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Catalytic Isomerization of Ethylenic Hydrocarbons

XVIII. Effect of Drying and Reaction Temperature on the Isomerization of Deuterated Butenes over Magnesium Oxide

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The isomerization of selectively deuterated *cis*-2-butenes was investigated at 60 and 250°C on magnesium oxide predried between 300 and 550°C. A rise in the drying temperature increases the number of active sites, but modifies neither their nature, nor their strength. The working temperature has a marked influence on the reactions observed. At 60°C, magnesium oxide catalyzes only double-bond migration without exchange of hydrogen between the olefin and the catalyst; at 250°C, a multiple exchange of hydrogen occurs during double-bond migration. In both cases the active sites are basic O^{2-} ions associated with weak acid Mg^{2+} ions, but adjacent OH groups participate in the reaction at 250°C. Some strong basic O^{2-} ions are also active at 250°C, but they deactivate very rapidly: on these sites, double-bond migration and *cis–trans* isomerization, both without exchange, are observed.

INTRODUCTION

A previous study (*1*) of the isomerization of selectively deuterated *cis*-2-butenes at 60°C showed that magnesium oxide prepared by dehydrating the hydroxide at 500°C had a behavior similar to that of homogeneous bases: the only reaction observed was a double-bond migration of *cis*-2-butene. This reaction occurred without any exchange of hydrogen between the olefin and the catalyst, since (1,4-D_6)-*cis*-2-butene yielded (D_6)-1-butene, and (2,3-D_2)-*cis*-2-butene yielded (D_2)-1-butene; an important isotope effect was measured when the reactant was labeled in the allylic position. All these results were explained by a π-allylic carbanion mechanism similar to the one proposed for the isomerization in a homogeneous basic medium (*2–4*).

However, the catalytic activity of acid–base oxides depends on the amount, the strength, and the kind of acidic and basic sites on the surface, all these depending in turn on the drying temperature of the oxide (*5, 6*). This surface heterogeneity implies that several types of reaction generally occur simultaneously; as the activation energies of these reactions are different, the working temperature will be an important parameter for the selectivity of the catalyst.

For these reasons, the aim of the present work is to study the effect of the drying temperature (from 300 to 550°C) and of the reaction temperature (60 and 250°C) on the acid–base properties of magnesium oxide, and on its selectivity for the isomerization of nondeuterated and selectively deuterated *cis*-2-butenes. Poisoning experiments were also carried out to obtain information on the nature of the active sites.

EXPERIMENTAL METHODS

The magnesium oxide was prepared by dehydrating magnesium hydroxide *in situ* in a flow of nitrogen. Nitrogen was dried by flowing down through a 5A molecular sieve column: a dewpoint of −75°C was reached,

0021-9517/84 $3.00

TABLE 1

Effect of Drying Temperature on the Dehydration of Magnesium Hydroxide and on the Surface Area of the Resulting Magnesium Oxide

Drying temperature[a] (°C)	300	350	400	500	550
Percentage of dehydration	17.5	97.7	98.8	99.1	99.3
Area (m^2g^{-1})	127	256	166	145	139

[a] 12-hour drying.

the carbon dioxide level being reduced at the same time to less than 1 ppm. Oxygen was eliminated by means of Cu deposited on a 5A molecular sieve. As has already been observed by others (*7*, *8*), the dehydration began at 300°C and was nearly completed at 350°C (Table 1). A 2-hr pretreatment was sufficient to obtain maximum dehydration; however, magnesium hydroxide was dehydrated overnight before each experiment. The specific surface area of the catalysts increased when the drying temperature was raised from 300 to 350°C, and then decreased rapidly (Table 1).

The catalysts will be designated MO-t, where t is the drying temperature: for instance, MO-350 will represent the magnesium oxide obtained by dehydrating the hydroxide at 350°C.

The basic properties of the catalysts were determined using Hammett indicators. The acidity of the catalysts was measured by thermodesorption of pyridine: the catalysts were first saturated with pyridine at 150°C, then the temperature was raised 50°C at a time, and the pyridine desorbed was detected by a flame ionization detector.

