

Evaluation of the acid–base surface properties of several oxides and supported metal catalysts by means of model reactions

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Abstract

Acid–base properties of oxides (Al_2O_3 , SiO_2 , ZrO_2 , CeO_2 , MgO , $\text{SiO}_2\text{–Al}_2\text{O}_3$ and $\text{CeO}_2\text{–Al}_2\text{O}_3$) were investigated by means of model reactions: 3,3-dimethylbut-1-ene isomerization (33DMB1), methylene cyclohexane isomerization (MECH), cyclohexanol conversion (CHOL) and CO_2 chemisorption at room temperature. The effect of acid (Cl^- , SO_4^{2-}) and basic (K^+) promoters on certain oxides (Al_2O_3 , ZrO_2) was also studied. Surface acidity was evaluated by means of 33DMB1 or MECH isomerization and of CHOL dehydration into cyclohexene. CO_2 chemisorption as well as the cyclohexanone to cyclohexene ratio in CHOL conversion were used to measure the surface basicity of the solids. Except for very few cases, all the tests gave coherent results which led to well-defined scales of acidity and of basicity. Contrary to what could be observed with the conventional isopropanol test, the CHOL test proves to be little sensitive to the redox sites of the oxides. The presence of metals can create significant perturbations in these acid–base tests, except in the case of 33DMB1 isomerization. The latter reaction is not catalyzed by Pt and Rh surfaces, which allows to measure (in the presence of these metals) the acid properties of the support and to investigate the changes in surface acidity, resulting from the metal impregnations (metal \rightarrow support electronic effect, presence of anions,...).

Keywords: Acid–base properties of oxides and supported metal catalysts; 3,3-dimethylbut-1-ene isomerization; Methylene cyclohexane isomerization; Cyclohexanol dehydration and dehydrogenation; CO_2 chemisorption; Alumina; Ceria–alumina; Silica; Silica–alumina; Zirconia; Ceria; Magnesia

1. Introduction

In recent studies about oxygen mobility at the surface of supported metal catalysts [1,2], we have shown that there existed a correlation between the oxygen mobility and the basicity of the oxide used as a support. We are at present investigating the hydrogen surface mobility on

the same catalysts. A possible correlation between hydrogen surface mobility and oxide acidity is envisioned. For this purpose, we have looked for chemical methods which allow us to measure the acid–base properties of oxides impregnated or not with noble metals.

Many chemical methods for measuring the acid–base surface properties of oxides have been developed [3–8]. Three main groups of methods can be used. The first concerns the titration methods based on the use of colored indicators

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in liquid phase [5,8]. However, the methods are not well adapted to the characterization of the acid–base properties of catalysts normally used in gas phase. The second group is based on gas phase adsorption of basic [6–9] or acidic [8–10] probe molecules. In the third group of methods, the acid–base properties of oxides are deduced from their catalytic behavior in model reactions. A great deal of acidity test-reactions have been reported [11–14]. For this purpose, alkene isomerization (double-bond shift or skeletal isomerization) are widely employed. In contrast, model reactions capable of characterizing the surface basicity are relatively scarce. In fact these reactions are generally sensitive to acid and base properties of the solid, as is the case for the conversion of secondary alcohols [15–23]. Owing to the amphoteric character of the alcohols, two main reactions can occur: (i) the dehydration into alkene and (ii) the dehydrogenation into ketone.

In the present study, three model reactions were used to investigate the acid–base properties of oxides (impregnated or not with noble metals): (i) the skeletal isomerization of 3,3-dimethylbut-1-ene (33DMB1), (ii) the double-bond shift isomerization of methylene cyclohexane (MECH), (iii) the cyclohexanol (CHOL) conversion. The 33DMB1 test is a well-adapted reaction for characterizing the acid centers with a medium strength, desorbing pyridine at 220°C [24,25]. Owing to the weak acidity of certain oxides inactive for 33DMB1 isomerization, we also used the isomerization of methylene cyclohexane (MECH) into methyl cyclohexenes (MCHE). Because of the exocyclic position of the double bond, the MECH is thermodynamically unstable and the formation of the 1-methyl cyclohexene (1MCHE) isomer is extremely favored [26]. The conversion of the cyclohexanol (CHOL) allowed us to evaluate the acid–base surface properties of the oxides. To obtain a measurement of the surface basicity independently of its acidity, the oxides were also characterized by gas phase chemisorption of CO₂ [9,10,27,28].

2. Reaction mechanisms

2.1. DMB1 isomerization

At temperatures of about 200°C, the reaction scheme (Fig. 1) is relatively simple with only two main products: 2,3-dimethylbut-1-ene (23DMB1) and 2,3-dimethylbut-2-ene (23DMB2) [11]. Methylpentenes appear at higher temperatures (> 300°C) and their formation requires relatively strong acid sites [11,13]. It is one of the isomerization reactions for which the mechanism through secondary carbenium ions on Brønsted sites is the most likely [11,13,29,30]. The slow step of the reaction is probably the isomerization of the carbenium ion intermediate through a methyl group migration (see Fig. 1). Kemball et al. [29–31], who studied the effect of hydrogen, water and hydrogen sulfide on the reaction rate, concluded that, most likely, the 33DMB1 isomerization did not occur on the Lewis centers of alumina. The most convincing result obtained was that the reaction was not poisoned by water or hydrogen sulfide. Moreover, it can be noted that the mechanism through a π -allylic intermediate which has often been proposed to explain alkene isomerization, is not possible in the case of 33DMB1 which has a quaternary carbon atom in the β position of the double bond. Therefore

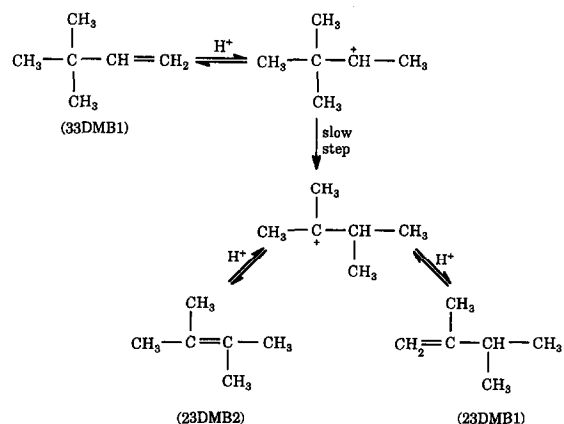


Fig. 1. 3,3-dimethylbut-1-ene (33DMB1) isomerization scheme, according to Ref. [11].

