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Hydrogen Activation by Magnesia Catalysts

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Hydrogen activation by magnesia catalysts was investigated by studying H_2–D_2 exchange. The number of active sites, surface composition, rate, and mechanism of the reaction were investigated as a function of the activation temperature. Behavior of a commercial magnesia and a catalyst synthesized from $Mg(OH)_2$ were similar, although the latter catalyst had a much larger surface area. The upper limit for the number of active sites was determined in the classical manner by using selective poisoning by CO. A novel technique involving monitoring the *stoichiometric* reaction between magnesia and $D_2(g)$ enabled the very unusual determination of the lower limit for the number of active sites. Thus, the true number of active sites is bracketed within the upper and lower limits. Maximal activity occurred after activation at 700°C. The number of active sites is about $10^{12}/cm^2$, which is 10^3-fold higher than formerly reported on the basis of EPR data. The turnover frequency at 273 K and a partial pressure of 20 Torr of an equimolar mixture of H_2–D_2 is $4\ s^{-1}$, roughly 10^3-fold less than previously reported. The site density and activity are now consistent with expected values, rather than the anomalous values previously reported. The hydroxyl coverage of the surface was determined in a novel manner using thermogravimetric analysis over the temperature range of 300 to 1400 K. The catalysts are of low activity when the surface is either of very high or very low hydroxyl content. A mechanism in which the active site includes an ensemble consisting of a Mg^{2+} center and neighboring surface OH and O^{2-} is proposed.

INTRODUCTION

The hydrogen–deuterium exchange reaction, $H_2 + D_2 \rightleftharpoons 2HD$, is a convenient means of studying the important process of hydrogen activation by catalysts. This reaction is known to be catalyzed by a small number of homogeneous complexes, many transition metals, and a moderate number of both transition and main group metal oxides. Magnesia (amorphous MgO) can be active for this reaction (*1–4*). The most detailed study of the exchange reaction over MgO was reported by Boudart *et al.* (*1*). They noted that a good correlation existed between catalytic activity and the intensity of a paramagnetic center that was detected by EPR after pretreatments between 500 and 900°C. Such a correlation is a necessary but not sufficient condition for the EPR center to also be an active site for the reaction. A model for the active site that consists of a triangular array of three O^- radical ions and an adjacent hydroxyl ion on a (111) face was proposed. However, more recent work suggests that the EPR signal may be due to impurities, as Mn^{2+} (*2*). In addition, the density of active sites determined by this method was extremely low, $\sim 10^9/cm^2$, and the turnover frequency was extraordinarily high, about $1000\ s^{-1}$ at 78 K for a 1 : 1 mixture of $H_2 : D_2$ at a pressure of 1 atm. Their model is also somewhat surprising in that it does not include a metal center. Coluccra *et al.* (*5*) have published IR data that show that magnesium hydride and hydroxyl groups are formed when H_2 adsorbs on magnesia, indicating a bonding interaction between H_2 and Mg^{2+}. Analogous chemistry has also been demonstrated on ZnO, which is a weak catalyst for H_2–D_2 exchange (*11*). Also, an ensemble containing an Al^{3+} ion and neighboring surface OH and O^{2-} is believed to be

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the active site on γ-Al_2O_3, which can be quite active for H_2–D_2 exchange (*6, 10*).

A comprehensive study of hydrogen activation by a large number of homogeneous catalysts, transition metals, and metal oxides reveals some clear trends in reactivity and site densities. In particular, oxides typically have a site density of roughly $10^{12}/cm^2$ and the activity of oxides is usually less than that of transition metals (*6*). However, the reported activity of MgO is far higher than the most active transition metal and its site density is very low. In order to resolve these discrepancies with magnesia, we have reinvestigated its activity for H_2–D_2 exchange. Of particular note is that a methodology has been developed for determining both the upper and lower limits for the density of active sites. For the first time this enables the true number of active sites to be bracketed within two bounds and therefore also provides a much more accurate measurement of the turnover frequency of a catalyst.

EXPERIMENTAL

Catalysts and chemicals. Two catalysts were studied. The first, designated MgO-WSU, was prepared from $Mg(NO_3)_2 \cdot 6H_2O$ (MCB reagent grade, catalog No. MX0060-1). The salt was dissolved in distilled water and ammonium hydroxide was added until a precipitate formed. After filtering and thorough washing with distilled water, the product was dried at 120°C for 18 h. The second catalyst, MgO-JM, was Johnson and Matthey puratronic grade MgO obtained from Alfa (catalog No. 400208). D_2 (g) was obtained from Scott Speciality Gases and was of 99.7% atomic purity (this corresponds to 99.4% mol purity).

