Hydrogenation of 1,3-Butadiene over CaO Catalyst Treated with Methanol

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When calcium oxide was treated with methanol at low temperature, calcium methoxides i.e., calcium dimethoxide and, calcium hydroxide methoxide, could be easily formed. The catalyst produced by the thermal decomposition of these compounds exhibited remarkably high activity to the hydrogenation of 1,3-butadiene. With the aim to investigate the cause of the high activity, two other calcium oxide catalysts were used for a comparison. The cause was ascribed to the formation of a large amount of electron-donating sites, including both basic ones and those with a high surface area.

Solid base catalysts, such as CaO and MgO, are known to catalyze the isomerization of butenes,[1] the dehydrogenation of alcohols,[2] the hydrogenation of dienes,[3-6] as well as H_2-D_2[7] and CH_4-D_2[8,9] exchange reactions. Tanaka et al.[3] pointed out that CaO prepared by the evacuation of $Ca(OH)_2$ above 1073 K gave a high catalytic activity for the hydrogenation of 1,3-butadiene at 273 K. Miyahara et al.[4] have also shown that the maximum activity for the hydrogenation of 1,3-butadiene is obtained when MgO is prepared around 1073—1273 K under vacum. Thus, treatment at higher temperatures than 1073 K under vacuum are necessary for the appearance of hydrogenation activity. We recently found a remarkably highly active CaO catalyst for the hydrogenation of 1,3-butadiene. The preparation method of the catalyst does not require a higher temperature than 1073 K. By heating under vacum at a rather lower temperature (873 K) after a treatment with methanol, a very high activity could be developed. Why such a high activity appeared through such a simple method as a methanol treatment is a very interestng problem. The aim of this paper is to answer the above question by comparing the three kinds of CaO catalysts.

Experimental

Materials. Three kinds of calcium oxide catalysts were used for a comparion. The calcium oxide purchased from Wako Junyaku Co. was calcined at 1173 K for 15 h in air in order to decompose the calcium carbonate and hydroxide impurities into CaO. This is called CaO(I). The second catalyst, CaO(II), was prepared by the decomposition of $Ca(OH)_2$, which was formed by refluxing a CaO(I) suspension in water for 3 h. In place of water CaO(I) was suspended in methanol, followed by stirring for 24 h at room temperature; methanol was then removed to dryness in an evaporator at ca. 333 K. This catalyst is called CaO-M. All of the catalysts were stored in a desiccator. Just before the reaction all of the catalysts used were slowly heated *in situ* under a vacuum and increasing temperature at a rate of 5 K min^{-1} to 873 K; this temperature was maintained for 1 h. This procesure is abbreviated as a pretreatment hereafter. The surface areas of CaO(I), (II) and CaO-M were measured by the BET method, giving 7.71, 55.2 and 139 $m^2 g^{-1}$, respectively.

1.3-Butadiene (Takacio Co., more than 99% purity) was purified by a repeated freeze-and-thaw technique. Hydrogen with a purity of more than 99.9999% (Takachio Co.)was dried using a trap containig a moleculare sieve (5A) kept at 77 K.

Reaction Procedures. The reaction was carried out in an all-glass static reactor with a volume of ca. 225 ml in a closed recirculation reactor equipped with a sampling manifold. A weighed amount of catalyst specimen (0.05 g as CaO) was placed in a qualtz glass reactor. The weight loss of CaO(II) and CaO-M due to the pretreatment was examined beforehand. A typical hydrogenation mixture of 1,3-butadine : hydrogen=50 : 100 Torr, (1 Torr=133.322 Pa) was used in the reaction. The reaction was carried out at 273 K, and the reaction products analyzed by a gas chromatograph equipped with a 5 m column of VZ-7 at 313 K

IR Measurement, A thin disk of the catalyst sample was treated using the same procedure as in the pretreatment. The IR spectra were recorded with a JASCO Model 810 spectrometer without exposing the sample to air.

