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Catalytic Properties of Lanthanide Metals on Silica

Hayao IMAMURA,* Tomohiro KONISHI, Yu-ichi TOKUNAGA,
Yoshihisa SAKATA, and Susumu TSUCHIYA
Department of Advanced Materials Science and Engineering, Faculty of Engineering,
Yamaguchi University, Tokiwadai, Ube 755

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Silica (SiO_2) powders reacted readily with Eu and Yb which were dissolved in liquid ammonia, resulting in the formation of active lanthanide/SiO_2 catalysts (Eu/SiO_2 and Yb/SiO_2). The reactions of dissolved lanthanide metals in liquid ammonia with SiO_2 were characterized by FT-IR studies and various catalytic reactions. The catalytic behavior varied markedly with varied levels of lanthanide loading. At low loadings ($<$ ca. 15 wt%), the dissolved lanthanide selectively reacted with the hydroxyl groups on SiO_2 to form $\equiv$SiO–MNH_2 species (M=Eu or Yb). The thermal treatment above 573 K led to the decomposition of this species to the inactive nitride MN. The catalyst with low loadings exhibited very high activity for the disproportionation of cyclohexadiene at room temperature. At high loadings ($>$ ca. 15 wt%), after the first portion of added lanthanide was consumed for the reaction with surface hydroxyl groups, subsequent lanthanide seems to deposit on SiO_2 in an active metallic form. The catalytic properties were very similar to those reported for lanthanide metal particles prepared by the metal vapor technique. The catalyst with high loadings discriminated between internal and terminal C–C triple bonds for the hydrogenation of alkyne; thus, 2-butyne was readily converted to *cis*-2-butene, whereas 1-butyne, propyne, and acetylene were not hydrogenated at all.

There has been a growing interest in heterogeneous, catalytic properties of lanthanide (rare earths) metals and related compounds.[1-2] By the use of dissolution of lanthanide (Eu and Yb) metal in liquid ammonia, we have described that novel lanthanide-containing bimetallic catalysts can be prepared.[3-5] Further, the catalytic study is extended to include the lanthanide-dosed oxide systems.[6] Catalysts prepared by the reaction of dissolved lanthanide metals in liquid ammonia with various oxides exhibit extraordinarily high specific activities. In particular, the lanthanide-dosed MnO yields extremely active catalysts for olefin hydrogenation although manganese(II) oxide is entirely inactive. The present paper describes an investigation of the Eu/SiO_2 and Yb/SiO_2 catalysts obtained by impregnating SiO_2 with the solution of lanthanide metals in liquid ammonia. The results reported here provide information on the nature of the lanthanide present on the SiO_2 surface using FT-IR technique. They also provide the necessary information as to the catalytic properties which vary with changes in the state of lanthanides on SiO_2.

Experimental

Materials. Lanthanide metals (Eu and Yb: 99.9 %) were supplied by Shin-etsu Chemical Co., Ltd. SiO_2 was commercially available Degussa aerosil. Prior to the reaction with the lanthanides SiO_2 was subjected to thermal treatment in vacuo at elevated temperatures. Triphenylsilanol was commercially obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. Ammonia (>99.9%; Iwatani Ind., Ltd.) which was dried through calcium oxide and subsequently through a sodium hydroxide column was used. Ethylene, acetylene, propyne, 1-butyne, 2-butyne, and 1,3-cyclohexadiene (1,3-CHD) were of research purity. These reactants were further purified by degassing, followed by a triple distillation. Hydrogen (99.975%) and dueterium (99.9 %) were stored in a reservoir for use as a reactant after having been passed through a molecular sieve column and liquid nitrogen trap.

Procedures. In a typical preparation of the catalysts (Eu/SiO_2 and Yb/SiO_2), SiO_2 which had been previously evacuated at 1073 K for 10 h was placed in a Schlenk reactor flushed thoroughly with dry argon. Eu or Yb was added to the oxide powders suspended in liquid ammonia (ca. 20 cm^3) with vigorous stirring at 195 K. Upon dissolution of the lanthanide metals in liquid ammonia, a blue homogeneous solution was formed, which is characteristic of the solvated electron.[7] The blue color gradually disappeared as a result of the reaction of dissolved lanthanides with SiO_2. On completion of the reaction, the vessel was allowed to warm to room temperature and the excess ammonia was vaporized. All operations were conducted in an atmosphere of dry argon, or else the catalysts became unreactive.