The isomerization experiments were carried out on fresh samples of catalyst in the microreactor described previously (*9*); the catalyst weight ranged between 0.2 and 0.5 g. The activities and selectivities were determined using nondeuterated *cis*-2-butene and 1-butene. In order to avoid secondary reactions, the activities of the catalysts were measured under conditions where conversion was less than 10%. Each injection of butene contained about 1 cm^3 (4.5×10^{-5} mole) of reactant.

The preparation of deuterated *cis*-2-butenes has already been described (*10*). To measure the isotope effects (IE), the deuterated *cis*-2-butenes were injected between two runs of light *cis*-2-butene under the same conditions (catalyst weight, carrier gas space velocity). The amount of each isomer produced from light *cis*-2-butene was plotted against the amount of the same isomer formed from deuterated *cis*-2-butene. The isotope effect k_H/k_D is given by the slope of the curve at zero conversion.

To estimate the poisoning effect a series of butene runs was carried out, and the poisons injected in the reactor about 5 sec before one of these runs.

RESULTS

Effect of the Drying Temperature on the Acid–Base Properties of Magnesium Oxide

Figure 1 presents the number of pyridine molecules which remain adsorbed on the catalysts after desorption at different temperatures. The number of acid sites which adsorb pyridine at 150°C increases from MO-300 to MO-350, then remains constant

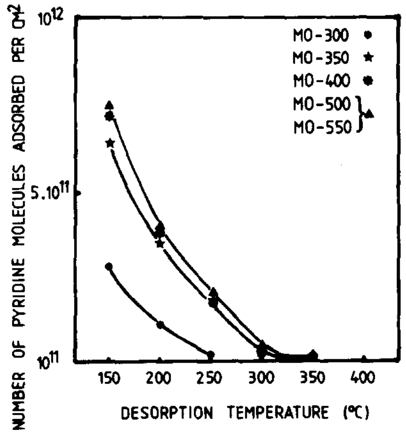

FIG. 1. Effect of drying temperature on the acidity of magnesium oxide: thermodesorption of pyridine.

TABLE 2

Isomerization of Butenes on Magnesium Oxide at 60°C; Effect of Drying Temperature

Reactant	Property	Catalyst				
		MO-300	MO-350	MO-400	MO-500	MO-550
(D_0)-*cis*-2-Butene	Activity at 60°C[a]	0.3	12	26	42	46
	Activity at 250°C[a]		19		37[b]	
$(2,3\text{-}D_2)$-*cis*-2-Butene	Isotope effect[c]	—	1.0	1.0	1.0	1.0
$(1,4\text{-}D_6)$-*cis*-2-Butene	Isotope effect[d]	—	5.0	5.3	5.5	5.2

[a] Units: micromole butene isomerized h^{-1} m^{-2}; [1-butene]/[*trans*-2-butene] formed from (D_0)-*cis*-2-butene >50; [*cis*-2-butene]/[*trans*-2-butene] formed from (D_0)-1-butene = 4.

[b] After deactivation.

[c] Product of isomerization, extrapolated to zero conversion = $C_4H_6D_2$.

[d] Product of isomerization, extrapolated to zero conversion = $C_4H_2D_6$.

from MO-350 to MO-550. Pyridine is retained up to 350°C on all the catalysts, but only up to 250°C on MO-300. These results indicate that the number and the strength of the acid sites are very similar on all the catalysts, but less numerous and less strong on MO-300.

The adsorption of Hammett indicators indicated that all the catalysts from MO-300 to MO-550 exhibited important basic properties: the H_0 of the surface ranges from 17.2 to 18.4, corresponding to the pK_a of 4-chloro 2-nitroaniline and 4-nitroaniline, respectively.

Effect of the Drying Temperature on the Isomerization of Butenes on Magnesium Oxide at 60°C

All the catalysts presented a very stable activity at 60°C; as shown in Table 2, the activity of magnesium oxide rapidly increases from MO-300 to MO-500 then stabilizes. A similar increase in activity with drying temperature has already been observed on magnesium oxide (*7, 8*) and on other basic catalysts such as La_2O_3 (*11, 12*). It should also be noted that there is no relationship between the activity of the catalyst and the number and the strength of the acid sites (Fig. 1), or the basic strength H_0 of the surface. This suggests that the increase in activity observed with the rise in drying temperature is linked to an increase in the number of basic sites. Whatever the drying temperature, magnesium oxide catalyzes only double-bond migration: the ratio of 1-butene to *trans*-2-butene formed from light *cis*-2-butene ($S_{1/t}$) is greater than 50 on all the catalysts. On the other hand, the isomerization of light 1-butene yields *cis*-2-butene rather than *trans*-2-butene ($S_{c/t}$ = 4.0).