Pretreatments. About 0.1 g of MgO-JM or 0.03 g of MgO-WSU was put into a reactor made of fused quartz and the sample was supported on a frit of porous fused quartz. The reactor was connected to a grease-free, high-vacuum, reaction/adsorption system constructed with stainless-steel bellows seal valves. The system has a base pressure of 10^{-7} Torr and a leak rate of $<1 \times 10^{-7}$ ml · atm/s. Catalysts were activated by successive evacuations at increasing temperatures from 300 to 900°C. This treatment gradually decreases the hydroxyl content of the surface and causes a modest drop in surface area.

Measurement of catalytic activity. After activation, adsorption and reactivity studies were performed without removing a catalyst from the reaction/adsorption system or exposing a catalyst to air. The catalytic exchange reaction was carried out using a flow system. The gas mixture (1.33% H_2, 1.33% D_2, and 97.33% He) was purified by passage through a trap of silica gel at 77 K after passing through a mass flow controller and immediately before entering the reaction system. The use of He precludes the measurement of mass 4 (D_2) during a flow reaction, but ultrahigh purity of the reaction gas is necessary for obtaining reliable results on catalysts that have a low concentration of active sites. A flow of 120 ml/min at a total pressure of 1 atm (partial pressure of (H_2 + D_2) = 20 Torr) was controlled by a Brooks Instrument Model 5842 electronic mass flow controller and passed through the reactor. Cryogenic baths and a furnace were used to adjust the temperature of the reactor between 77 and 1200 K. The effluent from the reactor continuously flowed past the high-pressure side of a molecular leak to a UTI model 100C quadrupole mass spectrometer. The response time of the system is about 1 s. The spectrometer and data analysis were controlled by an Apple II$^+$ computer with a DAS System 5 A/D-D/A interface board and our own software. Pure gases were used to obtain calibration factors to correct for the different sensitivities of the mass spectrometer for H_2, D_2, and HD. Correction was made for the background signal at mass 3 due to the background of the mass spectrometer measured with the reaction system evacuated (this term is negligible), a slight contribution from the leading edge of the very large He peak at mass 4 (~1/600 the size of the He peak), and impurity HD in the D_2. The typical background signal at mass

3 is equivalent to the $H_2 + D_2$ component of the feed stream containing 0.9% HD (which corresponds to a background conversion of 0.9%) and an increase of 0.02% in this value could be detected.

The activity for H_2–D_2 exchange was calculated from the relative amounts of H_2 and HD. The decrease in the H_2 signal was consistent with the increase in the HD signal based on the stoichiometry of the exchange reaction. The formula for calculating the percent conversion of H_2 is

$$\% \text{ conversion} = \{0.5\,[\text{HD}]/(0.5[\text{HD}] + [\text{H}_2])\} \times 100,$$

where [HD] and $[H_2]$ are the mol/liter of HD and H_2, respectively, in the reactor effluent.

The turnover frequency, N, is the number of H_2 molecules reacting per unit time per site and is given by the expression

$$N = (F/A) \times X_e \times \ln(1/(1 - X_t/X_e)),$$

where F is the number of molecules of H_2 or D_2 entering the reactor per unit time, A is the number of active sites, X_t is the fraction of H_2 that reacted (mol H_2 reacted/initial mol H_2), and X_e is the fraction of H_2 converted at equilibrium. The value of X_e is given by the expression

$$X_e = \sqrt{K}/(\sqrt{K} + 2),$$

where the equilibrium constant, K, is given by (*13*)

$$K = \exp([1.455T - 78.096]/T),$$

where T has units of K. The values of X_e at 77 and 295 K are 0.384 and 0.475, respectively. The specific activity, N', is computed with the same expression except that the term A is now defined as the surface area of the catalyst.

Surface area measurements. The surface area of catalysts was measured by the BET technique using N_2 at 77 K. The amount of adsorption was determined with an accuracy of ~0.0005 ml using the ideal gas law and a Setra Model 204 electronic pressure transducer to measure the pressure.