ESR Measurement. The ESR spectra were recorded on a Varian E-9 spectrometer (X-band with 100 kHz field modulation) at room temperature. The sample was prepared in an apparatus equipped with both greaseless stop valves and a trap used to cut the vapor from grease. For the *g*-value and spin concentration calibration, DPPH was used as a standard probe in a dual cavity. The relative concentration was estimated as being the ratio of the spin concentration per unit gram of sample vs. the spin concentration of DPPH. An approximate method to measure the spin concentration was adopted comprising the product of the square of the line width and the peak-to-peak height in order to estimate the area under the ESR absorption curve.[10] The electron-donating property of the catalysts was examined with the radical produced by the adsorption of nitrobenzene.

The sample was placed in a qualtz adsorption chamber equipped with a side ESR tube; at room temperature nitrobenzene vapor was adsorbed for 30 min and then evacuated for 15 min at the same temperature. The proper amount of the sample was transfered into the tube and then sealed for an ESR measurement.

XPS Measurement. The X-ray photoelectron spectra were recorded at room temperature on a Ulvac-Phi Model UP ESCA and Auger spectrometer using monochromatic Mg-α exciting radiation with an energy of 1253.6 eV. The spectrometer vacuum was better than 10^{-9} Torr. A thin

disk pressed from powder was treated using the same method as in the pretreatment. The Cls level of a trace of contaminant carbon, 285.0 eV, was taken as a reference.

Basicity Measurement. A CaO-M catalyst after the pretreatment showed a slight dark-gray color. Two other calcium oxide catalysts were white. Consequently, it was impossible to measure the surface basicity of CaO-M by the indicator method. Therefore, the basicity was estimated from the irreversible adsorption amount of CO_2. CO_2 was adsobed at 273 K on the catalyst sample; after attaining equilibrium, it was evacuated at 873 K for 1 h. Again, CO_2 was adsorbed on the sample at 273 K at the same presure as in the case of the initial adsorption. The irreversible adsorption amount of CO_2 was thus estimated from the difference of the adsorbed amount during the initial and secondary adsorption.

Results

Hydrogenation of 1,3-Butadiene. Carbon dioxide and oxygen inhibited the reaction when they were adsorbed on the catalysts. Hydrogenation of 1,3-butadiene over three kinds of CaO catalysts was carried out at 273 K. The conversion vs. the reaction-time plots are shown in Fig. 1. Though no reaction proceeded on CaO(I), the activity appeared on CaO(II) and CaO-M. Especially CaO-M catalyst exhibited a remarkably high activity, while attaining a conversion of 100% in only 2—3 min. Though the activity of CaO(II) was less than that of CaO-M, the conversion reached ca. 100% within 40 min after starting the reaction. The product distribution is shown in Table 1, showing that *trans*-2-butene was preferentially formed on both CaO(II) and CaO-M catalysts. This result agrees with those of Miyahara et al.[4] or of Shima and Yamaguchi.[5] The equilibrium composition of the hydrogenation products at 273 K can be calculated as 1-butene : *trans*-2-butene : *cis*-2-butene=2.3 : 76.1 : 21.6 (%). It can therefore be supposed that the experimental results regarding both CaO(II) and CaO-M catalysts nearly attained the thermodynamic equilibrium state due to the very high reaction rate. The conversion to 2-butene was higher than 96%, indicating that a 1,4-addition of hydrogen on 1,3-butadiene dominated. Strictly, it can also be considered that 1-butene was formed by a 1,2-addition during the initial stage, and then rapidly isomerized to 2-butenes, since the reaction rate was so high. However, from the results concerning the reaction of 1,3-butadiene and deuterium,[6] the 1,4-addition reaction predominantly proceeds on solid-base catalysts, such as MgO and CaO. It is consequently rational to regard that the hydrogenation in this study proceeded by the 1,4-addition mechanism. The reaction temperature of hydrogenation was so low that no further hydrogenation to butane could proceed, although CaO-M was the most active catalyst, as already described. However, if the reaction temperature was increased to as high temperature as 523 K,[11] the formation of butane would be detected. Also, in this study the rate from butenes to butane appears to be remarkably slow compared to the hydrogenation of butadiene. The initial rates of the hydrogenation, which were obtained from a decline of the linear region in 1.5-min intervals from the start of the reaction in the curve of the conversion vs. reaction time plots, are shown in Table 2. The rate on CaO-M was 2-times greater in magnitude than that on CaO(II).

