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Catalysis by Alkaline Earth Metal Oxides. III. X-Ray Photoelectron Spectroscopic Study of Catalytically Active MgO, CaO, and BaO Surfaces

Yasunobu INOUE* and Iwao YASUMORI

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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X-Ray photoelectron spectroscopy was used to reveal the surface states of MgO, CaO, and BaO oxides, which are catalytically active for ethylene hydrogenation. The catalytic activity of CaO exposed to H_2O changed with an increase in the temperature of evacuation in a way similar to that of $Ca(OH)_2$ decomposed by heat treatment. The photoelectron spectrum of CaO evacuated at 1223 K showed a peak of O 1s at 529.6 eV, while those of Ca $2p_{3/2}$ were at 346.3 eV and Ca $2p_{1/2}$ at 349.8 eV. The adsorption of H_2O at room temperature gave rise to an additional peak of O 1s at 532.4 eV and one of Ca $2p_{3/2}$ at 348.6 eV, which were attributed to a Ca–O–H structure. With an increase in the temperature of evacuation from 553 to 1053 K, at which the catalytic activity attained a maximum, the latter O 1s peak shifted to the lower binding-energy side by 0.4 eV, and the corresponding Ca 2p peak became broader. These spectral variations were ascribable to the formation of O^- species. Evacuation above 1273 K destroyed both the catalytic activity and characteristic peaks. BaO provided three O 1s peaks, at 528.5, 530.6, and 532.1 eV, after evacuation at 1373 K; these peaks were assigned to lattice oxygen of the oxide, O^-, and OH^- species respectively. The Ba 4d spectra showed correspondingly superposed peaks. The XPS peak due to O^- was observed only when BaO was evacuated at temperatures high enough to generate the catalytic activity. Such spectral features were less pronounced in the case of MgO. The structural analysis of CaO showed that the coordinatively unsaturated cations also play a role in the catalytic hydrogenation. On the basis of these findings, it was concluded that a combined structure of O^- and the cations is responsible for the hydrogenation activity.

It has been recently established that alkaline earth metal oxides became catalytically active for the hydrogenation of olefins and dienes when the oxides are subjected to heat treatment *in vacuo* within definite ranges of temperature;[1] in the case of olefin hydrogenations, the temperature ranges for activation were 1200—1400 K for MgO, 850—1200 K for CaO and 1200—1400 K for BaO. In our previous studies,[2,3] the mechanism of ethylene hydrogenation on such thermally activated CaO[2] and MgO[3] was analyzed on the basis of the detailed kinetics as well as the deuterium distributions in the reaction with D_2. In view of the similarities in the kinetic behavior of the reactions on the two oxides, we predicted the presence of active sites possessing common features in their structures and nature.

The surface states of alkaline earth metal oxides, especially MgO, and their changes upon the adsorption of electron-donor or acceptor molecules have been extensively studied by means of ESR and IR techniques,[4] but the information so far accumulated is not necessarily definitive in elucidating the catalytic behavior of the oxides described above. Thus, the present study was undertaken in order to characterize the surface states of catalytically active MgO, CaO, and BaO oxides by X-ray photoelectron spectroscopy (XPS), which is capable of revealing the electronic state of metals and oxides. A few experiments using XPS have so far been done on alkaline earth metal oxides in connection with their catalytic properties.[5] The most interesting aspect of the catalytic behavior of these metal oxides is that the activity is lost by heat treatment at temperatures higher than the activation range, but can be recovered by exposing the oxides to water vapor and by then re-evacuating at temperatures in the activation range. Since these phenomena well reflect the characteristics of the active sites present on the oxides, it is important to investigate the changes in the surface states of the oxides with H_2O-adsorption and subsequent evacuation at various temperatures. The present work was mainly concentrated on CaO because its catalytic properties were well clarified in a previous study.[2] Scanning-electron microscopic observation and X-ray diffraction were also employed for the structure analysis.