The deuterated *cis*-2-butene isomerization experiments were carried out at 60°C on all the catalysts except MO-300: the activity of the latter was so low that an accurate mass spectrometric analysis of the products would have been impossible. As shown in Table 2, on all the catalysts double-bond migration occurs with no exchange of H(D) between the olefin and the catalyst. There is formation of (D_2)-1-butene or (D_6)-1-butene only. This latter reaction gives rise to a very marked isotope effect (5.0–5.5), close to the maximum value at 60°C (5.6) calculated from the difference of energy between the C–H and C–D bonds at 0 K (*13*).

The possibility that the absence of exchange might be due to an isotopic dilution of the hydrogen of the catalyst was ruled out by including the reactant in a large slug of propene: no significant change arose in the isotopic distribution in the 1-butene produced.

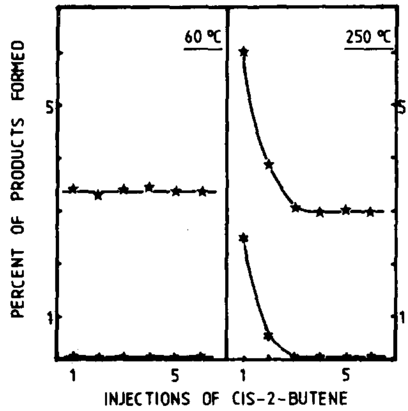

FIG. 2. Effect of reaction temperature on the activity of MO-500. ★, 1-Butene; *, *trans*-2-butene.

Effect of the Reaction Temperature on the Isomerization of Butenes on Magnesium Oxide

The effect of the reaction temperature (60 and 250°C) was examined on MO-350 and MO-500 (see Table 2).

MO-350 presents a stable activity at 250°C, slightly greater than at 60°C (apparent activation energy = 1.0 kcal mole^{-1}). On the other hand, MO-500 exhibits a rapid deactivation at 250°C during the first runs, before reaching an almost stable activity (Fig. 2). The initial activity of MO-500 at 250°C is three times greater than its activity at 60°C (activation energy = 2.3 kcal mole^{-1}) but after deactivation MO-500 is less active at 250°C than at 60°C (Table 2). It should be noted that if the activities are measured once more at 60°C, after being measured at 250°C, MO-350 has lost about 70% of its initial activity, whereas MO-500 has deactivated completely. Consequently, it seems that both catalysts deactivate very rapidly at 250°C, which explains the low activation energies measured.

At 250°C, the $S_{1/t}$ and $S_{c/t}$ selectivities of MO-350 and MO-500 (deactivated) are the same as those observed at 60°C: *cis*-2-butene yields only 1-butene, and 1-butene preferentially *cis*-2-butene. However, before deactivation at 250°C, MO-500 yields a significant amount of *trans*-2-butene (Fig. 2).

The isotope distribution in the 1-butene produced at 250°C on MO-350 does not change with working time and is identical to that observed on MO-500 (deactivated). However, both are different from those observed at 60°C.

Figure 3 shows that 1-butene produced by isomerization of (1,4-D_6)-*cis*-2-butene at 250°C contains unexchanged species, 10% (D_6), as well as exchanged species, 61% (D_5), 20% (D_4), 7% (D_3), and 2% (D_2). The isotope distribution does not change with the percentage of conversion. The 1-butene contains about 4.6 D per molecule, which corresponds to a loss of 1.3 D with respect to the reactant. The *cis*-2-butene recovered at low conversion is not exchanged (Fig. 3), but has lost 0.3 D per molecule at 10% conversion. The isomerization of (1,4-D_6)-*cis*-2-butene gives rise to an important isotope effect, namely 2.3 on MO-350 and 1.9 on MO-500 (maximum value at 250°C = 3.0).