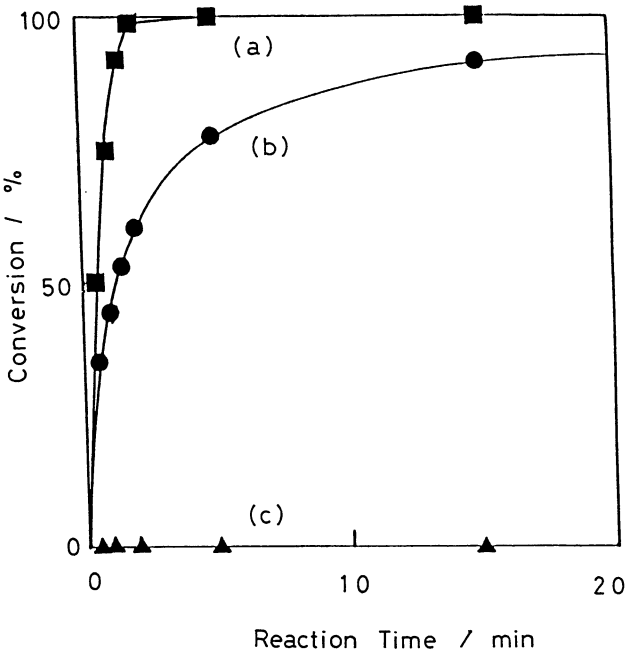

Fig. 1. The plot of conversion of 1,3-butadiene vs. reaction time.
(a) CaO-M, (b) CaO(II), (c) CaO(I).

Table 1. Product Distribution in Hydrogenation of 1,3-Butadiene

Catalyst	Reaction time/min	Conversion	Product/%		
		%	1-Butene	*trans*-2-Butene	*cis*-2-Butene
CaO-M	2	98.8	3.65	72.4	24.0
	5	100	3.26	71.8	25.0
	15	100	3.09	72.6	24.3
CaO(II)	2	60.8	3.73	72.4	22.9
	5	76.5	3.43	72.7	24.3
	15	90.9	3.16	72.3	24.6

Table 2. The Relative Spin Concentration and Initial Rate of the Hydrogenation on the Three CaO Catalysts

Catalyst	Initial rate	Relative spin concentration
	mmol g^{-1} min^{-1}	g^{-1}
CaO-M	8.93	3.59×10^{2} a)
CaO(II)	4.20	1.45×10^{2}
CaO(I)	0	4.01×10^{-2}

a) The caliblated value with the relative concentration of graphite carbon.

XRD Measurements. CaO(I) exhibited only CaO peaks as expected. Though before the pretreatment, CaO(II) mainly comprised $Ca(OH)_2$, after heating at 873 K under vacuum it turned to CaO accompanyed by a small amount of $Ca(OH)_2$, although the crystal structure was somewhat distorted. In the case of CaO-M, the XRD pattern exhibited relatively good crystallinity before the pretreatment, in which the peaks corresponded to CaO, $Ca(OH)_2$ and calcium dimethoxide, ($Ca(OCH_3)_2$) or calcium hydroxide methoxide ($Ca(OH)(OCH_3)$) were observed, as shown in Fig.2. However, $Ca(OH)(OCH_3)$ could not be distinguished from $Ca(OCH_3)_2$ by XRD. By the pretreatment the crystal state was remarkably distorted to be amorphous. Whether other alcohols, (for instance, ethanol and propanol) could similarly react with calcium oxide or not was examined. No calcium alcohoxides of ethanol and 2-propanol could be produced. Only the CaO peak was detected by XRD.