Experimental

The X-ray photoelectron spectra were recorded at room temperature on a Hewlett-Packard 5950A ESCA spectrometer, using monochromatic Al $K\alpha$ exciting radiation. The magnesium, calcium, and barium oxides were prepared from the respective hydroxides. The magnesium and calcium hydroxides of an extra pure grade were the same as those used in the previous kinetic studies.[2,3] Barium hydroxide and barium oxide of an extra pure grade were purchased from Wako Chemical Ind. and the Rare Metallic Co. respectively. The hydroxides, after being pressed into discs and placed on a recessed quartz plate, were transferred into the preparation chamber of the spectrometer and subsequently subjected to *in situ* decomposition into the respective oxides and then to prolonged evacuation at various temperatures up to 1400 K in a vacuum below 3×10^{-7} Torr (1 Torr=133.3 Pa). For H_2O adsorption, the vapor was admitted to the preparation chamber through a leak valve. The samples were heated with a halogen infrared lamp, Osram 25, which had been placed inside the chamber at a distance of 2.5 cm from the sample surface. The irradiation permitted a rapid and fine control of heating over a wide temperature range, 400—1400 K. The temperature of the smaple surface was monitored by means of a calibrated Pt–Pt/13%Rh thermocouple which was brought into contact with the samples on the occasion of measurement. The experimental conditions of the heat treatment were analogous to those used previously in the kinetic studies.[2,3]

The shift of X-ray photoelectron peaks caused by the positive charging of the surface was compensated for, or at least minimized, by showering electron beams from a "flood gun." The electric current and accelerating voltage of the beam were adjusted in the ranges of 0.1—0.5 mA and 0—4 eV so as to yield peaks with the narrowest full width at half maximum(fwhm) as optimum. The C 1s level of a trace of contaminant carbons, 285.0 eV, was taken as a reference. During XPS measurements, the background pressure was maintained below 2×10^{-9} Torr. For X-ray diffraction and scanning-electron microscopic observation, the calcium hydroxide was decomposed and subjected to heat treatment *in vacuo* at various temperatures. The pretreated samples were stored *in vacuo* in a quartz vessel until just before measurement. The procedures and apparatus used for the measurement of the catalytic activity of the oxides were the same as those reported previously.[2,3]

Results

Figure 1 compares the variations in the catalytic activity of MgO,[1] CaO,[2] and BaO[1] for olefin hydrogenations when the oxides were subjected to heat treatment *in vacuo* at various temperatures. These oxides possess different temperature ranges for the generation of the activity. The figure also shows the effect of pretreatment upon the recovery of the catalytic activity of CaO, which was almost completely deactivated by evacuation at 1273 K. The subsequent evacuation of the oxide at 1073 K had no effect at all. However, when the oxide was exposed to water vapor at room temperature to such a extent that its surface was nearly covered by a monolayer, followed by evacuation at high temperatures, the activity was regained at around 800 K and attained a maximum at around 1073 K. It should be noted that the H_2O-exposed oxide exhibits a similar pattern of the catalytic activity *vs.* the evacuation temperature, although the highest activity at 273 K was about a half of the original level, 3.6×10^{18} molecules m^{-2} min^{-1}.

Calcium Oxide. Figures 2 and 3 show the X-ray photoelectron spectra in the O 1s and Ca 2p regions respectively for CaO subjected to various treatments. The spectra of CaO evacuated at 1223 K gave a single peak of the O 1s, A, at 529.6 eV and a pair of Ca $2p_{3/2}$ and $2p_{1/2}$ peaks, A, at 346.3 and 349.8 eV respectively (Spectrum 6 in Figs. 2 and 3). The subsequent adsorption of H_2O on the oxide surface at room temperature produced a new O 1s peak, B, with a larger fwhm value of 3.0 eV at around 532.4 eV, in addition to the original A peak, the fwhm of which was 1.9 eV. In the Ca 2p region, the adsorption of H_2O gave rise to three peaks, the central one of which was apparently derived from a superposition of two peaks; the substraction of the original A peak from the superposed spectrum provided a pair of new peaks, B, *i.e.*, Ca $2p_{3/2}$ at 348.6 and $2p_{1/2}$ at 352.0 eV, which were similar in fwhm to those of $Ca(OH)_2$, 2.0 eV. Upon the evacuation of the catalyst at 553 K for 30 min, the intensity of the higher-binding-energy side of the O 1s B peak diminished; from the difference between Spectra 1 and 2, this was regarded as reflecting the disappearance of the B_h peak, whereas the Ca 2p spectra remained almost unchanged. The evacua-