Figure 4 presents the change of the isotope distribution in 1-butene formed and in *cis*-2-butene recovered by isomerization of (2,3-D_2)-*cis*-2-butene on MO-350 and MO-500 (deactivated) at 250°C. At 2% conversion, 1-butene contains about 1.86 D per molecule, which corresponds to a loss of 0.1 D with respect to the reactant; the *cis*-2-

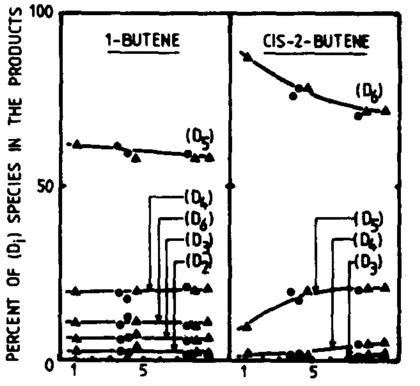

FIG. 3. Isomerization of (1,4-D_6)-*cis*-2-butene at 250°C on MO-350 (▲) and MO-500 (●). Starting material (%): 0.9 (D_4), 10.7 (D_5), 88.4 (D_6).

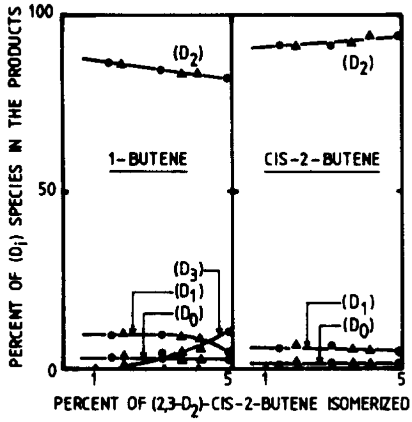

FIG. 4. Isomerization of (2,3-D_2)-*cis*-2-butene at 250°C on MO-350 (▲) and MO-500 (●). Starting material (%): 0.2 (D_0), 1.6 (D_1), 98.2 (D_2).

butene recovered is not much exchanged either. No isotope effect is measured for the isomerization of (2,3-D_2)-*cis*-2-butene.

TABLE 3

Isomerization of (1,4-D_6)-*cis*-2-Butene on MO-500 at 250°C: Percentage of Each Deuterated 1-Butene Species Formed

Pulse number	1-Butene formed (%)				
	(D_6)	(D_5)	(D_4)	(D_3)	Total
1	5.36	2.00	0.64	0	8.00
2	3.15	2.00	0.62	0.18	5.95
3	1.22	1.90	0.62	0.20	3.94
4	0.35	1.80	0.58	0.18	2.91
5	0.36	1.78	0.63	0.19	2.96
6	0.34	1.81	0.57	0.17	2.89

The isomerization of (1,4-D_6)-*cis*-2-butene was also performed at 250°C on MO-500 during the deactivation (Fig. 5). The amount of exchanged species in 1-butene, viz. (D_5), (D_4), and (D_3), is small in the first run, then increases rapidly when the catalyst deactivates. However, Table 3 indicates that there is a constant yield in exchanged 1-butene from pulse 1 to pulse 6, whereas the yield in (D_6)-1-butene decreases from pulse 1 to pulse 4. On the other hand, the *trans*-2-butene produced during runs 1 and 2 is not exchanged. The $S_{1/t}$ selectivity measured during the isomerization of (1,4-D_6)-*cis*-2-butene is the same as that measured during the isomerization of light *cis*-2-butene; this indicates that double-bond migration and *cis–trans* isomerization observed initially occur with the same isotope effect.

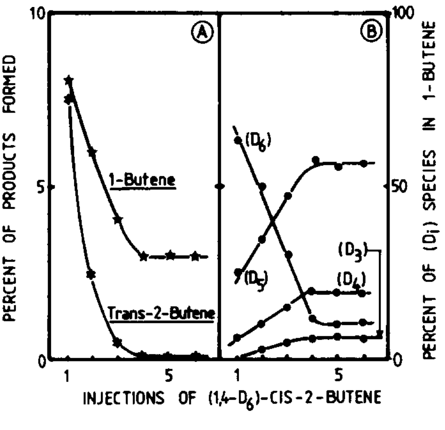

FIG. 5. Isomerization of (1,4-D_6)-*cis*-2-butene at 250°C on MO-500: activity of the catalyst (A) and isotope distribution in the 1-butene produced (B). Starting material (%): 0.9 (D_4), 10.7 (D_5), 88.4 (D_6).