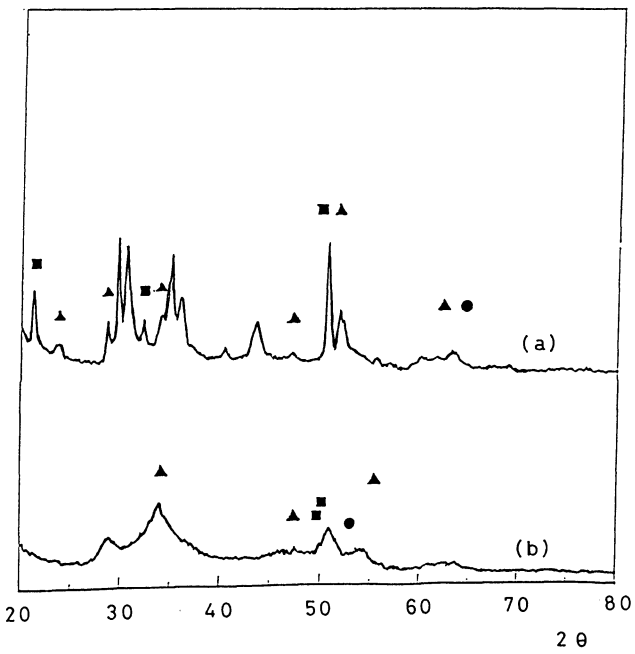

Fig. 2. XRD data of CaO-M (a) before (b) after the pretreatment.
●: CaO, ▲: $Ca(OH)_2$, ■: $Ca(OCH_3)_2$.

IR Measurement. Typical IR spectra of CaO-M measured after the treatment at room temperature and from 373 to 873 K at intervals of 100 K for 30 min under vacuum are shown in Fig. 3. From this data the formation of $Ca(OCH_3)_2$ and $Ca(OH)(OCH_3)$ could be clearly confirmed; i.e. the absorption bands at 1076 and 3640 cm^{-1} were assigned to $Ca(OH)(OCH_3)$[12] and those at 1079, 1159, 1410, 1472, 2072, 2192, 2306, 2592, 2777, 2818, 2864, and 2929 cm^{-1} also assigned to $Ca(OCH_3)_2$[13] (see Fig. 3 (a), (b), and (c)). It can be seen that both $Ca(OCH_3)_2$ and $Ca(OH)(OCH_3)$ were stable until 773 K, then gradually decreasing their strength with increasing temperature; at 873 K they were almost decomposed into CaO, leaving a small amount of $Ca(OH)_2$ (see Fig. 3(d)) which could be derived from the band at 3720 cm^{-1} shifted from 3670 cm^{-1}. The band shifted to 3720 cm^{-1} exhibits an isolated OH on the surface.[14] It is rather surprising that calcium methoxides can be eas-

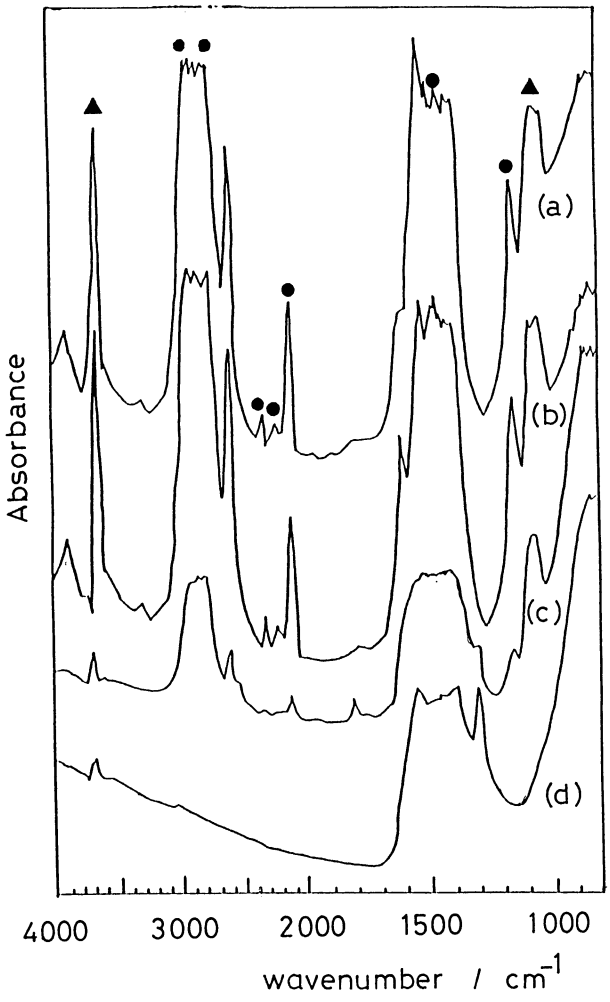

Fig. 3. IR spectra change of CaO-M treated under vacuum, (a): at room temperatures, (b): 573 K, (c): 773 K, (d): 873 K.
●: $Ca(OCH_3)_2$, ▲: $Ca(OH)(OCH_3)$.

ily produced by treatment with methanol at a relatively low temperature and are stable against heat. IR spectra of CaO(I) and (II) are also shown in Fig. 4 for a comparison. The bands between 500 and 1000 cm^{-1} characteristic for CaO, although the assignment was not known. As can be seen in CaO(II), the band at 3670 cm^{-1} can be assigned to basic OH, and that between 1300 and 1600 cm^{-1} probably to the OH of $Ca(OH)_2$.