CO poisoning. Selective poisoning with CO was used to determine the upper limit for the number of active sites for H_2–D_2 exchange. Immediately after running a reaction the reactor was evacuated to 10^{-7} Torr at room temperature. A known amount of CO was then added to the reactor at room temperature and allowed to adsorb for 5 min. The amount of CO added was calculated with an accuracy of ~0.0002 ml using the ideal gas law. Helium gas was then flowed through the reactor at room temperature for 10 min to collect unadsorbed CO, which was condensed on a small amount (~0.1 g) of silica gel at 77 K. The trap was then rapidly heated by immersing it in a water bath at room temperature and the evolved CO gas was analyzed by gas chromatography using a 2 ft × $\frac{1}{8}'$ in. o.d. column of Spherocarb at room temperature. In order to minimize the effects of nonselective poisoning and the slow desorption of adsorbed CO, the number of active sites was calculated by extrapolating the initial part of a plot of activity versus CO adsorbed to zero activity.

Amount of exchangeable OH. Some of the OH groups on the surface (σ-OH) of the MgO will exchange with $D_2(g)$ to form σ-OD + HD(g). This is defined as exchangeable OH. The amount of exchangeable OH was determined by exposing a catalyst to a known amount (measured in the same manner as CO) of pure $D_2(g)$ at 273 K. In a typical experiment, ~0.5 g of catalyst was exposed to ~50 Torr of $D_2(g)$ (~0.7 ml STP). The gas in the reactor was analyzed by passing through a small orifice placed inside the reactor, which allowed $\sim 1 \times 10^{-5}$ ml · atm/s of gas to bleed into the mass spectrometer, which continuously analyzed the isotopic composition of the gas. The analysis was performed every second for the first 50 s of reaction so the amount of rapid exchange could be followed, and subsequently the mixture was analyzed every minute until the rate of reaction was negligible. Due to the lag time for diffusion of gas from the surface of the catalyst to the orifice, the response time of this analysis is about 4 s and exchange occurring in the first 1 to 2 s would

TABLE 1

Physical and Activity Parameters for MgO at T_{max}

Sample	T_{max}[a] (°C)	S (m^2/g)	N' ($HD/cm^2 \cdot s$)	N[b] ($HD/site \cdot s$)	CO adsorbed (10^{12} CO/cm^2)	Exchangeable σ-OH ($10^{12}/cm^2$)		
						Fast	Slow	Total
MgO-JM	700°C	20.1	1.5×10^{13}	3.82	3.9	0.1	0.06	0.16
MgO-WSU	700°C	89.8	1.3×10^{13}	3.90	3.4	3.4	0.5	3.9

[a] T_{max} is the pretreatment temperature that gave the maximum activity.

[b] N is the turnover frequency, where the number of sites is based on CO poisoning.

distort the initial response enough to be detected. Exchange occurring in <1 s just results in a nonzero y-intercept when the conversion is plotted against time. Correction was made for the amount of gas that was evacuated during the analysis. The sensitivity of the analysis is about 3×10^{15} exchangeable OH. For a typical sample (0.5 g of MgO and $S = 80$ m^2/g), this corresponds to 7×10^9 exchangeable OH/cm^2, which is $7 \times 10^{-4}\%$ of a monolayer. It should be noted that due to the small amount of $D_2(g)$ used and the stability of the mass spectrometer, this technique is much more sensitive than related methods in which a catalyst is exposed to relatively large amounts of $D_2(g)$ in a circulating system (*12*). The accumulative amount of exchangeable σ-OH is termed the *total* exchangeable σ-OH, the amount of exchange extrapolated to time zero (based on the first 50 s of reaction) is termed the *fast* exchangeable σ-OH, and the amount of *total* minus *fast* exchange is the *slow* exchangeable σ-OH.

EPR. Catalyst samples were examined using a Varian E-109 EPR spectrometer (X-band, 100-kHz field modulation and a rectangular cavity). Catalysts were pretreated in a sample tube of fused quartz (6.4 mm o.d. × 4 mm I.D.). Spectra were taken after pretreatment (either *in vacuo* or in air) at room temperature. The background of the quartz tube was removed from the recorded spectra.