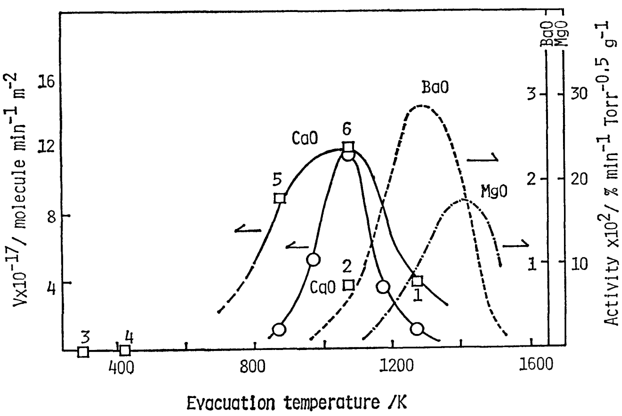


Fig. 1. Catalytic activities *vs.* evacuation temperature. Squares and full line: ethylene hydrogenation on CaO exposed to H_2O and then evacuated. Reaction temperature=273 K. The numbers denote the experimental sequence; CaO was first evacuated at 1273 K (No. 1), then at 1073 K (No. 2), and exposed to H_2O at room temperature (No. 3) followed by evacuation (from No. 4 to 6).
Circles and full line: ethylene hydrogenation on CaO prepared by the decomposition of $Ca(OH)_2$. Reaction temperature=573 K. See Ref. 2. The rate of the hydrogenation at 273 K on this 1073 K-evacuated CaO was 3.6×10^{18} molecules m^{-2} min^{-1}.
Doubly dashed line: ethylene hydrogenation on MgO. See Ref. 1.
Simple dashed line: 1-butene hydrogenation on BaO. See Ref. 1.

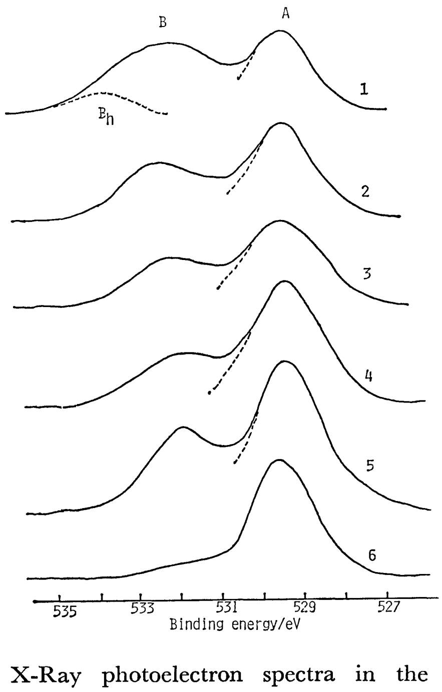


Fig. 2. X-Ray photoelectron spectra in the O 1s region of CaO.
1: After being evacuated at 1223 K for 30 min, CaO was exposed to 5 Torr of H_2O at room temperature and evacuated at the same temperature, 2: evacuated at 553 K for 30 min, 3: evacuated at 883 K for 30 min, 4: evacuated at 1053 K for 30 min, 5: $Ca(OH)_2$ was decomposed and evacuated at 1063 K for 30 min, 6: evacuated at 1223 K for 30 min.

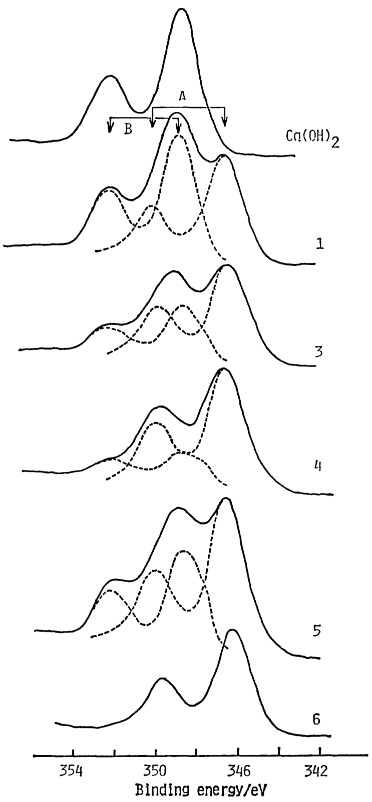


Fig. 3. X-Ray photoelectron spectra in the Ca 2p region. The pretreatments of CaO with respect to spectrum 1 to 6 are the same as those described in Fig. 2 except for the absence of a spectrum corresponding to No. 2.