Effect of Poisons on the Isomerization of Butenes on Magnesium Oxide

The effect of CO_2, NH_3, and H_2O was studied at 60 and 250°C on MO-350 and MO-500 (deactivated); the results are reported in Table 4.

TABLE 4

Effect of Poisons on MO-350 and MO-500 at 60 and 250°C: Percentage of 1-Butene Produced

	Reaction temperature (°C)		60	250
MO-350 0.50 g	Initial		3.8	4.1
	after	2.5 cm^3 CO_2	0.15^a	0.08^a
		10 cm^3 NH_3	3.50	3.75
		1 μl H_2O	2.55^a	2.75
MO-500 0.23 g	Initial		3.5	2.8
	after	2 cm^3 CO_2	0.35^a	0^a
		10 cm^3 NH_3	3.20	2.60
		1 μl H_2O	2.04^a	0.80

^{a} Irreversible modification.

CO_2 strongly deactivates MO-350 and MO-500 at 60 and 250°C, without changing the $S_{1/t}$ selectivity. A total deactivation of the catalyst at 60°C would need 5.5×10^{13} molecules cm^{-2} on MO-350 and 1.8×10^{14} on MO-500, which indicates that MO-500 has 3.3 times as many active sites as MO-350. The isotope distribution in the 1-butene produced after CO_2 poisoning is identical to the initial one.

NH_3 has only a weak deactivation effect on MO-350 and MO-500, both at 60 and at 250°C; this effect is immediately reversible and does not modify the selectivity of the catalysts.

H_2O deactivates MO-350 and MO-500 irreversibly at 60°C, but momentarily at 250°C. A total deactivation at 60°C would need 8×10^{13} molecules cm^{-2} on MO-350 and 2.4×10^{14} on MO-500: the active sites which adsorb water are consequently 3.0 times more numerous on MO-500 than on MO-350. The isotope distribution in the 1-butene produced at 60°C and the $S_{1/t}$ selectivity at 60 and 250°C are not modified by H_2O adsorption.

The effect of CO_2 and H_2O was also studied on MO-500 at 250°C before deactivation: 2 cm^3 CO_2 or 1 μl H_2O was added to the catalyst about 10 min before the first *cis*-2-butene run. Under these conditions, the catalyst treated by CO_2 presents no activity, and that treated by H_2O exhibits the same deactivation period, poisoned or not.

DISCUSSION

All our results confirm that, whatever the drying temperature, magnesium oxide possesses strong basic sites, as shown by H_0 close to 18, high sensitivity to CO_2, and selective double-bond migration as in the case of homogeneous bases (*2–4*). Nevertheless, the participation of weak acid sites of the catalyst cannot be ruled out since one observes a slight deactivating effect of ammonia and a small chemisorption of pyridine.

On the other hand, the isotope distribution in the 1-butene produced depends a great deal on the reaction temperature: no exchange is observed at 60°C, whereas multiexchanged species are obtained at 250°C. Reactions with exchange of hydrogen are consequently favored by an increasing reaction temperature, as already observed on alumina (*5*).

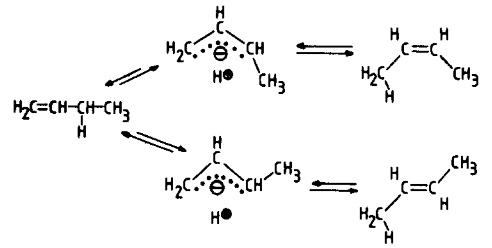

FIG. 6. Isomerization of butenes through allylic carbanion intermediates.

First we shall discuss the results obtained at 60°C, then those obtained at 250°C. This discussion will be limited to MO-350 and MO-500; the similarity in the behavior of all our samples allows us to believe that the conclusions of this discussion may be extended to MO-300, MO-400, and MO-550.