TGA. Thermogravimetric analysis (TGA) was used to determine the hydroxyl content of MgO-WSU as a function of temperature. Temperature was controlled by a temperature programmer (TECO Model TP-2000). The electrobalance (Cahn Model 2000) was contained in a evacuable glass vessel and was mounted on a platform to provide vibration isolation. The sensitivity is 0.1 μg. About 5 mg of sample was supported in a boat suspended from a hangdown wire, each constructed of fused quartz. The sample could be evacuated to 1×10^{-6} Torr and exposed to a variety of gases. The temperature of a sample was increased in steps. At each temperature the weight loss was followed until the rate became negligible (about 15 min) and then the process was repeated at higher temperatures until no further weight loss occurred.

In a separate experiment about 0.25 g of MgO-WSU was heated at 30 K/min and then held for 30 min at 500, 700, and 900°C and the evolved gases continuously analyzed in the range of 1 to 60 amu by the mass spectrometer (the transfer lines were heated to 120°C). The data for each mass were integrated over time and the weight percent that each species contributed in a given temperature range was calculated using response factors determined from analysis of mixtures of known concentrations.

RESULTS AND DISCUSSION

Variation of activity with pretreatment temperature. Previous work in this laboratory and by others (*1*, *5*) has shown that

TABLE 2

Physical and Activity Parameters for MgO-WSU

Sample	Pretreatment	% Conversion		S (m^2/g)	Exchangeable σ-OH ($10^{11}/cm^2$)		
		195 K	273 K		Fast	Slow	Total
A (0.03120 g)	300°C *in vacuo*	0	0.18	—	—	—	
A	400°C *in vacuo*	0	0.22	—	—	—	
A	500°C *in vacuo*	0	0.29	79.3	0.7	0.5	1.2
A	700°C *in vacuo*	14.1	31.1	75.9	34	5	39
A	800°C *in vacuo*	0.65	4.78	78.7	12	15	27
A[a]	Rehydrated	9.66	20.4	72.9	57	2	59
B (0.03337 g)	700°C *in vacuo*	18.7	37.7	—	—	—	—
B[b]	CO poisoning	3.06	8.84	77.7	5.2	45	50

[a] After 800°C pretreatment, sample A was rehydrated and then evacuated at 700°C.

[b] After 700°C pretreatment, sample B was poisoned with CO.

the catalytic activity of a metal oxide can strongly depend on its pretreatment temperature. Therefore, the activity for H_2–D_2 exchange was determined as a function of the temperature of activation. Tables 1 and 2 summarize some of the physical and activity data, and Fig. 1 shows the activity as a function of activation temperature. The activity of an empty reactor is zero. It is clear that both catalysts are of low activity when heated below 500 or above 800°C and are highly active when heated between 600 and 750°C. The temperature at which the activity is maximum, defined as T_{max}, is 700°C for both catalysts. The surface area of the catalysts changes negligibly between 500 and 800°C (Table 2), suggesting that the activity is very sensitive to certain species present on the surface. The activation energy was found to be 1.7 ± 0.3 kcal/mol. This is in good agreement with the value of 2.2 ± 0.1 kcal/mol reported by Boudart *et al.* (*1*).

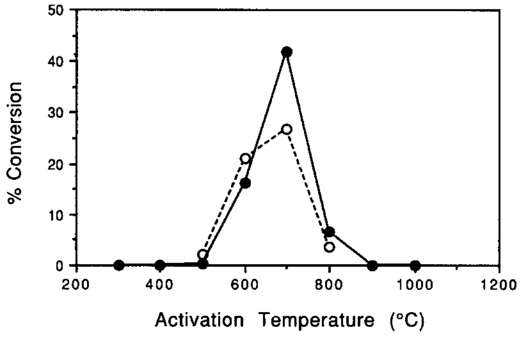

FIG. 1. Activity of MgO for H_2–D_2 exchange at 273 K. (○) MgO-JM, 0.19196 g; (●) MgO-WSU, 0.01217 g.

Surface hydroxyl groups on MgO. Unless heated to high temperature, the surface of magnesia is covered with σ-OH groups. At higher temperatures these groups condense to evolve H_2O and form exposed O^{2-} and Mg^{2+} species. The hydroxyl content of magnesia has been previously studied (*7–9*), but it has been shown that the results are strongly dependent on the method used to synthesize the sample and its exact pretreatment. Therefore, the hydroxyl content of MgO-WSU was determined by TGA over the temperature range of 300 to 1400 K. Figure 2 shows the weight loss as a function of temperature.The weight loss is very low about 800°C and is zero above 900°C. Mass spectrometric analysis detected only negligible amounts of NO_2 and a small amount of NO, in addition to H_2O being evolved during dehydroxylation. With respect to the *total* weight change over the *entire* experiment