tion of the sample at 883 K for 30 min, caused significant changes in both O 1s and Ca 2p spectra; the A peak of O 1s became broader by 0.4 eV, and the position of the O 1s-B peak shifted by 0.3 eV to the lower-binding-energy side. In the Ca 2p region, the substraction of the A peak from the observed spectra gave a pair of peaks, the fwhm values of which were broader by 0.2 eV than those of $Ca(OH)_2$ (Spectrum 3 in Fig. 3). Further evacuation at 1053 K considerably enhanced the intensity of the O 1s-A peak, decreasing its fwhm value by 0.2 eV. The B peak of Ca 2p became broader. For evacuation at 1273 K, these characteristic structures in the O 1s and Ca 2p regions vanished, and Spectra 6 in Figs. 2 and 3 were regained. In another experiment in which $Ca(OH)_2$ was decomposed *in vacuo* at various temperatures up to 1273 K, the spectral features of the activated CaO were quite similar to those of the abovementioned CaO (cf. Spectra 5 in Figs. 2 and 3).

The X-ray diffraction of CaO showed that the relative intensities of lines from such index plane as (111), (220), and (200) remained nearly unchanged on heating *in vacuo* from 873 to 1073 K, but evacuation at 1273 K caused a considerable enhancement of the diffraction intensity from the (111) plane, compared to that from the (220) and (200) planes. Scanning-electron microscopic observation also indicated the preferential growth of particles, probably related to the (111) orientation, upon pretreatment at 1273 K.

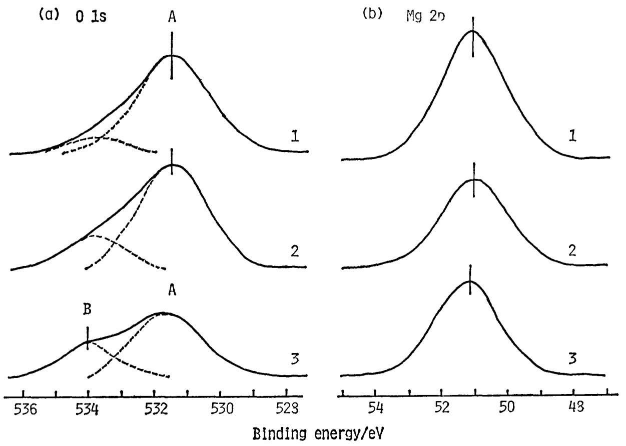


Fig. 4. X-Ray photoelectron spectra in the O 1s (a) and Mg 2p (b) regions of MgO. 1: $Mg(OH)_2$ was evacuated at 1373 K for 30 min, 2: exposed to 5 Torr of H_2O at room temperature for 30 min and evacuated at the same temperature, 3: $Mg(OH)_2$ was evacuated at 873 K for 30 min.