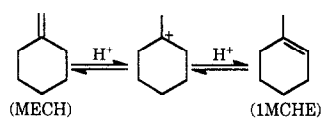


Fig. 2. Mechanism of the isomerization of the methylene cyclohexane (MECH) to the 1-methyl cyclohexene (1MCHE) with carbenium ions as intermediates.

the proposition that the 33DMB1 isomerization occurs through a pure protonic mechanism is the most likely.

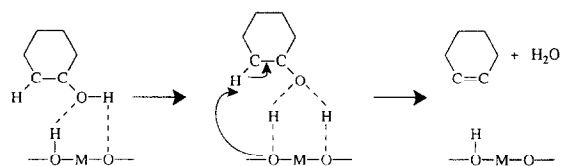
2.2. MECH isomerization

The most likely mechanism of the MECH isomerization involves carbenium ions as intermediates (Fig. 2). Nevertheless, the mechanism through a π -allylic intermediate and the mechanism on Lewis acid centers are possible. Irvine et al. [30] who studied the methylene cyclopentane isomerization on alumina, show that the mechanism involving carbenium ions on Brønsted acid centers predominates, whereas the mechanism involving the formation of a π -allylic intermediate on the Lewis acid sites is the most probable in the case of the isomerization of the 3-methylcyclopent-1-ene.

2.3. CHOL conversion

This reaction allows us to characterize the acid–base surface properties of the oxides. The dehydrogenation activity would be linked to the presence of basic sites formed by surface oxygen ions of the oxide lattice [23]. As suggested by Ai [18] in the case of isopropanol and confirmed later by several authors [20,32–36], the dehydration of cyclohexanol (CHOL) leading to cyclohexene (CHENE) would be catalyzed by the acid centers, whereas its dehydrogenation leading to cyclohexanone (CHONE) would be catalyzed both by acid and basic sites through a concerted mechanism (Fig. 3). According to these authors the dehydration activity (A_{CHENE}) could be related to the surface acidity, whereas the ratio between the activity in dehydrogena-

1) Dehydration of CHOL to CHENE on the acid sites



2) Dehydrogenation of CHOL to CHONE on the acid and basic sites

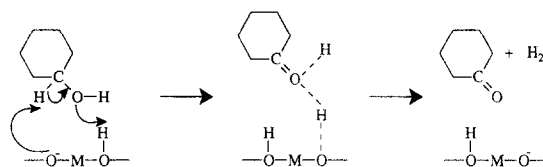


Fig. 3. Mechanism of the cyclohexanol conversion in accordance with the sites involved; both of these mechanisms can be written either with a Brønsted (like here) or a Lewis acid site.

tion and the activity in dehydration (A_{CHONE}/A_{CHENE}) would represent the surface basicity.

2.4. CO₂ chemisorption

As previously mentioned by several authors [9,10,27], the chemisorption of CO₂ at the oxide surface could lead to several species depending on the surface site involved and on the surface basicity of the oxides (Fig. 4). According to Auroux and Gervasini [9], different surface species can result from the CO₂ adsorption on

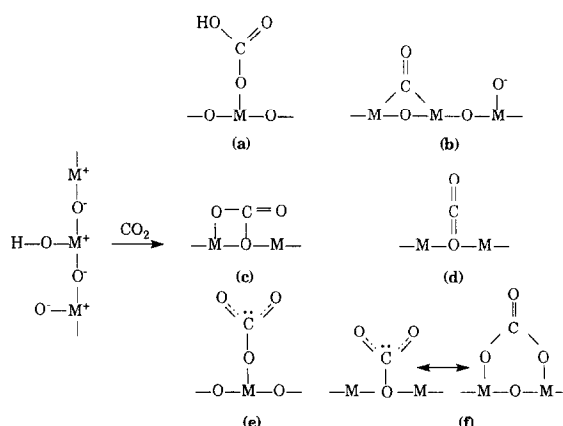


Fig. 4. Possible species formed during CO₂ chemisorption on oxides.

Table 1
Nomenclature and characteristics of the bare and modified oxides

Oxide	Provided by and (code)	Main impurities (ppm)	Structure	BET area ($\text{m}^2 \text{g}^{-1}$)	Name of bare oxides	Modified by	Name of the modified oxides
25 wt% SiO_2 / Al_2O_3	Akzo Chemie (HA HPV)	n.d.	amorphous	525	25 SiAl	—	—
5.5 wt% SiO_2 / Al_2O_3	Akzo Chemie (007–0.75E)	n.d.	amorphous	320	5.5 SiAl	—	—
SiO_2	Degussa (Aerosil D200)	Al: 500, Ti: 300, Cl: 250	amorphous	200	SiD	—	—
SiO_2	Rhône-Poulenc (DBM 250)	Na: 5920, S: < 400	amorphous	250	SiP	—	—
Al_2O_3	Institut Français du Pétrole (E 1633)	Na: 460, Ca: 560, Si: 310	gamma	100	AlI	12 wt% CeO_2	CeAlI
Al_2O_3	Rhône-Poulenc (GFS-C)	Na + Fe + S: < 200	gamma	200	AlG	0.2 wt% K^+	KAlI
ZrO_2	Degussa (zirkonoxid)	Al: 2000, Si: 100, Ti: 100, Cl: 1000	monoclinic	40	ZrD	0.5 wt% Cl^-	ClAlG
						0.2 wt% SO_4^{2-}	0.2 SO_4 ZrD
						0.8 wt% SO_4^{2-}	0.8 SO_4 ZrD
MgO	UBE (100A)	Si: 20, Ca: 20	cubic	150	MgU	0.2 wt% K^+	KZrD
CeO_2	Rhône-Poulenc (HSA)	La: 1500	cubic	60	CeP	—	—