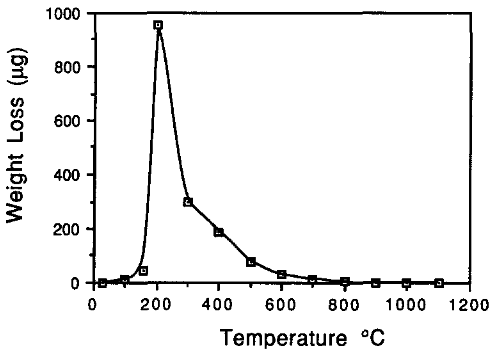

FIG. 2. TGA data for MgO-WSU. Initial weight of sample was 4.882 mg.

being defined as 100%, then 92% of the weight loss was due to H_2O and 8% was due to NO. Up to 500°C, the component values are 70% H_2O and 4.5% NO, in the range of 500 to 700°C the values are 13.4% H_2O and 3.3% NO, and in the range 700 to 900°C the values are 8.6% H_2O and 0.4% NO. Thus, NO has a small effect on the calculation of the percentage hydroxylation and at temperatures near and above T_{max} the effect is negligible.

Figure 3 shows the hydroxyl content as a function of temperature. Determination of the hydroxyl content is not trivial. Most frequently, some independent technique, such as IR spectroscopy, is used to discriminate between adsorbed H_2O and σ-OH. However, it is generally difficult to do this accurately. In this analysis we use a novel approach that is easy and can yield relatively accurate data. The sample is heated to such a high temperature that there is no more weight loss. It is necessary that the sample does not decompose during this heating. The hydroxyl content is then assigned the value of zero at the maximum temperature. Weight uptake at moderately lower temperatures is then attributed to σ-OH.

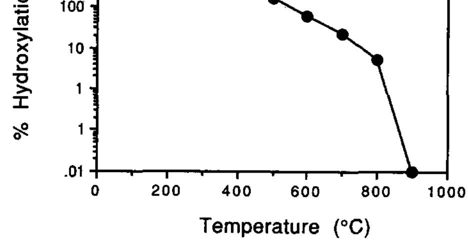

FIG. 3. Surface hydroxyl content of MgO-WSU. It is assumed that 100% hydroxylation equals 22 σ-OH/nm^2.

The monolayer coverage of the surface by σ-OH can be calculated if the weight of a monolayer is known. This can be calculated from the crystal structure of the material. This is an approximation, as an estimate must be made of the crystal faces that are exposed on the sample. However, these errors are generally small compared to the amount of adsorbed water that can be present (note that at 100°C, about 10 monolayers are present). The main crystal faces believed present on MgO are the (100), (110), and (111) faces (*7*). These have surface densities of 2.2×10^{15}, 1.6×10^{15}, and 1.3×10^{15} σ-OH/cm^2, respectively. Most experimental data support the (100) face as being dominant on MgO. The data of Fig. 3 are based on the (100) face of MgO. This face has a density of 1.1×10^{15} Mg^{2+} ions/cm^2 and 1.1×10^{15} O^{2-} ions/cm^2. It is assumed that 100% hydroxylation corresponds to an OH group attached to each surface cation and an H attached to each surface O^{2-} (thereby forming a second σ-OH), yielding a σ-OH density of 2.2×10^{15} σ-OH/cm^2 and a surface stoichiometry of $Mg(OH)_2$, or equivalently, $MgO \cdot H_2O$.

Figure 3 shows that a monolayer of σ-OH remains at ~550°C. This is in good agreement with a recent report (*9*) that after outgassing magnesia for 50 h at 550°C the retained water corresponded to the stoichiometry of $MgO \cdot H_2O$. It is clear that large amounts of adsorbed H_2O are present at lower temperatures and above 800°C the σ-OH content is very low. The percentage hydroxylation at T_{max} is 20% and, at this high temperature, almost certainly does not include adsorbed H_2O. It appears likely that