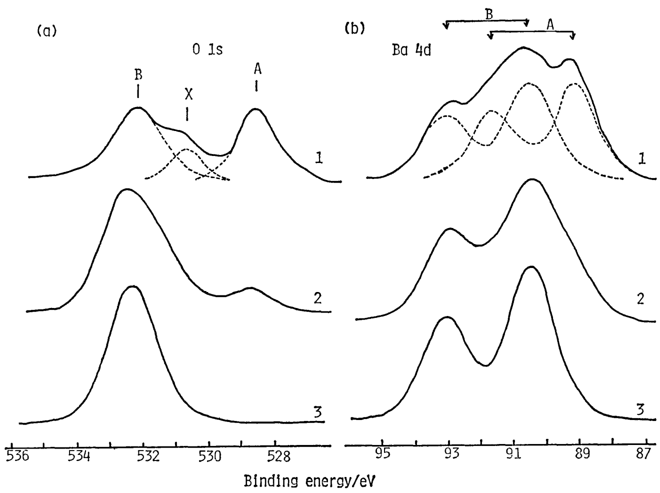


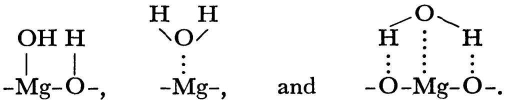
Fig. 5. X-Ray photoelectron spectra in the O 1s (a) and Ba 4d (b) regions of BaO. 1: evacuated at 1373 K for 40 min; the observed peak was roughly deconvoluted by assuming that the intensity ratio of the A to B peak in the Ba 4d line was the same as that in the O 1s line, 2: exposed to 3 Torr of H_2O at room temperature and evacuated at 853 K for 40 min, 3: exposed to air for a long time.

Magnesium Oxide. Figure 4 shows the X-ray photoelectron spectra of MgO pretreated in various ways. The heat treatment of $Mg(OH)_2$ *in vacuo* at 873 K gave rise to two peaks in the O 1s region, *i.e.*, A at 531.6 and B at 534.0 eV. Further treatment at 1373 K caused an appreciable development of the A peak at 531.4 eV and changed the B peak to a small one appearing at around 533.7 eV. The exposure of the oxide to 4 Torr of H_2O at room temperature for 30 min resulted in the appearance of a broad peak at almost the same position as that of the B peak, but its intensity was low. The temperature of H_2O adsorption was raised to 373 K, but no drastic development of the peak occurred. With the Mg 2p photoelectron peak, no appreciable change was observed upon such treatment except for the broadening of the peak upon the H_2O adsorption.

Barium Oxide. Figure 5 shows the O 1s and Ba 4d spectra of BaO evacuated at 1373 K for 40 min. In the O 1s region, there existed three peaks, *i.e.*, A at 528.5 eV, X at 530.6 eV, and B at 532.1 eV. The corresponding Ba 4d spectra also consisted of superposed peaks. The adsorption of H_2O on the oxide at room temperature and the following evacuation at 853 K led to a drastic decrease in the intensity of the A peak and the development of a broad B peak at 532.4 eV in the O 1s region. With the Ba 4d spectra, the corresponding peaks due to $4d_{5/2}$ and $4d_{3/2}$ were still broad, but the doublets were considerably separated. For comparison, the figure also involves the spectra of BaO exposed to air at room temperature; the O 1s level gave a single peak at 532.3 eV, whereas the Ba 4d levels showed well-separated peaks of Ba $4d_{5/2}$ at 90.5 eV and $4d_{3/2}$ at 93.0 eV. These spectra were substantially identical with those of $Ba(OH)_2$. Table 1 summarizes the values of the binding energies and fwhm of the photoelectron peaks described above.

Discussion

The adsorption of H_2O on the three oxides and subsequent evacuation caused similar variations in their X-ray photoelectron spectra. Deane *et al.* studied the adsorption of H_2O at room temperature on MgO by IR spectroscopy and classified the produced surface species into several kinds of groups,[6] such as



$$\begin{array}{c}\mathrm{OH\ \ H}\\ |\quad\ |\\ \text{-Mg-O-},\end{array}\quad \begin{array}{c}\mathrm{H\ \ H}\\ \diagdown\mathrm{O}\diagup\\ \vdots\\ \text{-Mg-},\end{array}\quad \text{and}\quad \begin{array}{c}\mathrm{O}\\ \mathrm{H}\ \vdots\ \mathrm{H}\\ \vdots\quad\vdots\quad\vdots\\ \text{-O-Mg-O-}.\end{array}$$