EPMA (Electron Probe Microanalysis). The surface states of CaO(I),(II) and CaO-M were examined by EPMA. On CaO-M the deposition of free carbon was detected at the wavelength position of ca. 11.5 Å, which would cause the appearance of the dark-gray color on the catalyst after the pretreatment. On CaO(I) and (II) carbon deposition could not be entirely observed. It is therefore clear that the carbon on CaO-M is deposited by the decomposition of calcium methoxides.

ESR. The ESR spectra of CaO(I) and (II) exhibited nothing, except for that due to a Mn impurity.

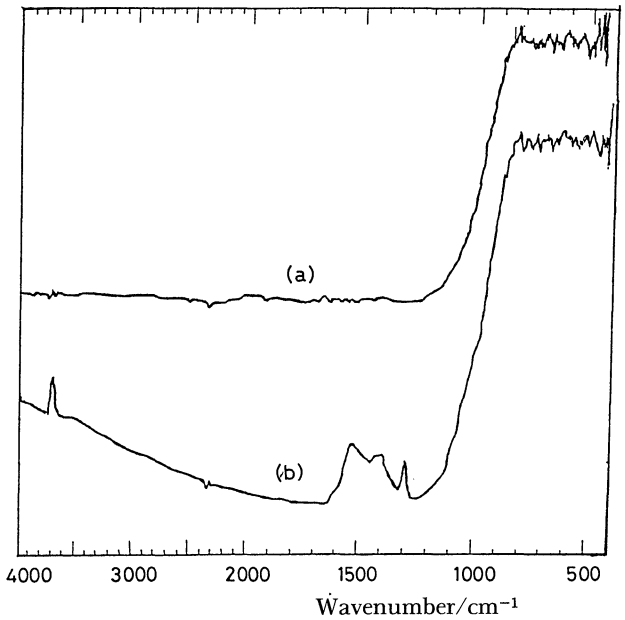

Fig. 4. IR spectra of (a) CaO(I) and (b) CaO(II) after the pretreatment.