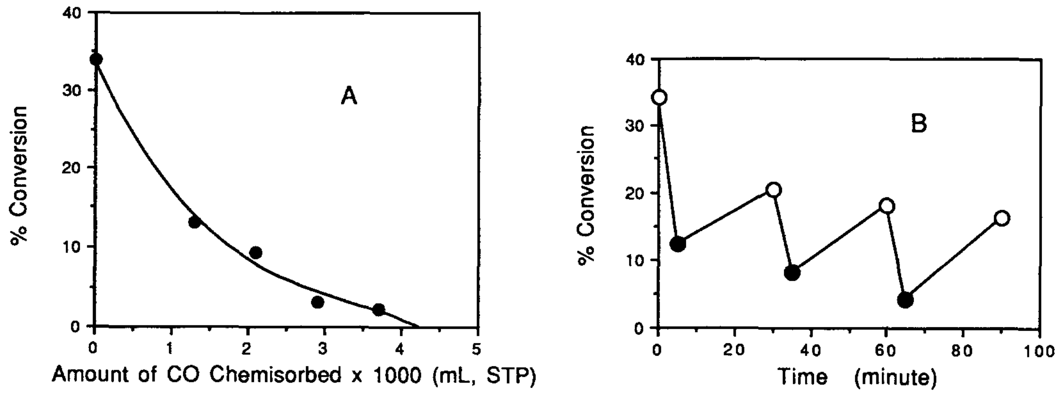

FIG. 4. CO poisoning of MgO after activation at 700°C. (A) MgO-WSU, 0.01534 g; (B) MgO-JM, 0.21290 g. Solid circles represent activities immediately after adding each dose of CO and open circles represent activities 30 min later. Amount of CO chemisorbed in doses 1 through 3 are 0.0015, 0.0044, and 0.0174 ml (STP), respectively.

both σ-OH and exposed ions (formed by dehydroxylation) are necessary for catalytic activity. A similar result has been found for γ-alumina (*10*).

Selective CO poisoning. The number of active sites of a catalyst is of intrinsic interest as well as necessary for calculating a turnover frequency. Poisoning by selective adsorption of a gas yields an upper limit to the number of active sites since some of the gas can adsorb on inactive sites. CO has been shown to be a good selective poison for H_2–D_2 exchange over alumina (*10, 12*). The use of CO_2 as a poison resulted in a 10-fold higher value for the number of active sites on alumina. It was therefore felt that CO is a better poison and this effect is likely to be even more pronounced on magnesia since it is more basic and should therefore give less selective adsorption. Figure 4 shows typical data for CO poisoning over the catalysts. As shown in Fig. 4B, on the MgO-JM sample (but not on MgO-WSU) the activity dropped substantially with the addition of CO but then slowly increased with time. This indicates that the adsorption of CO is weaker on this sample and the CO is slowly desorbing during the subsequent measurement of catalytic activity (or possibly migrating from the active sites). Due to the low concentration of active sites, as the active sites become substantially poisoned the surface remains largely bare, so it is expected that the selectivity of the poison will substantially decrease and give rise to a tail in the poison plot. Therefore, for these reasons on both catalysts the first data point was extrapolated to zero activity to obtain the number of active sites. The first exposure to CO was always chosen so as to substantially (usually 50 to 70%) but not completely reduce the activity, thereby minimizing extrapolation error without adding excess CO. Due to the errors inherent in extrapolating the poison curve to zero activity, it is estimated that the number of active sites is only accurate to about 50% (but comparisons between catalysts should be much more accurate). CO poisoning yields an upper limit for the site densities of 3.9×10^{12} sites/cm^2 for MgO-JM and 3.4×10^{12} sites/cm^2 for MgO-WSU. It is interesting that within the experimental error the site densities are identical, even though the surface areas are quite different.

Exchangeable σ-OH groups. When an oxide is exposed to D_2(g), some of the σ-OH can exchange to form σ-OD + HD(g). What is most unusual is that any site that can undergo this *stoichiometric* reaction must also be a site for the *catalytic* H_2–D_2 exchange reaction, as shown by

$$\frac{\begin{array}{l} D_2(g) + \sigma\text{-OH} \leftrightharpoons HD(g) + \sigma\text{-OD} \\ H_2(g) + \sigma\text{-OD} \leftrightharpoons HD(g) + \sigma\text{-OH} \end{array}}{D_2(g) + H_2(g) \leftrightharpoons 2HD(g)}$$

Since there might also be some active sites for the catalytic exchange reaction that do not undergo this stoichiometric reaction, it is clear that the quantity of exchangeable σ-OH is a lower limit to the number of active sites. By combining this value with the upper limit of the number of active sites as determined by selective poisoning, the true number of active sites is bracketed within the two limits. To our knowledge this is the first time that it has been possible to bracket the number of active sites within two bounds.