Table 2
Nomenclature and characteristics of the supported metal catalysts

Carrier	Metal loading (wt%)	N_{metal} ($\mu\text{mol g}^{-1}$)	Metal dispersion (%)	Catalyst name
SiD	0.6 Rh	58.3	38	Rh0.6SiD
	1.2 Pt	67.0	57	Pt1.2SiD
AlI	0.5 Rh	48.5	87	Rh0.5AlI
	1.2 Pt	67.0	37	Pt1.2AlI
CeAlI	0.5 Rh	48.5	89	Rh0.5CeAlI
	1.0 Pt	55.8	84	Pt1.0CeAlI
ZrD	0.6 Rh	58.3	66	Rh0.6ZrD
	1.2 Pt	67.0	26	Pt1.2ZrD

the oxides (see Fig. 4): (a) formation of a surface hydrogenocarbonyl ion on a basic hydroxyl group, (b) adsorption on a metal cation and dissociation of the resulting bond, (c) formation of a bidentate carbonate on a metal–oxygen ion pair, (d) formation of a surface carbonyl group on an oxygen vacancy and (e), (f) formation of a monodentate carbonate on metal ions with the participation of excess oxygen. Similar surface species were proposed by Lavalley [10]. Except when it leads to the formation of bulk carbonates, the amount of chemisorbed CO_2 is considered as a good measurement of the basic site density.

3. Experimental

3.1. Materials

Several oxides (Table 1) provided by different firms were used in this study. Some of them were modified with ceria, sulfate, chlorine or potassium to evaluate the sensitivity of the model reactions to a slight modification of the

acid–base surface properties. The whole series of bare oxides (modified or not) were studied first. Later, rhodium and platinum catalysts were prepared using some of the bare oxides as carriers (Table 2). These catalysts were prepared by impregnation with aqueous solutions of rhodium (III) nitrate and of dinitrodiamine platinum (II). They were dried overnight at 120°C and calcined for 4 h in air at 450°C . Dispersion measurements were carried out on the reduced catalysts (H_2 , 450°C) in a pulse chromatographic system previously described [37]. For the ceria free samples, metal dispersion was deduced from oxygen titration of the chemisorbed hydrogen using the following stoichiometries: $\text{H}/\text{Rh}_s = 1$, $\text{O}/\text{Rh}_s = 1.5$ and $\text{H}/\text{Pt}_s = \text{O}/\text{Pt}_s = 1$ (Table 2). On ceria-containing catalysts, only hydrogen chemisorption could be used to determine metal dispersion because oxygen could titrate the reduced sites of ceria formed during the pretreatment [38].

3.2. Catalytic test reactions

All the three catalytic test reactions were performed in a plug flow reactor at atmospheric pressure. The reactants (33DMB1, MECH or CHOL) were diluted in nitrogen by bubbling the gas through the liquid reactant in a saturator maintained at different temperatures (Table 3). To obtain a good reproducibility, the oxide samples were calcined in situ at 450°C in air before each experiment. The products were analyzed by on line gas chromatography (FID) using a capillary Squalane column (50 m, 0.25 i.d.) maintained at 30°C for 33DMB1 and at 50°C for MECH and CHOL reactions. Activity and selectivity were extrapolated at time zero.

Table 3
Experimental conditions used during catalytic test reactions

	Reaction		
	33DMB1 isomerization	MECH isomerization	CHOL conversion
Reactant partial pressure (kPa)	21.2	1.8	0.23
Reactant flow (mmol h^{-1})	15.3	1.3	0.17

3.3. CO₂ chemisorption

CO₂ chemisorption measurements were carried out on the calcined bare oxides in a pulse chromatographic system previously described [37]. The oxide sample (0.1 g) was first flushed with He for 0.25 h at 500°C and cooled down to room temperature. Pulses of CO₂ (0.260 ± 0.005 cm³) were injected into a He flow (30 cm³ min⁻¹) every three minutes till saturation. Following this chemisorption, the amount of CO₂ desorbed between 25 and 500°C (23°C min⁻¹) was measured. After cooling the reactor down to room temperature under a He flow, a second chemisorption was carried out following the same procedure as the preceding one.

4. Results

4.1. DMB1 isomerization

4.1.1. Oxide activities

The reaction was performed at a temperature between 60 and 400°C, so as to remain below a 10% conversion. Table 4 gives the activities and the temperature of reaction for each oxide. In every case the activation energy was close to 95 kJ mol⁻¹, which allows us to establish a classification of the acidity based on an extrapolation of the activity at 300°C (Fig. 5).

Table 4
Activity of the oxides in 33DMB1 isomerization

Oxide	Reaction temperature <i>T</i> (°C)	Activity at <i>T</i> °C (μmol m ⁻² h ⁻¹)
25SiAl	60	24
0.8SO ₄ ZrD	100	470
5.5SiAl	150	61
ClAlG	250	150
AlG	250	130
0.2SO ₄ ZrD	300	145
AlI	400	193
CeAlI	400	75
ZrD	400	65
CeP	400	0
SiD	400	0
SiP	400	0

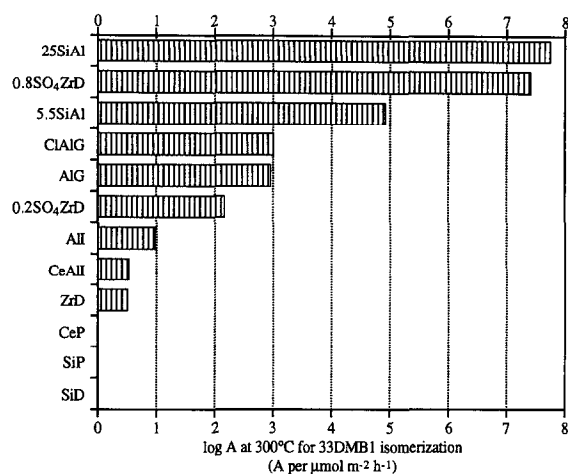


Fig. 5. Classification of the various oxides by decreasing acidity, based on the extrapolation of their activity for 33DMB1 isomerization at 300°C. Ceria and silica samples have a not available activity so $\log A \ll 0$.