Similar situations are likely to hold for the other alkaline earth metal oxides. In Spectrum 1 in Fig. 2, the close similarities in the binding energy and fwhm to those of anhydrated CaO permit us to assign the A peak of O 1s to the lattice oxygen of the oxide. The broad B peak is evidently composed of more than one kind of peak and is attributable to the oxygen atoms in the hydroxyl groups and adsorbed water, by analogy with the above-mentioned IR results, since these species are substantially associated with a common unit structure, Ca–O–H, but with slightly different binding energies in their O 1s levels. The peak on the higher-binding-energy side of the B peak is attributable to the oxygen of the adsorbed water, because the value of the binding energy was close to that of condensed water (534—535 eV); the peak readily disappeared upon heat treatment at temperatures as low as 553 K. In the Ca 2p region, the three peaks were well resolved into the Ca 2p peaks due to CaO and $Ca(OH)_2$; the A peak is evidently to be assigned to the Ca ion of the oxide, whereas the B

Table 1. Binding energies and fwhm

Catalysts	Pretreatment	Peaks	O 1s		Cations	
			B. E./eV	fwhm/eV	B. E./eV	fwhm/eV
					Mg 2p	
MgO	Evac. at 1373 K	A	531.4±0.1	2.5	51.0±0.1	2.2
		B	533.7±0.2	1.9		
	Exposed to H_2O and evac. at r. t.	A	531.4±0.1	2.5	51.0±0.1	2.4
		B	533.8±0.2	2.2		
	Decomp. of $Mg(OH)_2$ and evac. at 873 K	A	531.6±0.1$_5$	2.5	51.1±0.1	2.2
		B	534.0±0.1$_5$	1.9		
					Ca $2p_{3/2}$	
CaO	Exposed to H_2O and evac. at r. t.	A	529.5±0.1	1.8	346.4±0.1	1.9
		B	532.4±0.1$_5$	3.0	348.6±0.1$_5$	2.0
		(as B_h)	533.8±0.2	1.9		
	Evac. at 553 K	A	529.5±0.1	1.8	346.6±0.1	1.9
		B	532.5±0.1$_5$	2.3	348.8±0.1$_5$	2.0
	Evac. at 883 K	A	529.6±0.1	2.2	346.3±0.1	1.9
		B, X	532.2±0.1$_5$	≈2.2	348.5±0.1$_5$	2.2
	Evac. at 1053 K	A	529.4±0.1	2.0	346.5±0.1	1.9
		B, X	532.1±0.1$_5$	≈2.0	348.6±0.2	≈2.3
	Decomp. of $Ca(OH)_2$ and evac. at 1063 K	A	529.5±0.1	2.0	346.5±0.1	1.9
		B, X	532.1±0.1$_5$	≈2.0	348.5±0.1$_5$	2.2
	Evac. at 1223 K	A	529.6±0.1	1.8	346.3±0.1	1.9
					Ba $4d_{5/2}$	
BaO	Evac. at 1373 K	A	528.5±0.1	1.4	≈89.2	1.6
		X	530.6±0.1$_5$	1.2		
		B	532.1±0.1	1.8	≈90.6	
	Exposed to H_2O at r. t. and evac. at 853 K	A	528.7±0.2	1.3		
		B	532.4±0.1	≈2.3	≈90.5	
	Exposed to air	B	532.3±0.1	1.8	90.5±0.1	1.8

C 1s=285.0 eV as reference.

peak was considered to combine with hydroxyl groups (and presumably involves Ca ions combining with adsorbed water). The intensity of the i peak, I_i, was evaluated from each peak area and the I_A/I_B ratios were calculated to be 0.7±0.1 for the O 1s peak and 0.8±0.1 for Ca 2p peak. From these intensity ratios and the escape depth of the electrons ejected, the thickness of the hydroxide layer was estimated to correspond to several monolayers.

The most significant changes caused by evacuation at 883 K were the broadening of the O 1s-A and Ca 2p-B peaks and the shift of the O 1s-B peak toward the lower-binding-energy side. The findings that these characteristic variations proceeded further upon evacuation at temperatures up to 1073 K, while the heat treatment at 1273 K destroyed the resulting spectral fine structures, strongly suggest that a new oxygen species is formed on the surface treated in this definite range of temperature, *viz.*, 900—1073 K.