The amount of exchangeable σ-OH was measured immediately after activation to avoid any complication due to exchange of the catalyst during the catalytic reaction. The amount of exchangeable σ-OH of an empty reactor is zero. Experiments on MgO as well as on many other oxides showed a very rapid exchange that occurred within the time resolution of the technique (1 s) followed by a much slower rate of exchange. This is the basis for dividing the exchangeable σ-OH into two groups, but is not meant to imply that the activity of all sites within a group is the same. The rate of production of HD(g) was negligible after roughly 1 h, a typical result being shown in Fig. 5 (the first 50 s of data is averaged to a single point for this graph). Tables 1 and 2 show the amount of fast, slow, and total exchangeable σ-OH for the catalysts. After activation at T_{max}, the amount of fast exchangeable σ-OH corresponds to 0.7% of the residual σ-OH on MgO-WSU.

The contribution of the fast and slow exchangeable σ-OH to the total rate of the H_2–D_2 exchange reaction is proportional to the product of the number of sites and the average activity per site within each group. Due to the time constant of the mass spectroscopic analysis, an accurate measure of the relative activity per site of the two sets of sites cannot be obtained. However, it is sufficient to note that the fast exchange occurred in no more than about 1 s and the slow exchange occurred in about 3600 s. The ratio of the two types of contributions to the catalytic activity for H_2–D_2 exchange is given by the following formula

$$(f/f_t)/(s/s_t) \cong 3600\ (f/s),$$

where f is the amount of fast exchange that occurs in time f_t, and s is the amount of slow exchange that occurs in time s_t. The ratio is typically >1000, so for this catalyst it is only necessary to focus on the fast exchangeable σ-OH. The amount of fast exchangeable σ-OH varies in the same manner with the temperature of activation as does the activity for the exchange reaction (Fig. 6).

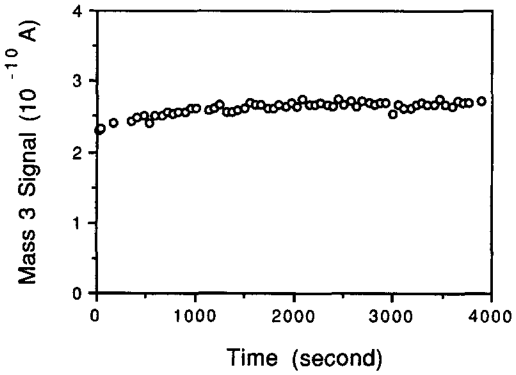

FIG. 5. Accumulative exchange of σ-OH on MgO-WSU. The background signal at mass 3 is 1.71×10^{-10} A.

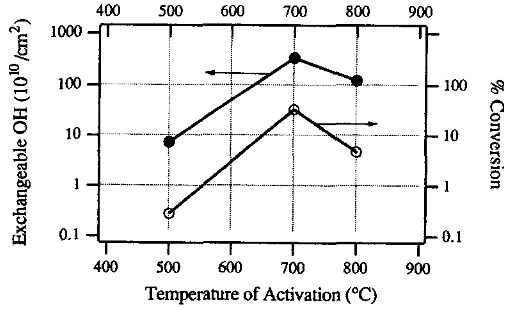

FIG. 6. Effect of temperature of activation on activity and amount of exchangeable OH on MgO-WSU. (●) Exchangeable OH; (○) percentage conversion.

After activation at 800°C and having its activity measured, a catalyst was rehydroxylated (Table 2). Helium gas was passed through a bubbler at room temperature and flowed through the reactor for 10 min at 300°C. The catalyst was then heated to 700°C *in vacuo*. This procedure increased the activity by about 10-fold and increased the amount of fast exchangeable σ-OH by 5-fold. This demonstrates the importance of σ-OH groups. However, it is not expected that the catalyst will duplicate the original activity (after activation at 700°C) since it is not likely that the two surfaces are identical. In another experiment, the amount of exchangeable σ-OH was determined after CO poisoning (Table 2). The quantity of CO adsorbed was 0.0019 ml, corresponding to 2.0×10^{12} sites/cm^2 (the total site density, based on extrapolation of the poisoning data to zero conversion, was 2.6×10^{12} sites/cm^2). This caused the amount of fast exchangeable σ-OH to drop 10-fold and the activity dropped about 3-fold. The lack of a simple linear relationship between changes in the amount of fast exchangeable σ-OH and activity is not surprising since it is expected that the sites are not all of the same activity. Since the exchangeable σ-OH must be active sites for the catalytic reaction and the amount changes with temperature of pretreatment, rehydroxylation, and CO poisoning in the same manner as the catalytic activity, it appears likely that they are also the dominant source of the activity. This is required for MgO-WSU, since the lower and upper bounds for the number of active sites are identical within experimental error. A similar result has been reported for γ-alumina (*6*). In this case all of the activity for the exchange reaction could be ascribed to the fast exchangeable σ-OH.