This classification agrees with the results previously published in the literature concerning the surface Brønsted acid properties of these oxides. Owing to their strong acidity, the two silica–alumina samples show a substantial activity for the 33DMB1 isomerization in agreement with previous work [22]. It must be noted that the presence of chlorine at the surface of alumina increases its protonic acidity, as previously shown [39]. Alumina I which contains alkaline impurities in relatively large proportions (Table 1) is less acid than alumina G. This decrease of acidity with the increase of alkaline content of alumina has already been reported [19,21,39]. The presence of ceria supported on alumina decreases the protonic acidity of alumina probably by decreasing the number of hydroxyl groups bonded to alumina. The pure zirconia sample, which is usually considered as an amphoteric or basic oxide [9,40–42], presents an acidity comparable to that of the ceria–alumina sample. When zirconia is modified with different amounts of sulfate, its acidity increases and for a content of 0.8 wt%, the acidity is comparable to that of one of the silica–alumina samples in agreement with recent studies [42,43]. This ‘super-acidity’ of the

Table 5
Activity of silica, zirconia and supported metal catalysts for 33DMB1 isomerization at 400°C

Sample	Activity at 400°C ($\mu\text{mol m}^{-2} \text{h}^{-1}$)
SiD	0
Rh0.6SiD	0
Pt1.2SiD	0
ZrD	65
Rh0.6ZrD	0
Pt1.2ZrD	0

sulfated zirconia is due to the simultaneous presence of Lewis and Brønsted acid centers [44]. Hattori [45] have shown that in presence of platinum and hydrogen, the Lewis acid centers are transformed into Brønsted sites, which gives to these catalysts the possibility of storing hydrogen issued from the hydrogen and the water of the gas phase [46]. Silica is not able to isomerize the 33DMB1 even at 400°C, which shows that there are only very weak acid centers on this oxide [5,9,47,48], which adsorbs little or no pyridine [49,50]. Ceria is totally inactive for the 33DMB1 isomerization. This result is in accordance with previous works having shown that ceria is essentially basic [41,51].

4.1.2. Supported metal catalysts activities

Silica-supported platinum or rhodium catalysts are quite inactive in 33DMB1 isomerization as was the bare support (Table 5). These results show that there is no specific activity of the metals in this reaction. Thus it is possible to characterize the acidity of the supported platinum or rhodium catalysts by means of 33DMB1 isomerization experiments and to estimate the changes in surface acidity due to the metal impregnation by comparing the activities of the bare oxides and those of the metal supported catalysts. On alumina, we have studied the influence of the two metals and of the pretreatment conditions on the 33DMB1 isomerization (Fig. 6). The oxidized rhodium catalyst shows the same activity as the bare alumina sample. We can conclude that there is no significant change in the Brønsted acidity at alumina sur-

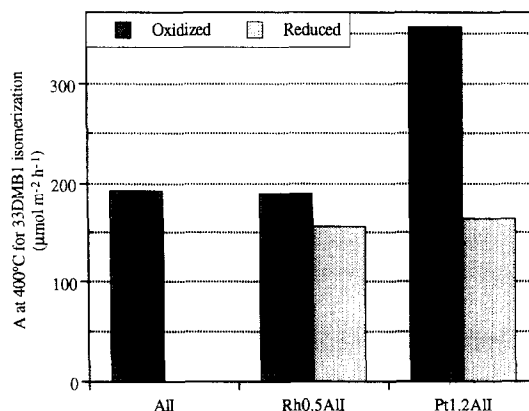


Fig. 6. Activity of the bare alumina and the alumina supported metal catalysts for 33DMB1 isomerization at 400°C.

face during rhodium impregnation. On the contrary, the oxidized platinum catalyst presents a much greater activity than the bare alumina. This result could be explained by a contribution of the acid sites created during oxidation in the vicinity of the platinum–alumina interface, as recently suggested by Sarkani et al. [52]. When the catalysts are reduced, their activity becomes slightly lower than those of the bare alumina. This is most likely due to an accelerated dehydroxylation of the support during reduction. The influence of the supported metal catalysts is more significant on ceria–alumina than on alumina: whatever the pretreatment, the activity is higher on the catalyst than on the bare ceria–alumina (Fig. 7). The rhodium and the platinum catalysts have greater acidity when oxidized.

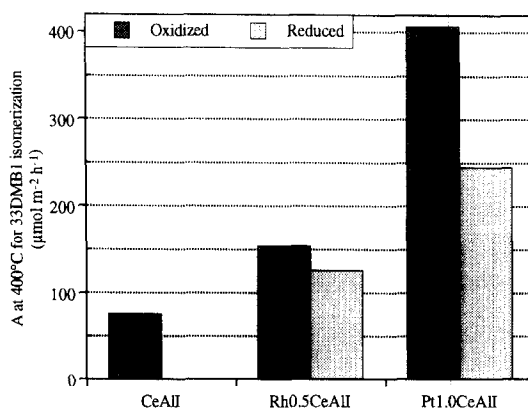


Fig. 7. Activity of the bare ceria–alumina and the ceria–alumina supported metal catalysts for 33DMB1 isomerization at 400°C.

Like on alumina and probably for the same reason, the oxidized platinum catalyst presents the higher activity. After a reducing treatment, the activity decreases but remains greater than the activity observed on the bare ceria–alumina sample and again greater for the platinum than for the rhodium catalyst. Concerning the activities of these ceria–alumina supported catalysts the pretreatment conditions seem to play an important role. Actually, during this treatment the ceria supported on alumina can be either oxidized by oxygen or partially reduced by hydrogen spilled over from the metal particles [38,53,54]. These different states of the ceria strongly modify the acidity of the ceria–alumina. On zirconia, the opposite effect can be observed (Table 5). The bare zirconia presents a low activity at 400°C corresponding to a weak Brønsted acidity, while rhodium and platinum catalysts supported on this support are totally inactive for 33DMB1 isomerization. This result clearly indicates that the surface acidity of zirconia is totally removed during metal impregnation.

4.2. MECH isomerization

As seen in Section 4.1.1 the 33DMB1 isomerization cannot characterize the oxides having a very weak acidity (silica) or a high basicity (ceria). To characterize these oxides we used the MECH isomerization.