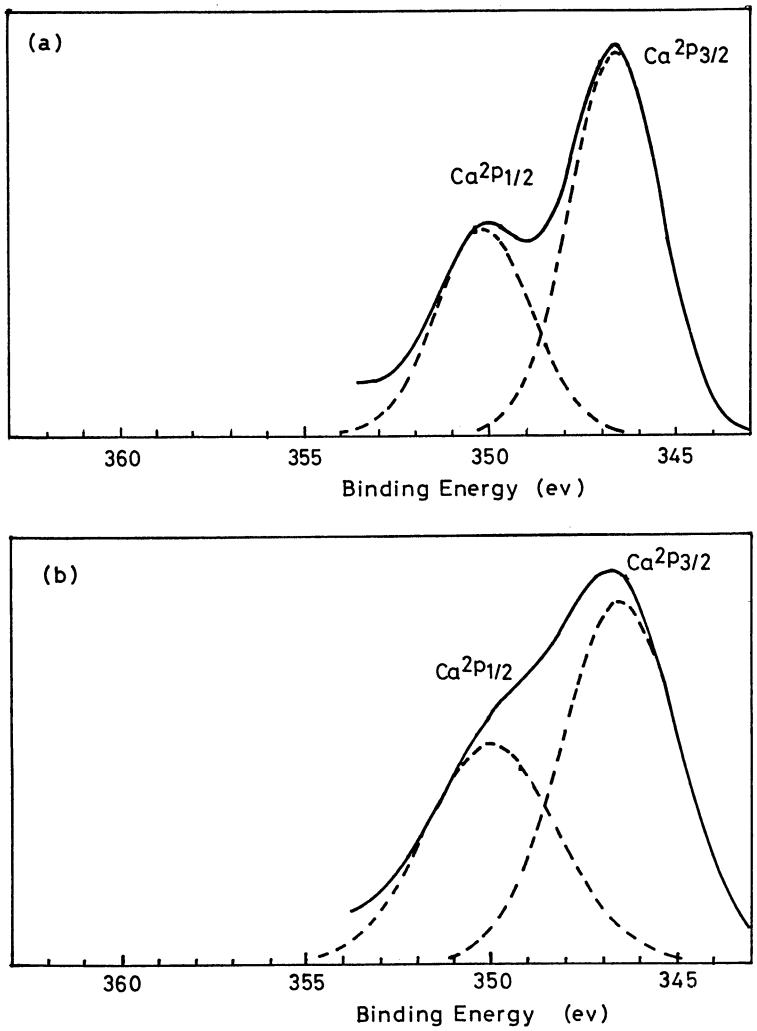

Fig. 5. XPS spectra of Ca $2P_{1/2}$ and Ca $2P_{3/2}$ of (a) CaO-M and of (b) CaO(I).

On the other hand, CaO-M gave a symmetrical Gaussian-shape signal at $g=2.0033$, which was assigned to graphite.[15,16] The relative spin concentration of the graphite carbon radical was estimated to be 4.31×10^2 per g of CaO-M. When butadiene, H_2 or CO_2 (being catalyst poison) was adsorbed on CaO-M, the carbon-radical signal did not entirely vary. This fact indicats that the carbon radical is not responsible for the hydrogenation. This conclusion was also derived from the fact that the carbon radical did not emerge on the CaO(II) catalyst. Therefore, other active sites should be expected to exist on the catalyst surface.

As described previously such electron-accepting molecules as oxygen inhibit hydrogenation, from which the electron-donating sites on CaO-M and CaO (II) may be active centers. It is further well-known that calcium oxides exhibit surface basicity. The basic sites are considered to be O^{2-} in the low-coordinatation sites.[17,18,19] Other electron-donating sites with the paramagnetic property, (for instance O^-) can be examined by an ESR measurement of the radical formed by the adsorption of an electron-accepting molecule, such as nitrobenzene.[14,20] When nitrobenzene was adsorbed on the three calcium oxide catalysts a relatively symmetrical signal with $g=2.0048$ could be detected. This also indicates that nitrobenzene adsorbs on graphite carbon on CaO-M to form its radical. By a comparison of the concentration of the nitrobenzene radical with that of DPPH, the relative spin concentrations of the electron-donating sites of these three catalysts were obtained (Table 2). The concentration of CaO-M is a value from which the value for the graphite carbon radical is subtracted. The concentration of CaO(II) and CaO-M were 3600- and 9000-times greater in magnitude than that of CaO(I). Though the existence of electron-donating sites can be detected in CaO(I), there is no hydrogenation activity. This may be due to the small amount of electron-donating sites.

XPS. Though the spectra of $Ca2P_{3/2}$, $Ca2P_{1/2}$, O1s and C1s showed similar binding energies in all samples, the size and shape of the spectra were different to some extent. In Figs. 5 and 6 the spectra derived from CaO(II) were omitted because of the similar behaviors to that of CaO-M and CaO(I). As shown in Fig. 6, the peak of O1s at 532.0 eV can be assigned to O^- derived from OH.[21,22] The peak assigned to O^{2-}, which can be seen at the position of 529.5 eV,[21,22] can not be clearly detected in Fig. 6. This seems to be due to an overlapping by the large O^- peak. The narrowest full width at half maximum (fwhm) of $Ca2P_{3/2}$, as the typical calcium band, O1s and C1s were measured and the ratios of the fwhm value of $Ca2P_{3/2}$ to O1s and to C1s, respectively, were calculated (Table 3). The ratio of $Ca2P_{3/2}$/O1s in CaO-M was the smallest, and increased in the order of CaO(II) and CaO(I). This fact indicates that the surface of CaO-M has somewhat more oxygen excess than does CaO(I) and (II). On the other hand, the ratio of $Ca2P_{3/2}$/C1s of CaO-M is smaller than that of the other two CaO catalysts. This fact indicates that carbon is deposited on the surface of CaO-M, which also agrees with the EPMA results.