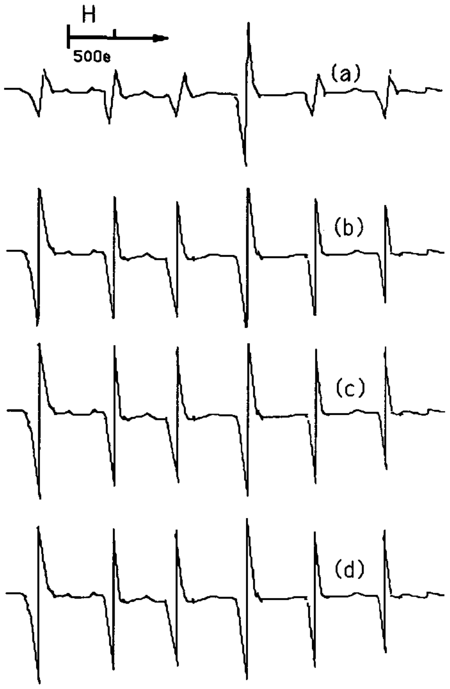

FIG. 7. EPR signal of MgO-JM at 298 K. Sample degassed at (a) 500°C; (b) 700°C; (c) 900°C. Curve (d) is after CO poisoning.

EPR measurements. The spectrographically pure sample, MgO-JM, was used for EPR measurements. In contrast to the signal described by Boudart *et al.* (*1*), this sample gave a seven-line EPR signal with a Lorentzian lineshape (Fig. 7). The intensity of the signal increased about 4-fold when the temperature of pretreatment increased from 500 to 700°C. This treatment causes the activity to increase by over 100-fold. Neither heating at 900°C nor exposure to 1 atm of CO or to air for 24 h decreased the EPR signal, although each of these treatments destroys the activity. Although there is an increase in the EPR signal during the initial dehydroxylation of the MgO and this fortuitously occurs as the activity is developing, it is clear that the EPR signal is not due to the active site.

Proposed mechanism of the H_2–D_2 exchange reaction. The foregoing data indicate that the active site for the H_2–D_2 exchange reaction over MgO probably requires both σ-OH as well as exposed Mg^{2+} and O^{2-} ions. The former species is destroyed and the latter species are created by dehydroxylation. Thus, the activity is maximum at an intermediate degree of hydroxylation. Since only a very small frac-

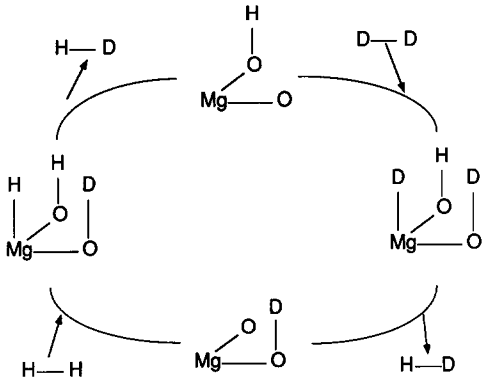

FIG. 8. Mechanism for H_2–D_2 exchange over MgO.

tion of the σ-OH are active, it appears that some special geometric arrangement or possibly some other species may also be involved in the active site. Based on what is known at this time, it is proposed that the active site is a multicenter ensemble, termed a *delta* site in recognition of its three known component species. This is similar to the site suggested by Boudart in that a multiplet center involving σ-OH is invoked, but we believe that Mg^{2+} is part of the active site. A mechanism for the exchange reaction is shown in Fig. 8. Although a triangular geometry is depicted for concreteness, the data do not differentiate between this and other geometries (including linear). A similar mechanism has been proposed for the reaction over γ-alumina, and it appears that this mechanism may have wide application for hydrogen activation over metal oxides.

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