For infrared studies, infrared spectra were recorded on a JASCO FT-IR 7000 spectrometer. For the preparation of the sample, the procedures were carried out in a similar manner as above. To a solution of Eu or Yb in ammonia at 195 K was added an IR pellet of SiO_2, which had been previously heated in vacuo at 973 K, treated in an oxygen flow at 723 K, and again evacuated at 723 K for 0.5 h. The sample thus pretreated was transferred to the IR cell without exposure to air. IR spectra were obtained from the ratio of the background spectrum of SiO_2 to that of Eu/SiO_2 or Yb/SiO_2.

The catalytic reactions were carried out using a Pyrex gas-circulation system. About 100 mg of catalyst was used in each run and this was mounted in the reactor between quartz wool plugs without exposure to air. Prior to the reaction the catalyst was evacuated at the prescribed temperatures for 2 h, and was then exposed to the reactant gases. The reacting gas in the system was collected by a gas sampler and analyzed by a gas chromatograph.

Results and Discussion

Reactions of Lanthanide with SiO_2. SiO_2 reacted readily with Eu and Yb metals which dissolved in liquid ammonia, resulting in the formation of active catalysts with varied levels of lanthanide loading. Figure 1(a)—(c) show infrared spectra of Yb/SiO_2 obtained when SiO_2 previously evacuated at 973 K was treated with dissolved ytterbium in liquid ammonia. Eu/SiO_2, as well as Yb/SiO_2, exhibited essentially the same behavior.

Hydroxyl group information derived from infrared spectra is characteristic. The vibration band at 3744 cm^{-1} of SiO_2 is assigned to free hydroxyl groups. It is accepted that for the evacuation at about 1023 K only free, unpaired ≡Si–OH groups are present.[8] As shown in Fig. 1, this band decreased immediately upon contact with lanthanide. The evolution of gas was simultaneously observed when the dissolved lanthanide in liquid ammonia reacted with SiO_2. These strongly suggest that a hydroxyl group on silica plays important roles for the reaction with dissolved lanthanide metals. To make sure this, attempts were made to perform the reaction of triphenylsilanol with dissolved lanthanide metals in liquid ammonia as a model reaction. The IR spectra of triphenylsilanol before and after the reaction showed a decrease in the absorption intensity of hydroxyl group as the addition of lanthanide increased. It now seems quite certain that the dissolved lanthanide reacts exclusively with hydroxyl groups.

In Fig. 1, the strong absorptions were also observed at 3384, 3288, and 1552 cm^{-1}, which were assigned to amide ($-NH_2$) bound at lanthanide on the basis of reference spectra of amide metal complexes.[9] In the absence of lanthanide on SiO_2, these bands were not observed at all. For the reaction of SiO_2 with ytterbium, the absorptions of amide were observed and their intensity increased as the quantity of ytterbium added increased. Thus, the interpretation of these data gives an indication that the dissolved lanthanide in liquid ammonia selectively reacts with the surface hydroxyl groups of SiO_2 at low temperature to give at least the following species evolving hydrogen.

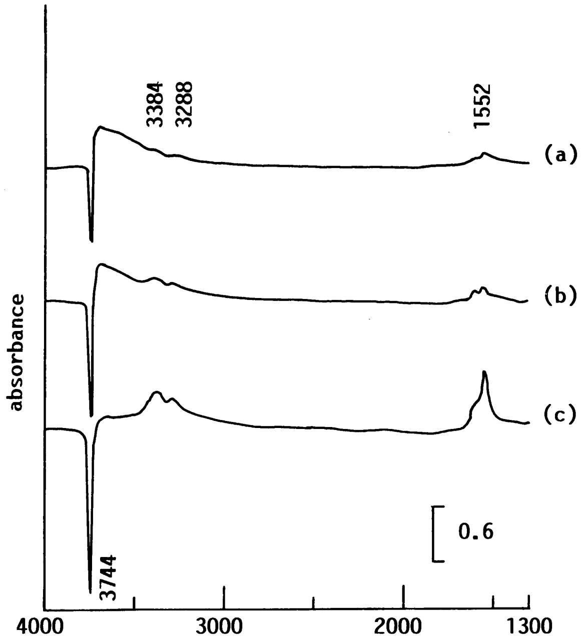
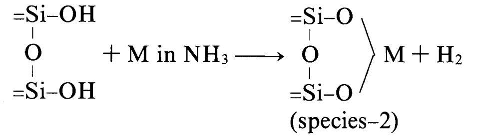