4.2.1. Activity of the bare oxides

As for the isomerization of 33DMB1, the results are given first at the temperature of reaction (Table 6) and a classification of the oxides based on an extrapolation of their activity at 100°C ($E_a = 58 \text{ kJ mol}^{-1}$) is presented in Fig. 8. The two acid scales (33DMB1 at 300°C and MECH at 100°C) can be directly compared by taking alumina I as a reference. This alumina sample has practically the same activity in the two reactions (about $10 \mu\text{mol m}^{-2} \text{ h}^{-1}$). Except for zirconia which shows a relatively high acidity in MECH isomerization, the order of

Table 6
Activity of the oxides in MECH isomerization

Oxide	Reaction temperature T (°C)	Activity at T °C ($\mu\text{mol m}^{-2} \text{ h}^{-1}$)
AlG	50	16
ZrD	100	13
AlI	100	11
CeAlI	100	9
CeP	200	2.5
SiD	150	2.5
SiP	150	1

acidity is practically the same for the two reactions. Concerning the strong acidity of zirconia for this reaction, two explanations can be proposed. The first is based on the presence of both Lewis and Brønsted acid sites at the surface of zirconia [9,42,55]. As mentioned in the introduction, the isomerization of MECH on Lewis acid sites cannot totally be excluded. In this case, Lewis sites could contribute to the activity measured for MECH isomerization on zirconia. The second explanation is based on the fact that the alkene isomerization on zirconia involves an acid–base pair site as previously mentioned [42,56]. In this second case, the initiation of the reaction could be either an allylic H abstraction by a basic site or an H^+ addition from a protonic acid site. The mechanism involving an allylic H abstraction is not possible with MECH due to the absence of hydrogen on the tertiary

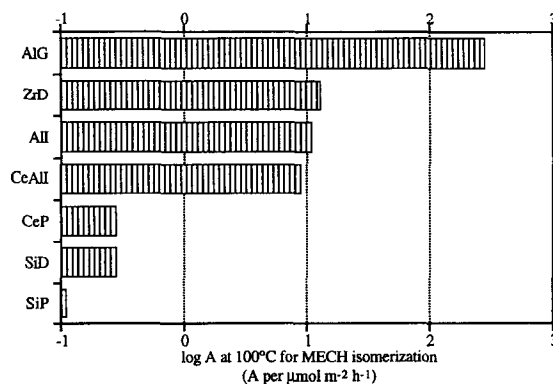


Fig. 8. Classification of the various oxides by decreasing acidity, based on the extrapolation of their activity for MECH isomerization at 100°C.

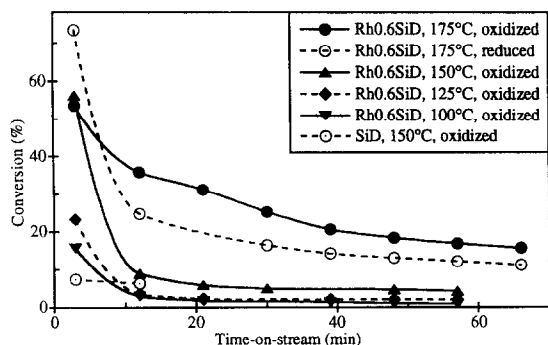


Fig. 9. Conversion of MECH on the bare silica (200 mg, 150°C) and on the silica supported rhodium catalysts (50 mg).

carbon of the double bond. So, in the case of zirconia, it seems that both Brønsted and Lewis acid centers play an important role for MECH isomerization. Except for zirconia, MECH isomerization allows us to evaluate the acidity of the very weakly acidic oxides: the silica and the ceria samples would have an acidity lower by a factor of 30 to 100 than the acidity of alumina I.

4.2.2. Activity of the supported metal catalysts

To study the influence of the supported noble metals (platinum and rhodium) on the oxide acidity determined by MECH isomerization, we tested the two samples Rh0.6SiD and Pt1.2SiD for which the carrier (SiD) presents a very low activity (Fig. 8). On Figs. 9 and 10, the variations of the conversion (%) as a function of time on stream are presented at different reaction temperatures for 50 mg of each catalyst sample.

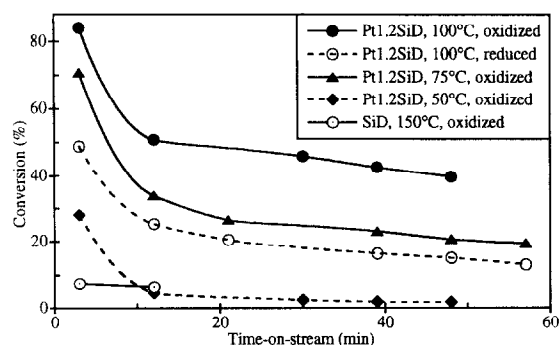


Fig. 10. Conversion of MECH on the bare silica (200 mg, 150°C) and on the silica supported platinum catalysts (50 mg).

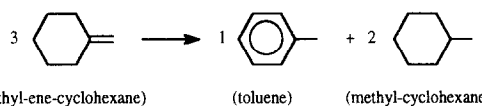


Fig. 11. MECH dismutation occurring on the metal catalysts supported on silica.

For the sake of comparison, the conversion (%) at 150°C for 200 mg of the SiD sample is also presented. Whether they are oxidized or reduced, the supported metals increase considerably the isomerization activity compared to the bare silica. A significant deactivation effect can be observed during the first 20 min for the two catalysts. It can be noticed that, above 200°C with a rhodium catalyst and above 150°C with a platinum catalyst, the isomerization reaction is accompanied by a MECH dismutation to toluene and to methyl-cyclohexane (Fig. 11). Contrarily to the 33DMB1 isomerization, the MECH isomerization does not allow to characterize the oxide surface acidity in the presence of supported rhodium or platinum metals.