Table 3. The Ratio of fwhm Values of $Ca2P_{3/2}$ to O1s and C1s

Catalyst	$Ca2P_{3/2}$/O1s	$Ca2P_{3/2}$/C1s
CaO-M	1.05	1.18
CaO(II)	1.09	1.82
CaO(I)	1.12	1.84

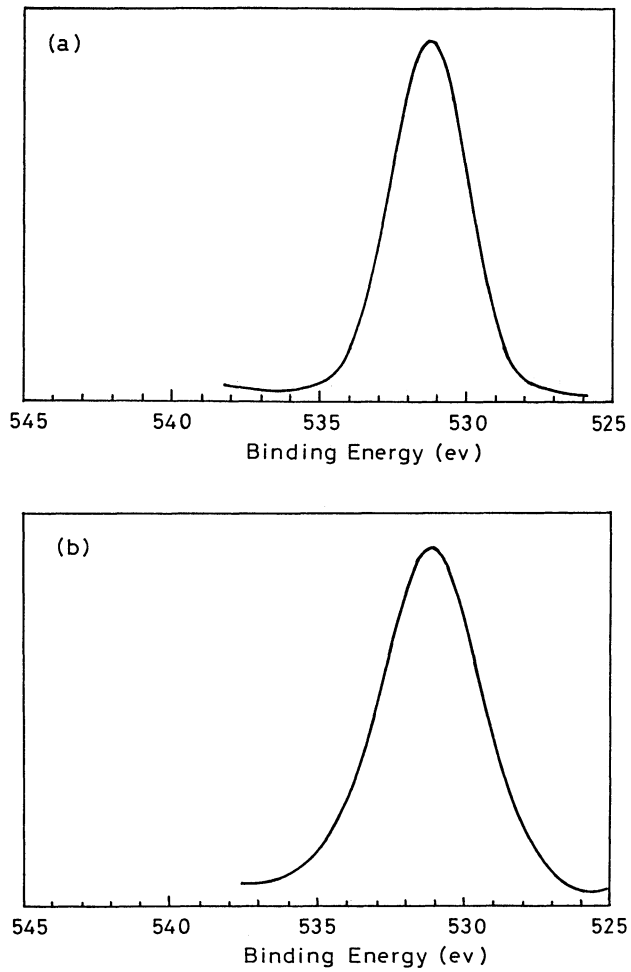

Fig. 6. XPS spectra of O1s of (a) CaO-M and of (b) CaO(I).

Basicity. A measure of the basicity from the amount of irreversible adsorption was obtained for the three CaO catalysts. The basicity of CaO-M, CaO(II) and (I) were 0.767, 0.277, and 0.019 mmol g^{-1}, respectively. As expected, the basicity of CaO-M was the largest. The correlation of the basicity between CaO-M and CaO(II) was 2.47 to 1 and that between the initial rates (Table 2) was 2.18 to 1. A relatively good

correlation could be obtained.

Discussion

Calcium oxide reacts with methanol to form calcium dimethoxide (I) and calcium hydroxide methoxide (II), as confirmed by XRD and IR measurements. These reaction schemes are described as follows, concurrently forming calcium hydroxide:

$$2CaO + 2CH_3OH \longrightarrow Ca(OCH_3)_2 + Ca(OH)_2, \quad \text{(I)}$$

and

$$CaO + CH_3OH \longrightarrow Ca(OH)(OCH_3). \quad \text{(II)}$$

When CaO treated with methanol was heated at 673 K under vacuum, the calcium methoxides remained. The CaO in this state did not entirely reveal any hydrogenation activity. This fact suggests that these calcium methoxides have no direct connection with activity. However, by a heat-treatment at 773 K under vacuum, in which the decomposition of calcium methoxides seemed to vigorously occur, a slight hydrogenation activity began to appear. At a temperature of 873 K most of the calcium methoxides converted to CaO, and remarkable activity was found. This fact indicates that the active sites are produced by the decomposition of calcium methoxides into CaO. The preparation of CaO by the decomposition of calcium methoxides is similar to the process in the sol-gel method. Generally, this method accompanying the hydrolysis of metal alcohoxides and calcination at a relative low temperature has been used to obtain both ceramics[23] and carriers[24] of high purity and activity; there has, however, been no report concerning a method to prepare highly active catalysts having a high surface area by a direct decomposition of metal alcohoxides.