Fig. 1. IR spectra of Yb/SiO_2 with varied levels of Yb loading. Prior to the measurement the catalysts were briefly evacuated at 473 K. (a) 15 wt%, (b) 24 wt%, (c) 39 wt%.

$$\equiv\text{Si–OH} + \text{M in NH}_3 \longrightarrow \equiv\text{Si–O–M–NH}_2 + \text{H}_2 \qquad (1)$$

$$\text{(species-1)}\ \text{M} = \text{Eu or Yb}$$

Thus, the lanthanide is immobilized on SiO_2. Moreover, taking into account the evolution of gas, some of the species-2 may be simultaneously formed according to the reaction (2).



$$\begin{array}{c}=\text{Si–OH}\\ |\\ \text{O}\\ |\\ =\text{Si–OH}\end{array} + \text{M in NH}_3 \longrightarrow \begin{array}{c}=\text{Si–O}\\ |\\ \text{O}\\ |\\ =\text{Si–O}\end{array}\Big\rangle \text{M} + \text{H}_2 \qquad (2)$$

$$\text{(species-2)}$$

However, there is no evidence for the formation of the species-2.

The variation in the amount of surface hydroxyl groups with the temperature is attributed to dehydroxylation effects. The density of the surface hydroxyl groups as a function of the evacuation temperature has already been thoroughly investigated, which shows that the hydroxyl density with varied temperature pretreatment is almost independent of the silica type.[8,10] Besides free, isolated hydroxyl groups, bridged, perturbed hydroxyl groups are present on a hydroxylated silica surface. At ca. 1023 K only free, unpaired ≡Si–OH groups are present.[8] Considering the evacuation temperature of SiO_2 used, the surface density of hydroxyl group is estimated as about 1.5 OH per nm^2.[10] Therefore, the number of hydroxyl groups on SiO_2 (380 $m^2\,g^{-1}$) is determined. The loading of 13 wt% Eu and 15 wt% Yb roughly corresponds to the total amount of hydroxyl groups present on the surface of SiO_2 by assuming a lanthanide metal to a hydroxyl group ratio of 1 : 1 in the surface complex. However, this is not necessarily satisfied (Fig. 1), since there exist distribution and concentration of the different types of hydroxyl groups on the surface of silica.

As shown in Fig. 2(a)—(d), further, the absorption intensity of amides gradually decreased as the evacuation temperature of Yb/SiO_2 increased in the range of 295 to 723 K, and their absorptions almost disappeared upon heating at 723 K. Upon this thermal treatment the spectra of hydroxyl groups changed in intensity at the same time; thus, the hydroxyl groups were found to gradually regenerate to a some extent. This indicates the decomposition of the lanthanide species-1 through surface hydroxyl groups, simultaneously resulting in

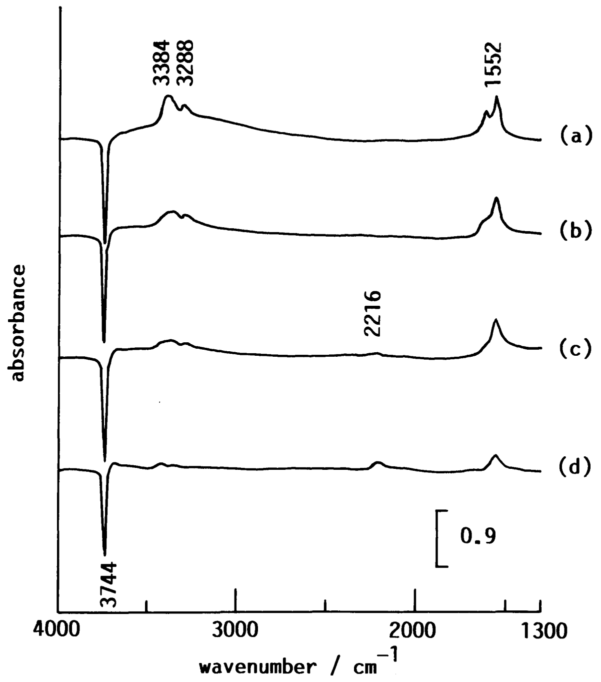


Fig. 2. IR spectra of 39 wt%-Yb/SiO$_2$ evacuated at elevated temperatures. (a) 295 K, (b) 473 K, (c) 573 K, (d) 723 K.

deactivation of Eu/SiO$_2$ and Yb/SiO$_2$ for the catalytic reactions (see the next section). It has been shown that the solutions of lanthanide metal in liquid ammonia decompose to form the diamide exclusively at low temperature, and finally, the nitride.[11] Thermal decomposition of Eu(NH$_2$)$_2$ or Yb(NH$_2$)$_2$ at 513—523 K gives the nitride EuN or YbN, respectively. A possible explanation for the results obtained is as follows; thus, during the thermal treatment the lanthanide species-1 decomposes to form the lanthanide nitride. However, the formation of the nitride could not be confirmed by X-ray diffraction (XRD) analyses, as described later.