Isomerization of Butenes on Magnesium Oxide at 60°C

The results obtained on MO-350 and MO-500 at 60°C may be explained (*1*) by a mechanism involving π-allylic carbanion intermediates similar to that proposed for the isomerization in a homogeneous basic medium (Fig. 6). Such intermediates explain why no *cis–trans* isomerization is observed, since the change from the *cis*-anion to the *trans*-anion would be prohibited (*2*). Moreover, the *cis*-anion is generally considered (*2–4*) to be more stable than the *trans*-anion, which explains the preferential formation of *cis*-2-butene from 1-butene. Indeed, high *cis*/*trans* ratios have been measured on many basic catalysts, for example, MgO (*7, 8, 14*), La_2O_3 (*11, 15*), and ZnO (*15–17*). Moreover, with our catalysts, we observe a selective *cis*-2-butene → 1-butene isomerization ($S_{1/t}$ > 50, Table 2). There is some discrepancy here between the present results and those found in the literature: $S_{1/t}$ ratios lower than unity have been measured on MgO (*7, 8*) and ZnO (*15–17*); however, high $S_{1/t}$ ratios have been observed on La_2O_3 (*12, 15*) and CdO (*18*). Although we have no definite explanation for these divergences, it should be noted that the above experiments were carried out at low reaction temperatures, where the thermodynamic equilibrium amount of 1-butene is very small. Under such conditions, the $S_{1/t}$ ratio measured could be nonrepresentative of the initial selectivity of the catalyst, in particular when high conversion levels of *cis*-2-butene are obtained. Moreover, the activation conditions (temperature, *in vacuo* or in a gas flow) were very different, which suggests that most of the investigations were probably carried out on different catalysts. Finally, the results obtained could depend on the manner in which the experiments were performed, as demonstrated by Goldwasser and Hall (*19*).

The reactions observed on MgO are inhibited by CO_2, which implies that basic sites are involved in isomerization; these sites may be either O^{2-} ions (*20, 21*), or OH^- ions (*20*). On the other hand, the slight deactivation provoked by NH_3 adsorption indicates that acid sites probably participate in the reaction. The isomerization of selectively deuterated butenes occurs without any exchange of hydrogen between the olefin and the catalyst. A similar result has been obtained using tracer studies on many basic catalysts, e.g., MgO (*14*), La_2O_3 (*12, 15*), and ZnO (*17*). This indicates that the active sites are nonprotonic and consequently the basic sites are O^{2-} ions and the acid sites are Lewis acid sites, i.e., Mg^{2+} ions. The basic sites on the surface can be destroyed by rehydroxylation (*22*), which explains the deactivation observed after H_2O adsorption (Table 4). It must be noted that the basic sites are about 3.3 times more numerous on MO-500 than on MO-350 (CO_2 and H_2O poisoning experiments), and that MO-500 is 3.5 times more

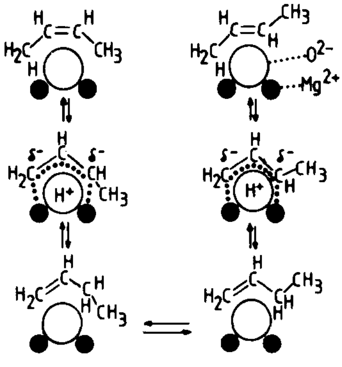

FIG. 7. Isomerization of butenes on magnesium oxide at 60°C.

active than MO-350 (Table 2). This indicates that the rise in the drying temperature increases the number but not the strength of the active sites on the surface, as has already been stated (*23*). Moreover, the number of CO_2 or H_2O molecules needed to deactivate MO-350 and MO-500 at 60°C compares closely with the number of sites responsible for tetracyanoethylene (*23*) or trinitrobenzene (*24*) radical formation; these electron donor sites were believed to be the O^{2-} ions located on the corners of the cubic oxide lattice (*25, 26*).