Calcium hydroxide also showed activity due to a treatment at 873 K under vacuum, although the activity was low, due to an inadequate decomposition of $Ca(OH)_2$ at that temperature. As indicated in the literature,[2] it may be necessary to perform treatments at a temperature higher than 1073 K under vacuum. Martens et al [25] pointed out that the thermal decomposition of $Mg(OH)_2$ under vacuum released water and hydrogen in the temperature range, 570—970 K, leaving O^- and O^{2-} on the surface. Also, in the case of $Ca(OH)_2$, water and hydrogen are released, forming O^- and O^{2-} sites at the same time. In the case of CaO-M CH_3OH, CH_3OCH_3, and other compounds including water, CO, and hydrogen are probably released, although the decomposition process of calcium methoxides has not yet been clarified yet. Regarding the decomposition process of calcium methoxides, the growth of crystalization into CaO is probably suppressed by the release of the decomposed gases, leading to the high surface area of CaO. At the same time, it can be considered that some extent of the point defects accompanying the low coordination sites located at the edges and corners on a surface are formed. This consideration is rational, since CaO-M exhibited a distorted XRD pattern (see Fig. 2) and the surface area increased greatly. By the formation of point defects and low coordination sites, basic sites (i.e., the lattice O^{2-} and electron-donating sites accompanied by a paramagnetic property) are produced on the surface. As previously mentioned, since hydrogenation is ceased by the adsorption of CO_2, the basic sites on the surface are responsible for the hydrogenation; i.e., the O^{2-} sites are active centers. The O^- species are derived from the OH which remains on the surface in the undecomposable state, or which is derived by the adsorption of a proton—an abstracted from, for instance, hydrocarbon—on O^{2-}.[21,22] In this case, the former can be related with the formation of O^- sites. It is known that by XPS O^- and the lattice O^{2-} can be distinguished.[21,22] As shown in Fig. 6, however, the contribution of O1s of O^- at 532.0 eV was so large that the O^{2-} peak could not be found at 529.5 eV. Consequently, though there seems to be no O^{2-} sites on the surface, since CO_2 adsorption could be detected as a measure of the basicity, there must be O^{2-} sites (although the sites could not be clearly found in XPS). Iizuka et al.[14] have suggested that a nitrobenzene radical measurement revealed the property of the reducing sites on the surface and Kijenskii et al.[20] mentioned the property of the one-electron donating sites, although the detailed properties of both sites are not yet well known. If the reducing or one-electron donating sites are O^-, nitrobenezene can be adsorbed on the sites to form the nitrobenzene radical. In our study the relative spin concentration of nitrobenzene and DPPH of the three CaO catalysts were obtained (Table 2). The correlation between the relative spin concentration in the ESR measurement and the initial rate of hydrogenation on both CaO-M and CaO(II) catalysts were sought. The ratios of the relative spin concentration and the initial rate were 1 : 2.48 and 1 : 2.13, respectively. A good correlation between them was obtained. The initial rates, basicity and relative spin concentrations on CaO-M and CaO(II) per unit surface area were obtained as 6.4×10^{-2}, 7.6×10^{-2}, (mmol m^{-2} min^{-1}), 5.0×10^{-3}, 5.5×10^{-3} (mmol m^{-2}), and 2.6, 2.6 (m^{-2}), respectively. Since relatively good correlations between the rates and basicity or spin concentration per unit surface area were also found, it can be considered that the active sites on CaO-M and CaO(II) for hydrogenation consist of the same kind of sites.

It is suspected that the O^- sites are the active center. This conclusion agrees with the fact that Inoue and Yasumori[21] assumed that the active center of the hydrogeantion of ethylene would be O^-. From the results of the basicity measurement the basic sites were correlated with the initial rate, indicating that the

basic sites are also another active center. Especially in the case of CaO-M, a large amount of the active center can be produced. From the results of XPS, it was found that fwhm values of $Ca2P_{3/2}$ and O1s of the three catalysts decrease in the order CaO(I), (II) and CaO-M (see Table 3). This result is responsible for the presence of the excess amount of O^- sites on the CaO-M catalyst, which results in the high activity. It may be concluded that the hydrogenation of 1,3-butadiene proceeds at both basic and paramagnetic sites (i.e., O^{2-} and O^-), which both can be derived from the decomposition of calcium methoxides that have a strong effect on hydrogenation.

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