other hand, in the case of silica-supported niobium oxide (entries 1-6), diethyl acetal was produced with a quite high selectivity accompanied by the formation of ethanal and acetic acid. The activity was significantly suppressed by UV light with wavelengths of λ > 320 nm (entry 8). In the absence of oxygen (entry 9), the selectivity to diethyl acetal in the oxidation was very high although the conversion was much suppressed. The slight evolution of hydrogen was found in the gas phase, indicating that dehydrogenation occurs in some extent on the irradiated catalyst. These results clearly show that UV-irradiation

Table 1. Photoassisted reaction of ethanol under atmospheric O_2 over Nb_2O_5 / SiO_2 [a)]

Entry	Nb_2O_5 loading / wt%[b)]	Conv. / %[c)]	Selectivity [d)]/ mol%			
			CH_3CHO	$CH_3CH(OC_2H_5)_2$	CH_3CO_2H	$CH_2=CH_2$
1	1	5.7	6.4	91.7	1.6	0.4
2	3	12.6	4.1	93.4	1.1	0.4
3	4.5	11.2	4.4	93.1	2.2	0.2
4	6.3	16.5	5.3	91.1	2.6	0.2
5	7	9.7	3.1	94.8	1.3	0.3
6	10	8.4	3.3	94.6	1.9	0.2
7	100	0.1	92.8	tr.	tr.	7.2
8[e)]	6.3	1.9	1.5	97.8	0.0	0.7
9[f)]	6.3	0.2	tr.	86.0	0.0	14.0
10[g)]	6.3	4.8	42.2	39.8	18.0	tr.
11[h)]	6.3	2.2	56.9	18.7	24.4	tr.

a) Catalyst 0.2 g, neat ethanol 1 cm^3, reaction time 7 h, reaction temperature 310 K. b) Wt% as Nb_2O_5. c) Based on ethanol. d) Product selectivity based on converted ethanol. Ethene was detected only in the gas phase. e) UV-irradiated through a glass filter permitting light with wavelengths of λ>320 nm. f) Ar purged and O_2-Free. Hydrogen gas was detected in the gas phase. g) 69.3 μmol of pyridine was added. h) 214 μmol of pyridine was added.

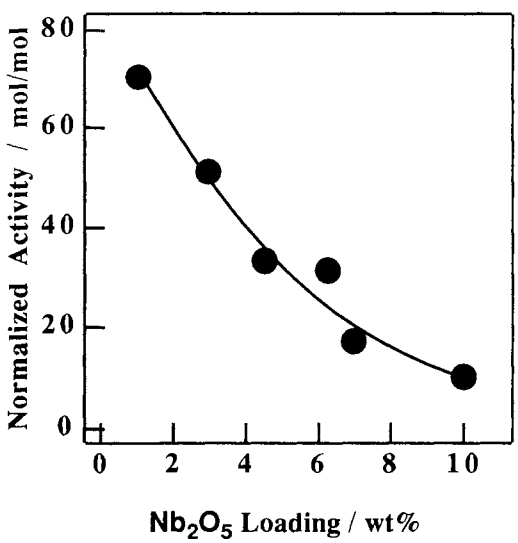


Fig. 1. Normalized activity of the catalyst. The ethanol conversion was divided by the amount of niobium ions.

the silica-supported niobium oxide with wavelengths of λ < 320 nm promotes the oxidation of ethanol to produce diethyl acetal.

As found in Table 1, entries 1-6, the conversion increases with an increase in the loading amount to a maximum at 6.6 wt% and then falls at higher loadings. At 10 wt% of loading, niobium ions should be aggregated to form polyniobate and bulk niobium oxide on the surface which is almost inactive (entry 7). Provided that niobium ions are dispersed atomically, loadings of Nb ions in all the supported samples are much less than that corresponding to the full coverage of silica. However, the conversion does not increase linearly, suggesting that Nb ions are supported inhomogeneously. We have concluded that surface monatomic niobates are the most active species in alkene photo-oxidation.[3)] When the loading amount of such metal oxides becomes larger, polymetalates form resulting in sluggish reaction rates.[4)] This may also be the case for the present catalyst system. This reasoning is supported by the activity normalized to the number of Nb ions as shown in Fig. 1. The normalized activity, which should correspond to the turnover number if all of Nb ions participated in the reaction, is the highest at 1

wt% of loading. At 1 wt% of loading, we have found that monomeric NbO_4 tetrahedra are the predominant species on the basis of the luminescence[3b] and Nb K-edge X-ray absorption[5] spectroscopies. Thus, we conclude that the active species in the reaction is the highly dispersed niobate.