The mechanism proposed by Baird and Lunsford (*23*) explains clearly all these observations (Fig. 7): *cis*-2-butene adsorbs on an exposed oxide ion which removes an allylic proton from the molecule and transfers it to a vinylic carbon atom. During this 1-3 transfer, the π-allylic carbanion is held in the *cis*-configuration by electrostatic interaction between the terminal carbon atoms and two magnesium cations. Such a mechanism excludes any possibility of direct *cis–trans* isomerization.

Isomerization of Butenes on Magnesium Oxide at 250°C

The isomerization selectivity at 250°C on MO-350 and MO-500 (deactivated) is identical to that observed at 60°C: no *cis–trans* isomerization occurs, and there is preferential formation of *cis*-2-butene from 1-butene. As at 60°C, the active sites are very sensitive to CO_2 and slightly to NH_3; the only difference is that the deactivating effect of H_2O is reversible at 250°C, and irreversible at 60°C. Consequently, it is reasonable to suppose that the sites active at 250°C are the same as those active at 60°C, i.e., strong basic sites associated with weak acid sites. In this case the reaction intermediates at 250°C would be π-allylic carbanions.

However, the isomerization of selectively deuterated *cis*-2-butenes gives very different results at 60 and at 250°C, since an important exchange of hydrogen between the olefin and the catalyst is observed at 250°C on MO-350 and MO-500. On the latter, the amount of exchanged 1-butene remains constant all through the deactivation period at 250°C, but initially the double-bond shift without exchange prevails (Table 3); this reaction, as opposed to the one with exchange, is strongly affected by deactivation (Table 3). A similar phenomenon has already been observed with titanium dioxide (*6*).

On MO-350 and MO-500 (deactivated), the isomerization of (1,4,D_6)-*cis*-2-butene yields 1-butene containing, in order of their importance, (D_5), (D_4), (D_6), and (D_3) species (1.3 D atom lost per molecule). The *cis*-2-butene recovered is partially exchanged, the exchange rate increasing with the conversion; on the other hand, the exchange rate in 1-butene remains constant (Fig. 3). These results suggest that the multiple hydrogen exchange occurs during a single adsorption of the molecule. If one assumes that the reaction mechanism is the same at 250 and at 60°C, it must be supposed that the D atom abstracted from (1,4-D_6)-*cis*-2-butene is rapidly exchanged by hydrogen atoms of the catalyst. The presence of multiexchanged species in the 1-butene implies that more than one hydrogen atom is required. This result can be accounted for if one assumes that the allylic carbanion rapidly isomerizes before desorbing. If this isomerization is rapid compared to desorption, and if the hydrogen atoms can migrate on the surface, then the molecule can exchange more than one deuterium atom. This hypothesis is shown in Fig. 8 to explain the formation of (D_6)-1-butene by isomerization without exchange, that of (D_5)-1-butene by single exchange, and that of (D_4)-1-butene by double exchange and isomerization of the carbanion. It must be noted that this mechanism explains the exchange observed in the *cis*-2-butene recovered from (1,4-D_6)-*cis*-2-butene isomerization, as well as the absence of exchange in the products of isomerization of (2,3-D_2)-*cis*-2-butene: effectively, the vinylic deuterium atoms are not involved in such a mechanism.

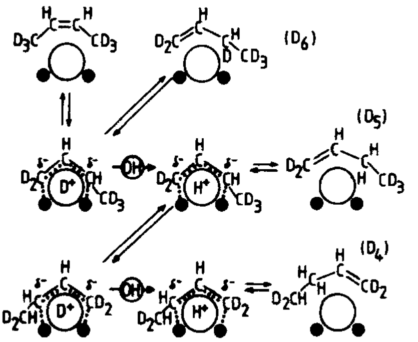

FIG. 8. Exchange and double-bond migration of (1,4-D_6)-*cis*-2-butene on magnesium oxide at 250°C.