4.3. CHOL conversion

Depending on the intrinsic oxide activity this reaction was carried out at 150, 200 or 300°C (Table 7). For a given temperature, the sample weight was varied so as to obtain a 10% conver-

Table 7
Activity of the oxides in CHOL conversion

Oxide	Reaction temperature T (°C)	A_G ($\mu\text{mol m}^{-2} \text{h}^{-1}$)	A_{CHENE} ($\mu\text{mol m}^{-2} \text{h}^{-1}$)	$A_{\text{CHONE}} / A_{\text{CHENE}}$
AlG	150	8.5	6.0	0.4
AlI	200	34	29	0.2
CeAlI	200	34	19	0.8
KAlI	200	3.4	1.6	1.1
0.2SO ₄ ZrD	300	85	60	0.4
ZrD	300	42	20	2.6
KZrD	300	17	2.4	6.1
CeP	300	28	2.0	13.3
SiD	300	1.1	0.9	0.3
SiP	300	0.3	0.1	2.6
MgU	300	7.5	0.1	49

sion. The oxides can be characterized by their activity in CHOL transformation (A_G , calculated at 10% conversion) and by their activities in CHENE (A_{CHENE}) and in CHONE (A_{CHONE}) formation. As previously mentioned (Section 2), the dehydration of CHOL to CHENE was catalyzed by the acid sites while the dehydrogenation of CHOL to CHONE was catalyzed by both the acid and the basic sites according to a concerted mechanism (Fig. 3). Besides A_G , Table 7 gives A_{CHENE} representative of the oxide acidity and the A_{CHONE} to A_{CHENE} ratio which is representative of the oxide basicity. Nevertheless it was not possible to study the oxide activities at the three temperatures with a conversion below 10%. Moreover the selectivity to CHENE seemed to increase with the conversion. For these reasons, the results obtained at different temperatures cannot be compared.

4.3.1. Activity at 150°C and at 200°C

At 150°C only the alumina G sample is active and its activity is mostly due to acid sites (high selectivity to CHENE). On the AII alumina sample which contains more alkaline impurities than the AIG sample (Table 1), CHOL conversion can only be observed at 200°C. As previously observed in 33DMB1 isomerization, the presence of ceria supported on the AII decreases its acidity (A_{CHENE}). At the same time, ceria increases alumina basicity ($A_{\text{CHONE}}/A_{\text{CHENE}}$). Nevertheless, this modification of the surface properties due to ceria impregnation occurs without any change in the overall activity (A_G). On the other hand, if the presence of potassium increases the basic properties of alumina, this effect is accompanied by a loss of the overall activity which is lower by a factor 10 than on the unmodified alumina. This decrease of the total activity accompanied by an increase of the basic properties was also observed by Siddhan and Narayanan [19] in the case of alcohol dehydrogenation on sodium modified aluminas. The authors explain this decrease of the total activity by a significant decrease of the protonic acidity of alumina, as

confirmed by 33DMB1 isomerization measurements. Similar phenomena were observed by Lauron-Pernot et al. [21] in the conversion of 2-methyl-but-3-yne-2-ol on pure and doped alumina. These authors showed there was an increase of the selectivity to acetylene and acetone when alumina was doped with sodium ions. This is characteristic of an increase of the surface basicity of the oxide upon Na doping. At the same time they showed that an increase of sodium content decreases the amount of pyridine adsorbed and decreases the temperature of pyridine desorption, which is a proof of the decrease of the number and of the strength of the acid sites. These alkaline effects on the acidity were also confirmed by Gervasini et al. [47] who showed that when alumina is modified with Li, the initial heat of ammonia adsorption decreases. Our results obtained with CHOL conversion show clearly that basic promoters can have very different effects on the acid–base properties of alumina: ceria increases the basic character of the alumina without changing its acidic properties, while the relative increase of basicity resulting from potassium addition is largely due to a decrease of the protonic surface acidity.

4.3.2. Activity at 300°C

At 300°C all the basic and amphoteric oxides used in this study present an activity for CHOL conversion. As previously observed in 33DMB1 isomerization, the presence of sulfates on zirconia increases its protonic acidity and decreases its basicity with a greater overall activity in CHOL conversion. The effects of adding potassium to zirconia are the same as those observed with alumina: an increase of the basic properties due to a decrease of the oxide protonic acidity. As already mentioned for MECH isomerization, the ceria sample presents an acidic activity greater than that of the two silica samples. On the other hand, ceria is one of the more basic oxide used in this study. The presence of large amounts of alkaline impurities at the surface of the SiP sample (compared to the SiD sample) is

clearly shown by an increase of the ratio (basic sites) and by a decrease of A_{CHENE} (acid character). Magnesia presents a practically zero acidity but the greatest basicity among the oxides investigated in this study. This is in agreement with the results obtained by Lauron-Pernot et al. [21] in the 2-methyl-but-3-yne-2-ol test. Recently, the conversion of isopropanol on several oxides was investigated by Lahousse et al. [36], who showed that MgO was totally inactive in this reaction. In contrast, ZnO was very active and gave high yields of acetone. They considered that these results were due to the fact that the dehydrogenation reaction required redox sites rather than basic sites. As MgO is active in CHOL conversion and presents a good selectivity to CHONE, we can state that CHOL dehydrogenation occurs on the basic sites of MgO.

4.4. CO₂ chemisorption

As discussed in the introduction, CO₂ chemisorption at room temperature is used to determine the oxide surface basicity independently of the surface acidity. To obtain a good precision in these measurements, we proceeded in the three steps described in the experimental part: chemisorption at 25°C, TPD between 25

Table 8

CO₂ chemisorption and thermodesorption (molecules per nm²)

Oxide	CO ₂ chemisorbed before TPD	CO ₂ thermo-desorbed	CO ₂ chemisorbed after TPD
SiD	0	0	0
25SiAl	0.01	n.a. ^a	0.01
SiP	0.02	n.a. ^a	0.01
5.5SiAl	0.08	0.08	0.07
ClAlG	0.12	0.12	0.11
AlI	0.17	0.18	0.18
AlG	0.18	0.19	0.19
CeAlI	0.44	0.43	0.42
ZrD	1.45	1.52	1.82
MgU	1.77	2.20	1.71
CeP	3.23	3.05	3.01

^a Not available: value too small to be accurate.

and 500°C followed by a second chemisorption at room temperature (Table 8). Before discussing these results, we must keep in mind that the adsorption of CO₂ leads to oxide surface species which depend on the nature of the basic sites [9,10,27] (see Section 2). When the adsorption occurs on a very basic surface oxide the formation of bulk carbonate species is also possible [10,57,58].