The following path is very likely for the formation of diethyl acetal as acetal formation from aldehydes and alcohols is a well known reaction.

$$C_2H_5OH \xrightarrow{O_2} CH_3CHO \quad \text{(step 1)} \qquad CH_3CHO \xrightarrow{C_2H_5OH} CH_3CH(OC_2H_5)_2 \quad \text{(step2)}$$

To find out which step involves the photoactivation, we have carried out the reaction between ethanol and ethanal. Catalyst samples were suspended in the ethanolic solution of 11.7 mol% ethanal under atmospheric oxygen. As shown in Table 2, there is no appreciable difference between UV-irradiated and dark reactions. This strongly suggests that the oxidative dehydrogenation of ethanol (step 1) is a photoprocess. The Nb=O bonds are thought to be active sites for photooxidation[1,3a,7b] as in the case of V_2O_5/SiO_2[3,7-9].

Table 2. Reactions of ethanolic solution of ethanal over 6.6 wt% Nb_2O_5/SiO_2[a]

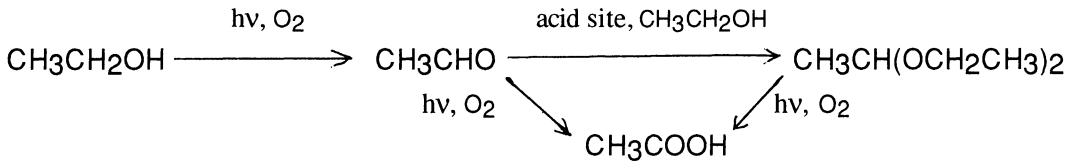
Entry	condition	Conversion[b]	Selectivity / %	
			$CH_3CH(OC_2H_5)_2$	CH_3COOH
1	UV	61.3	99.9	tr.
2	dark	59.5	99.9	tr.
3	dark, pyridine[c]	0.1	100	0

a) Catalyst 0.2 g, ethanolic solution(11.7 mol% CH_3CHO) 1.9 g, reaction time 1 h, reaction temperature 310 K. b) Based on CH_3CHO. c) Pyridine 263 μmol.

The formation of ethene, a product resulting from dehydration (Table 1, entries 1-9), should be noted. Dehydration is ordinarily promoted on the acid sites. Nb_2O_5 itself is almost neutral[10] and the yield of ethene is very low as found in entry 7 in Table 1. Therefore, the results suggest that acid sites also participate in the reaction or induce parallel reactions. It is well known that the dispersion of metal cations on inorganic carrier causes the generation of strong acid sites.[6] The thermal desorption profiles of pyridine from the catalyst sample have shown that strong acid sites are present on the catalyst sample although the amount is small. To examine the role of acid sites, the reaction was carried out in the presence of pyridine. The catalyst changed from white to yellow when being immersed into a pyridine-ethanol solution due to the adsorption of pyridine molecules on Nb ions. The results are shown in Table 1, entries 10 and 11. The activity decreased and the products distribution also significantly changed. Ethene formation was much suppressed. This presumably results from the poisoning of both acid sites and photoactive sites. By increasing the amount of pyridine, the selectivity to diethyl acetal decreased much more. These results strongly suggest that the formation of diethyl acetal is promoted on the acid sites on the catalyst surface. Actually, when pyridine is added to the ethanolic solution of 11.7 mol% ethanal and the solution mixture is stirred, the formation of diethyl acetal is much suppressed as shown in entry 3 of Table 2. Iseda *et al.* reported[2] that diethyl acetal is formed from liquid ethanol on irradiated $TiSe_2$ only in the presence of O_2 and the formation is enhanced by the addition of Pt on the $TiSe_2$ photocatalyst. They postulated that the formation of diethyl acetal requires photoformed O_2^-, which captures proton from ethanol. We conclude

that the mechanism for the formation of diethyl acetal is quite different from that on the $TiSe_2$ and involves a photooxidation step of ethanol and a consecutive acid-catalyzed reaction.

We have summarized the reaction scheme as follows:



Since the acid site is expected to exist closely to the highly dispersed Nb=O site for the photoassisted formation of CH_3CHO or its precursor, the consecutive formation of diethyl acetal is faster than further oxidation of CH_3CHO.

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