Upon the thermal treatment in the range of 573 to 773 K, another absorption band appeared at 2180—2230 cm^{-1} (Fig. 2(c),(d)). The bands observed here are assigned to azides, which have been found to absorp in the same frequency range.[12] Wokaun et al.[13] have recently shown that the bands in the region between 1950 and 2350 cm^{-1} are identified as surface-bound azides $N{=}N{=}N^-$ for the adsorption of ammonia on Cu/Al$_2$O$_3$ at 423—643 K. These species are suggested to be possible precursors in the copper nitride formation, strongly supporting the possibility of the formation of lanthanide nitride via azide intermediates in the present system.

For all the samples studied, the XRD spectra exhibited negligible changes upon the loading of 10 to 39 wt% lanthanide; the spectra showed only the existence of the parent SiO$_2$. For the Eu/SiO$_2$ and Yb/SiO$_2$ samples, no XRD peaks assigned to lanthanides such as metal, diamide, nitride or double oxide were observed even in the high lanthanide-added region; the lanthanide seems to be highly dispersed on the SiO$_2$ surface.

Catalytic Activity. Their catalytic properties have been characterized by various reactions (Table 1). For all the reactions studied, SiO$_2$ itself showed negligible activities, but upon the addition of lanthanide the catalytic activity appeared even under the same reaction conditions. The behavior of a less readily reducible oxide such as SiO$_2$ should have been quite different with varied levels of lanthanide loading.[6] The variation of activity (expressed by a first-order rate constant k) for ethene hydrogenation as a function of lanthanide loading on SiO$_2$ is shown in Fig. 3. The activity abruptly increased in the loading range of more than 15—20 wt% lanthanide even though the influence of the pretreatment temperatures on the activity was observed. There was an apparent difference in their catalytic behavior between the low (<ca. 15 wt%) and high (>ca. 15 wt%) lanthanide-added samples.

As described above, for low lanthanide-added region the preferential reaction of lanthanide with hydroxyl groups on SiO$_2$ is expected. This reflects the catalytic

Table 1. Results of Various Catalytic Reactions over Eu/SiO$_2$ and Yb/SiO$_2$

Reaction	Reactant	Catalyst[a]	Activity	Product
			mmol min^{-1} (g-cat)$^{-1}$	%
Hydrogenation[b] (353 K)	Acetylene	35wt%-Eu/SiO$_2$	—	
	Acetylene	39wt%-Yb/SiO$_2$	—	
	Propyne	35wt%-Eu/SiO$_2$	—[d]	Allene
	Propyne	39wt%-Yb/SiO$_2$	—[d]	Allene
	1-Butyne	39wt%-Yb/SiO$_2$	—[d]	1,2-Butadiene (37), 2-Butyne (63)
	2-Butyne[e]	39wt%-Yb/SiO$_2$	1.0×10^{-4}	*cis*-2-Butene (76), 1-Butene (24)
Disproportionation[c] (298 K)	1,3-CHD[e]	13wt%-Eu/SiO$_2$[f]	9.2×10^{-3}	CHE (32), Benzene (68)
	1,3-CHD[e]	15wt%-Yb/SiO$_2$[f]	9.8×10^{-3}	CHE (38), Benzene (62)
	1,3-CHD[e]	35wt%-Eu/SiO$_2$	3.0×10^{-5}	CHE (14), Benzene (86)
	1,3-CHD[e]	39wt%-Yb/SiO$_2$	2.1×10^{-3}	CHE (43), Benzene (57)

a) Prior to the reaction the catalysts were evacuated at 773 K for 2 h. b) Alkyne=20 Torr, H$_2$=40 Torr, 1 Torr=133.322 Pa. c) 1,3-CHD=15 Torr. d) Only isomerization occurred. e) Isomerization simultaneously occurred. f) The catalysts were evacuated at 373 K for 2 h.