There is a good coherence between the values of chemisorptions and of thermodesorption

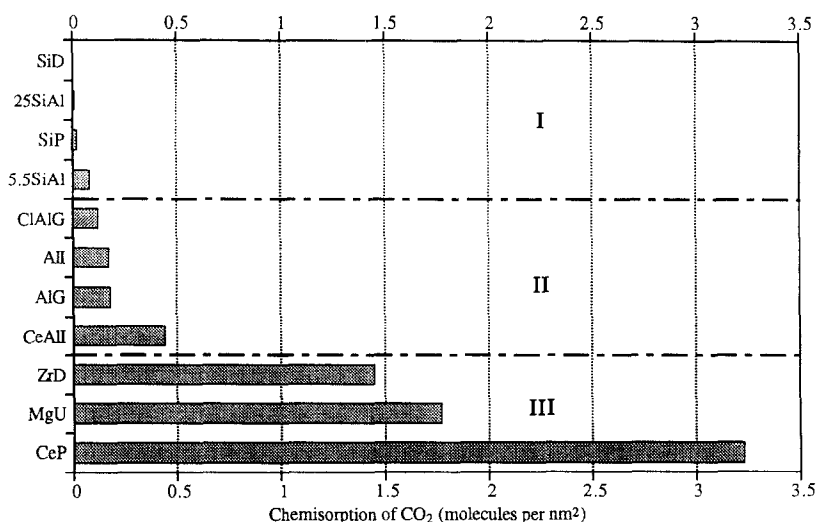


Fig. 12. Amount of CO₂ chemisorbed on oxides at room temperature.

(Table 8), which allows us to classify the oxides in three groups (Fig. 12):

Group I: is constituted by the silica and the silica–alumina samples on which the amount of CO_2 adsorbed is less than 0.1 molecule per nm^2 . As previously observed, pure silica cannot adsorb carbon dioxide [9,27,39] and the value measured on the sample SiP is due to its content of alkaline impurities (see Table 1). According to the results obtained by Berteau et al. [22], the basicity of the silica–alumina sample is low and decreases when the silica content increases.

Group II: is constituted by the aluminas (modified or not by ceria or chlorine) which chemisorb between 0.1 and 0.5 molecule of CO_2 per nm^2 . Similar values of CO_2 coverage were already observed [9,59], which shows that only a part of the hydroxyl groups of aluminas can chemisorb carbon dioxide. It must be noticed that the presence of a small amount of ceria (12 wt%) doubles the amount of CO_2 chemisorbed on alumina. The decrease of the basicity of the chlorine modified alumina sample is probably due to a substitution of the more basic hydroxyl groups of alumina by chloride ions [60].

Group III: is constituted by the zirconia, magnesia and ceria samples which chemisorb over 1 molecule of CO_2 per nm^2 . These oxides have a relatively strong surface basicity [9] that could lead to the formation of surface carbonate species [10,27]. The amount of CO_2 chemisorbed on ZrO_2 at room temperature agrees with previous work [42], confirming the significant basicity of this oxide. MgO known as a strong basic oxide [9,48] chemisorbs about two CO_2 molecules per nm^2 . Ceria appears to be more basic than magnesia. This could be due to a re-oxidation by CO_2 of partially reduced ceria sites associated with oxygen vacancies as previously mentioned by Lavalley [10] and presented by scheme (d) in Fig. 4. The adsorption of oxygen on pre-reduced ceria samples leads to a re-oxidation at room temperature [38] with formation of different oxygen species (mono- and di-atomic) at the ceria surface: oxygen anion (O^{2-}), superoxides (O_2^-) and peroxides (O_2^{2-}) [61]. Superoxides were detected by EPR [62,63], while FTIR showed the presence of peroxide species on a partially pre-reduced ceria sample after oxygen adsorption [64]. In this case, the large uptake of CO_2 could also result

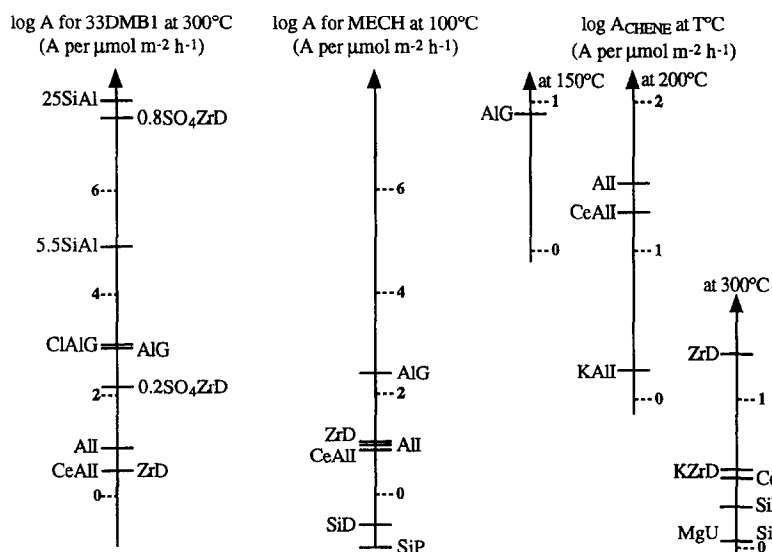


Fig. 13. Comparison of the acidity scales obtained using the three catalytic test reactions (there is no link between the two isomerization scales and the three scales used for the conversion of CHOL to CHENE).

from a chemisorption on the metal ion with the participation of certain adsorbed oxygen species (schemes (e), (f) in Fig. 4).

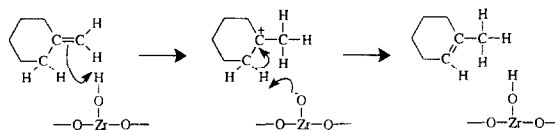
5. Discussion

5.1. Acidity and basicity of bare oxides

5.1.1. Acidity measurements

The acidic properties of the oxides were assessed by means of three catalytic tests: the 33DMB1 and MECH isomerization and the conversion of CHOL to CHENE. In Fig. 13 the acidity scales obtained with these three tests are compared. Except in the case of the zirconia which has been previously discussed (see Section 4.2.1), the various oxides are classified in the same order of acidity whatever the catalytic test used. Any of these tests can be used to evaluate the oxide acidity. Moreover, they give complementary information. The 33DMB1 isomerization allows us to measure the Brønsted acidity of the strong acidic oxides like silica-alumina, sulfated-zirconia and chlorinated-alumina and of the medium acidic oxides like alumina and zirconia. The MECH isomerization is well-adapted to determine the very weak acidity of oxides like silica and ceria. By conducting out the reaction at 50–100°C, MECH isomerization can also be used to characterize the acid sites of medium strength like those of alumina. However, there seem to be some problems with ZrO_2 . As previously suggested (see Section 4.2.1), the high acidity found for ZrO_2 with MECH isomerization (see Fig. 13) could be due to the participation of relatively strong Lewis sites as shown by the scheme in Fig. 14. For this reason, the results obtained with MECH isomerization on ZrO_2 deserve further investigation. The conversion of CHOL to CHENE and CHONE allows us to specify the role of the different additives used. For instance, the 33DMB1 isomerization test shows that alumina modified by ceria or alkaline ions is less acidic than the starting oxide. Using the CHOL con-