The O 1s A and B peaks which were observed after the evacuation of $Mg(OH)_2$ at 873 K were assinged to oxygen of the oxide and hydroxides respectively. The separation between the two peaks, 2.4 eV, was consistent with the value, 2.5 eV, obtained by Fuggle *et al.* in the case of H_2O[7a] or O_2[7b] adsorbed on evaporated magnesium films. Upon evacuation at 1373 K, the A peak developed whereas the B peak changed to a small one and merged into the tail of the main A peak. The spectral features of the produced oxygen species were not so clear as in the case of CaO, but it is not unreasonable to expect that these variations in the O 1s peak upon heating are correlated with the process of the catalytic activation.

The most striking features of BaO treated at 1373 K, which gives a maximum activity for 1-butene hydrogenation,[1] were clearly observed in the O 1s region where three oxygen peaks appeared; from a comparison with Spectra 2 and 3, the A and B peaks were assigned to oxygen of the oxide and hydroxides respectively, whereas the X peak was assigned to a new oxygen species. As for the cation, the corresponding Ba 4d photoelectron spectra provided superposed peaks similar to those observed in the Ca 2p region of the activated CaO. An additional peak due to anhydrated BaO was not obtained under the present heating conditions; the superposed peaks were analyzed by substracting the peaks of hydrated BaO (Fig. 5b, 3). This procedure gave rise to a pair peak which shifted by 1.4 eV to the lower-binding-energy side and was assigned to anhydrated BaO. Since neither broadening nor shoulder peaks were appreciably observed, the resulting peak appears to be insensitive to the influence of the newly-produced oxygen species.

It should be noted that there existed a similarity in the photoelectron spectra of these oxides when they were subjected to the heat treatment by which their catalytic activities were generated, in spite of the difference in the optimum temperature for activation. A recent mass-spectrometric analysis of gases evolved during the thermal decomposition of $Mg(OH)_2$ showed that hydrogen and water molecules are released in the temperature range, 570—970 K, and oxygen atoms above 770 K.[8] The following processes were proposed to occur:

$$2\,OH^- \rightarrow O^-\cdots O^- + H_2 \text{ and } 2\,OH^- \rightarrow O^{2-} + H_2O$$

at a lower temperature, and:

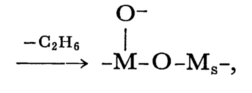
$$OH^- \rightarrow O^- + 1/2\,H_2 \text{ and } 2\,O^- \rightarrow O^{2-} + O$$

at a higher temperature. The formation of O^- species on CaO[9] and MgO[10] upon heat treatment *in vacuo* was also confirmed by ESR studies. The change in surface structures due to this process is not clearly reflected in the XPS spectra of MgO, probably because of the low concentration of the species formed. This view is in line with the fact that the density of O^- species was estimated to be less than $1\times10^{17}\,m^{-2}$ from the quantitative analysis of the hydrogen evolved.[8] The processes described above are likely to take place on CaO and BaO to a greater extent, since the formation of peroxide is more favored in both oxides. Accordingly, the broadening of the O 1s-A peak of CaO after evacuation at 883 K seems to result from a contribution of the surface O^{2-} species thus formed, the binding energy of which is probably not far from that of lattice oxygen. The variation in the OH-band intensity of $Ca(OH)_2$ with an increase in the evacuation temperature showed that most of the OH groups were removed by evacuation up to 773 K, but still remained as isolated OH groups even after evacuation at 1173 K.[11] By taking the charge distribuitons into account, the B peak of O 1s appears to be derived from the O^- species and the residual OH^- groups. The splitting in energy between O^{2-} and O^- levels is not clear in the present case, but falls within the range of 1.9—2.2 eV, as was also observed in the adsorption of oxygen on NiO and Cu_2O surfaces.[12] The broadening of the Ca 2p-B peak by evacuation at temperatures between 883 and 1053 K appears to be brought about as a result of the partial conversion of OH^- species to O^- (and surface O^{2-}) species; it is likely that the broadening of the B peak toward the lower-binding-energy side is due to a contribution from the Ca ions, which combine with these oxygen species in place of the hydroxyl group, since the binding energies of O 1s were in this order; $O^{2-}<O^-<OH^-$ and since the Ca 2p level was lower in CaO than in $Ca(OH)_2$.