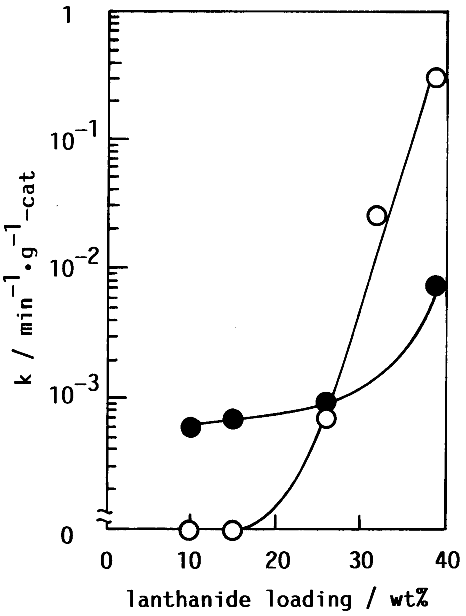


Fig. 3. Rate constant of ethene hydrogenation (373 K) vs. lanthanide loading (wt%). Prior to the reaction the catalysts were evacuated at 373 K (●) or 773 K (○) for 2 h: C_2H_4=20 Torr; H_2=40 Torr.

actions. The activity (● in Fig. 3) was almost proportional to the lanthanide loading in this range, indicating that the species-1 and/or 2 formed during the reactions (1) and (2) are operative for the hydrogenation of ethene. However, since the species-1 seems to be decomposed by the thermal treatemnt at 773 K, the activity (○ in Fig. 3) at low loadings is not observed. Upon contact with D_2, the exchange reaction of hydrogen between the amide ($-NH_2$) and gaseous D_2 readily occurred; IR spectra showed that the absorption bands of amide ($-ND_2$) at 2520 cm^{-1} began to appear above 373 K. This indicates that the catalyst has the ability to activate hydrogen molecules at 373 K, being consistent with the results of ethene hydrogenation.

The catalysts (13 wt%-Eu/SiO_2 and 15 wt%-Yb/SiO_2) exhibited high activity for the disproportionation of 1,3-cyclohexadiene (1,3-CHD) to benzene and cyclohexene (CHE) (Table 1). It has been shown that a number of homogeneous and heterogeneous catalyst systems are effective for the disproportionation.[14] The disproportionation rates of 13 wt%-Eu/SiO_2 and 15 wt%-Yb/SiO_2 at 298 K were comparable with that of the metallic nickel catalyst,[15] being fairly active for this reaction. The simultaneous dehydrogenation of 1,3-CHD to benzene increased the composition of benzene in the products (Table 1). Conversely, the catalysts with high loadings were less active. This strongly suggests that the species-1 or 2 is important to determine the disproportionation activity.

The SiO_2 catalysts with the loading of 20—39 wt% lanthanide exhibied different catalytic behavior. Evidently, for 39 wt%-Yb/SiO_2 the lanthanide exists sufficiently in excess for the total surface hydroxyl groups present on the silica. The sudden increase in hydrogenation activity at a certain loading of lanthanide suggests that the first portion of added lanthanide is consumed for the reaction with surface hydroxyl groups and sacrificed for the elevation of the activity. After this passivation of the surface is complete, subsequent lanthanide deposits on SiO_2 in an active form. From the results of lanthanide loading dependence for activity (Fig. 3), it seems that the loading of 15—20 wt% lanthanide roughly corresponds to the consumption of surface hydroxyl groups. Further, these values are very close to those estimated by assuming a 1 : 1 ratio of a lanthanide metal to surface hydroxyl group in the surface complex on the basis of the surface density of hydroxyl groups (1.5 OH per nm^2). As mentioned below, the catalytic behavior of the catalysts with high lanthanide loadings was very similar to that observed for the lanthanide metal particles which were prepared by the metal vapor technique in earlier works.[16] Therefore, in the catalysts with high loadings an excess of lanthanide present appears to be highly dispersed in almost metallic form, not amide or nitride form.

As shown in Fig. 3, the activity of ethene hydrogenation at high loadings was high by a factor of 20 or over 1000 compared to that at low loadings, and the specific activity was close to that for lanthanide metals.[16] Further, 39 wt%-Yb/SiO_2 discriminated between internal and terminal C–C triple bonds for the hydrogenation of alkyne (Table 1); thus, 2-butyne was readily converted to *cis*-2-butene in high selectivity at 353 K, whereas 1-butyne, propyne, and acetylene were not hydrogenated at all under the same conditions. The type of hydrogen addition for terminal and internal $C \equiv C$ bonds by the lanthanide was completely contrary to that of conventional transition-metal catalysts.[17] The activity for the hydrogenation at 353 K was very close to that observed for the ytterbium metal catalyst and the catalytic behavior was also very similar in the product selectivity (*cis*-2-butene: 76% and 1-butene: 24%).[18] The yield of *trans*-2-butene was negligible. Lanthanide surface gave preferential *cis*-2-butene formation. Relative yields of butene isomers formed by lanthanide-catalyzed butyne hydrogenation depend on the conformational characteristics of adsorbed precursors; no isomerization of butene takes plalce before desorption. These catalytic behavior is consistent with that observed for lanthanide metal catalysts.[16]