As for the nature of the active sites, it is necessary to invoke the participation of protonic sites on the catalyst, or at least hydrogen-containing sites, to explain the exchange observed. Hydroxyl groups have been detected on magnesium oxide (*22, 27*), even after pretreatment at 500°C in vacuum (*22, 28*). It has been reported (*27*) that dehydration proceeds through an increase of the dehydroxylated areas, and leaves OH clusters on the surface; such clusters could account for the rapid exchange of the D atom abstracted from the molecule. It must be noted that a surface proton has been considered (*29*) as essential to the H_2–D_2 equilibration on MgO; the active site was identified as an OH^- group, adjacent to a paramagnetic defect center consisting of three O^- ions (so-called V_I center). However, these V_I centers ap-

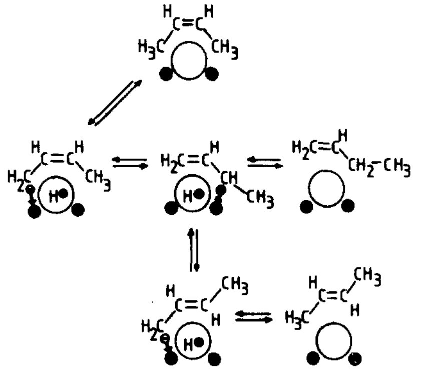

FIG. 9. Double-bond migration and *cis–trans* isomerization of *cis*-2-butene on magnesium oxide at 250°C.

peared only after pretreatment in vacuum at 500°C (*29*), and consequently could not be present on MO-350; moreover, they seem to be insufficiently basic to explain the results reported in the present paper. Therefore, an active site consisting of an O^{2-} ion adjacent to OH groups (*20*), associated with magnesium cations, is quite probable.

Nonprotonic sites are also active on MO-500 before deactivation, and responsible for double-bond migration and *cis-trans* isomerization, both without exchange. A similar reaction has already been observed on alumina (*5*): the active centers were proposed to be strong Lewis acid–base pair sites, the strong Lewis acid sites on alumina being readily destroyed by water adsorption at 250°C. This suggests that such sites do not exist on magnesium oxide, since the preadsorption of water does not modify the behavior of the catalyst. On the other hand, the active centers are obviously basic, since they are poisoned by preadsorption of CO_2. Consequently, these centers could be magnesium cations associated with weakly coordinated O^{2-} ions, similar to those observed by Che *et al.* (*24*): these O^{2-} ions adsorb the molecules strongly, and the electron is not delocalized over the whole molecule, but localized at one point. On such active centers, the reaction intermediates would be σ-allylic species instead of π-allylic ones, which would allow both a double-bond shift and a *cis–trans* isomerization without exchange (Fig. 9). The consumption of these centers during the first butene runs may be due to an irreversible adsorption of the olefin on the O^{2-} ions.

Finally, there are two types of sites which are active simultaneously on MO-500 at 250°C before deactivation:

(i) Strong basic centers, responsible for the double-bond shift and the *cis–trans* isomerization, both without exchange, and involving σ-allylic intermediates;

(ii) Strong basic O^{2-} ions associated with OH groups, catalyzing only a double-bond migration with a multiple hydrogen exchange, involving π-allylic intermediates.

The first type of site is destroyed during the first butene runs, and only the second type is active on the deactivated catalyst.

The apparent activation energy measured on MO-350 is similar to that measured on deactivated MO-500. This result definitely suggests that the sites initially active on MO-500 at 250°C also exist on MO-350, but they are not detected perhaps because they are few in number. In this case, MO-350 at 250°C would in fact be a deactivated catalyst.

CONCLUSION

The present work has enabled us to show that the selectivity of magnesium oxide is not influenced by the drying temperature. A rise in the drying temperature increases the number of active sites without modifying their nature or their strength, which is the contrary of what was observed with other acid–base oxides (*5, 6*). On the other hand, the reaction temperature has a marked influence on the selectivity of the catalyst. At 60°C, magnesium oxide catalyzes only double-bond migration without exchange of hydrogen between the olefin and the catalyst; at 250°C, a multiple exchange of hydrogen occurs during double-bond migration. The active sites are basic O^{2-} ions associated with weak acid Mg^{2+} cations, with additional OH groups for a reaction carried out at high temperature. Magnesium oxide also possesses strong basic O^{2-} ions which catalyze at 250°C double-bond migration and *cis–trans* isomerization, both without exchange; these sites are active only during the first butene runs, probably because of an irreversible adsorption of the olefin. All the reactions observed occur through carbanionic species formed by abstraction of an allylic hydrogen of the molecule by the basic sites of magnesium oxide.

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