A similar consideration of the activated BaO leads to the conclusion that the O 1s X peak is associated with the O^- species. This assignment is supported by the results of the XPS study of H_2O adsorbed on the Fe surface;[13] the O 1s peak at 530 eV was assigned to the chemisorbed oxygen, $O^{\delta-}$, and the peak at 532 eV to the $OH^{\delta-}$ species. The findings described above for the oxides evidently show that the conditions necessary for the catalytic activation are also effective in producing the common oxygen species, which are coordinatively unsaturated O^- and O^{2-}. The O^- species appears to be more responsible for the catalysis as a part of the active sites for the hydrogenation, since the density of the surface O^{2-} was attenuated with an increase in the catalytic activity of CaO, as is shown in the narrowing of the O 1s-A peak upon evacuation at temperatures from 883 to 1053 K, and since the active BaO surface provided exclusively the X peak associated with the O^- species. Besides, there is evidence that the species is able to contribute to the H_2-D_2 equilibration reaction.[14]

As was shown in a previous study,[2] evacuation following the calcination of $Ca(OH)_2$ in air gave rise to a low catalytic activity. This implies that the cations in specific positions also play an important role in the catalytic hydrogenation, because the UV reflectance spectra revealed that the sintering of CaO in O_2 at 1073 K preferentially decreased the intensities of the lower frequency bands which relate to ions with lower coordinations, indicating the preferential destruction of high-index faces and local imperfections.[15] The X-ray diffraction and electron microscopic results for the decomposition of $Ca(OH)_2$ demonstrated that the CaO produced by evacuation at temperatures between 873 and 1073 K was still in a crystallographically transient state, retaining many cations with a lower coordination, *e.g.*, those located at edges and corners, but it changed to an oxide with a well-developed (111) orientation upon heat treatment above 1273 K. These findings give support to the above view. Furthermore, the contribution of incompletely coordinated cations or oxygen-deficient sites of CaO to the exchange reaction of butene with D_2 has been pointed out.[16] Therefore, the consolidation of these findings leads to the conclusion that the active sites of the oxides are composed of the O^- species adjacent to the specific cations. This model apparently explains the fact that the fraction of the active sites was as small as 0.5% of the total surface ions.[2]

Evidence for the adsorption of H_2 and C_2H_4 on these sites was shown in the ESR study; the ESR signal of oxygen adsorbed on MgO and CaO was remarkably enhanced by the pre-exposure of MgO to H_2, C_2H_4, or CO[17] and by that of CaO to H_2,[9] and it was concluded that such effects were due to the adsorption of these reducing molecules on the coordinatively unsaturated ions. These considerations, as well as the above-mentioned conclusion as to the structure of the active sites, confirm the following pathway of ethylene hydrogenation, which was previously proposed on the basis of the kinetic results:[2]



$$\overset{O^-}{|}\!\!-M-O-\overset{|}{M_s}- \xrightarrow{H_2+C_2H_4} \overset{O^-\cdots H^{\delta+}\ \ H^{\delta-}}{-\overset{|}{M}-O-M_s \diagup\!\!\diagup C_2H_4} \xrightarrow{-C_2H_6} -\overset{O^-}{\overset{|}{M}}-O-M_s-,$$

where M_s denotes a metal cation with a lower coordination on such specific sites as edges or corners. It appears likely that this structure of the isolated active sites produces heterolytically split hydrogen, thus leading to the formation of a π-allyl carbanion proposed as an intermediate in the 1,3-butadiene hydrogenation on MgO.[18] A comparison of the intensities of the O 1s peaks attributable to O^- shows that its concentration relative to lattice oxygen becomes higher in the order of: BaO>CaO>MgO. The above-mentioned structure of the active sites predicts that the catalytic activity also increases in this order, provided that the contribution of M_s is similar in the three oxides. This prediction is in line with the observed results.[1] An XPS study by Vinek *et al.* revealed that the hydroxide layer on MgO catalysts is enhanced with the storage time, causing a change in selectivity from the dehydrogenation of buta-2-ol to dehydration.[5] We have at present no evidence confirming the contribution of the OH groups to the hydrogenation; further study of their role is needed.

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