We can give the evacuation temperature of the catalyst as one of those affecting the catalytic properties. For the low and high loading catalysts, there was a quite difference in the dependence of the pretreatment temperature on activity. For 13 wt%-Eu/SiO_2 and 15 wt%-Yb/SiO_2, an evacuation temperature of 573 K or above led to a rapid decrease in activity of the

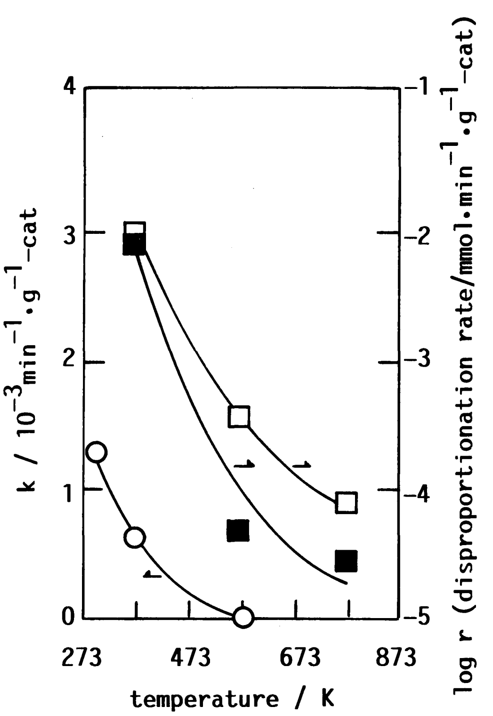


Fig. 4. Effect of evacuation temperatures on the activity of the hydrogenation (373 K) and disproportionation (298 K) over 13 wt%-Eu/SiO_2 (■) and 15 wt%-Yb/SiO_2 (○, □). The catalyst was evacuated for 2 h before use. Hydrogenation: C_2H_4=20 Torr, H_2=40 Torr. Disproportionation: 1,3-CHD=15 Torr.

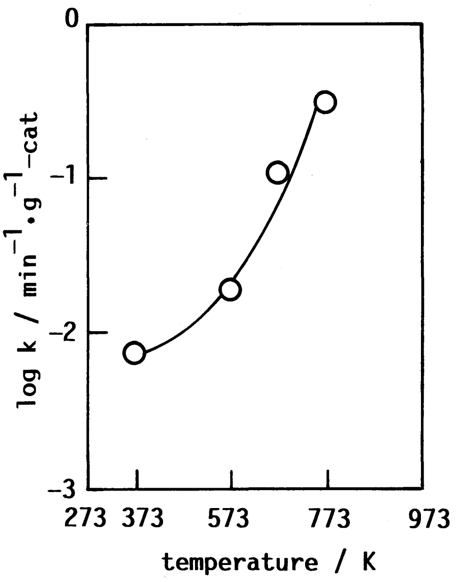


Fig. 5. Effect of evacuation temperatures on the activity of ethene hydrogenation (373 K) over 39 wt%-Yb/SiO_2. The catalyst was evacuated for 2 h before use. C_2H_4=20 Torr, H_2=40 Torr.

hydrogenation and disproportionation reactions to almost zero (Figs. 3 and 4). This probably corresponds to the decomposition of the species-1 by the thermal treatment, as shown by IR spectra. The evacuation treatment at elevated temperature was often accompanied by an observable color change of the catalyst, indicating the variation in the state of lanthanide present on the oxide. For example, for 15 wt%-Yb/SiO_2 the loading of lanthanide on SiO_2 gave a light green solid, which turned colorless on evacuation above 573 K and was completely deactivated at the same time. For 39 wt%-Yb/SiO_2, the hydrogenation activity increased with an increase in the temperature of the evacuation treatment conducted before the reaction (Fig. 5). It increased by more than two orders of magnitude with the temperature of 373 to 773 K. This is probably due to release of adsorbed ammonia or amide on the catalyst and/or changes in the surface or crystal structure with an increase in the evacuation temperature. However, the latter has not been confirmed by XRD analyses.

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