1) Isomerization of MECH on the Brønsted acid sites



2) Isomerization of MECH on the Lewis acid sites

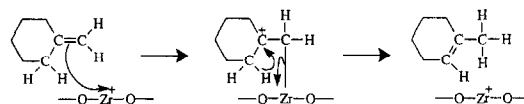


Fig. 14. Mechanisms of the isomerization of MECH on Brønsted and Lewis acid sites on zirconia.

version test we have shown that in the case of ceria additive the decrease of the acidity is accompanied by an increase of the basicity while in the case of alumina modified by alkaline ions, the decrease of the acidity is due only to an elimination of the protonic acidity.

5.1.2. Basicity measurements

The basic properties of the oxides were evaluated by means of two tests: CHOL conversion and CO_2 chemisorption. Fig. 15 shows the basicity scales obtained with these tests. Except in the case of CeO_2 , the CO_2 chemisorption gives a basicity order in agreement with the literature

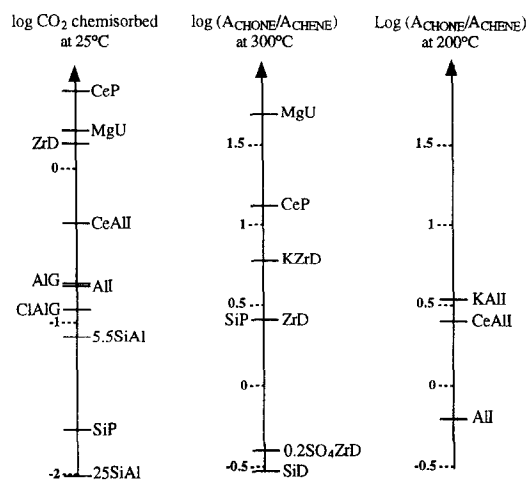


Fig. 15. Comparison of the basicity scales obtained using the CHOL conversion and the chemisorption of CO_2 (there is no link between the three scales).

data. The great amount of CO_2 chemisorbed on ceria could be due to a possible reoxidation of ceria by CO_2 or to a chemisorption of CO_2 on oxygen species present in excess at the ceria surface (see Section 4.4). The CHONE to CHENE activity ratio in CHOL conversion (Fig. 15), provides coherent data allowing to evaluate the oxide basicity. The isopropanol conversion to acetone is a test reaction often employed for characterizing oxide basicity. Actually, many mechanisms involving the redox properties have been proposed [65–67] and MgO is not active in this reaction [36]. By contrast, CHOL conversion to CHONE gives the following order for the basicity: $\text{MgO} > \text{CeO}_2 > \text{ZrO}_2$. The apparently higher basicity of ceria compared to magnesia observed with CO_2 chemisorption is not confirmed. This proves that the strong redox properties of ceria have no effect on the conversion of CHOL to CHONE contrary to what was observed by Zaki et al. [65] in the case of the conversion of isopropanol. From these results we can conclude that in CHOL conversion the ratio $A_{\text{CHONE}}/A_{\text{CHENE}}$ depends only on the basic properties of oxides. Moreover, the CHOL conversion is very sensitive to slight acid–base modifications and allows to determine the changes due to minute amounts of additives impregnated on the oxide surface. For example, the increase of basicity of the ceria modified alumina is clearly shown by this catalytic reaction.

5.2. Acidity of supported noble metals catalysts

As for the determination of the acid–base properties of oxides in the presence of supported noble metals (rhodium and platinum), the 33DMB1 isomerization is the only test which can be used. Since both SiO_2 and silica supported Rh and Pt catalysts are inactive in this reaction, it can be considered that there is no contribution of the metals in 33DMB1 isomerization. It is therefore possible to determine the changes in the acid properties of the supports due to metal impregnation. These changes are

the results of either the blockage of the support sites by the metal particles or of the effect of the counter-ions used during impregnation. It has been shown that when the alumina supported rhodium and platinum catalysts are pre-reduced, the acidity of the catalysts is about the same as that of the bare support. In this case the acid properties are not modified by the metal salt impregnation. As for the ceria–alumina supported catalysts, whatever the pretreatment (oxidation or reduction) the catalyst activities are always greater than the activity of the bare ceria–alumina. This result could be due to the different states of ceria supported on alumina which seem to induce large modifications of the acidity of the modified oxide. When ceria is totally oxidized, by gaseous oxygen or by oxygen spilled over from the metal particles, the catalyst acidity is greater than when ceria is partially reduced through hydrogen spillover. Concerning zirconia supported catalysts, the weak Brønsted acidity of zirconia is totally removed after metal impregnation, which supposes that the metal salts are preferentially bonded to the Brønsted acid sites of the zirconia.

6. Conclusion

In this work three catalytic tests as well as CO_2 chemisorption were used to assess the acid–base properties of various oxides and modified oxides. Cross-linked information on both acidity and basicity were then obtained. Two scales integrating the results of the different tests can be proposed for the acidity and basicity:

Acidity scale:

- silica–alumina > 0.8 wt% sulfated-zirconia
- > 0.5 wt% chlorinated-alumina \gg alumina
- > 12 wt% ceria–alumina
- > 0.2 wt% potassium doped alumina
- > zirconia

» 0.2 wt% potassium doped zirconia

> ceria > silica > magnesia.

Basicity scale:

magnesia > ceria > zirconia

» 0.2 wt% potassium doped alumina

> 12 wt% ceria–alumina > alumina

> 0.5 wt% chlorinated-alumina

» 0.2 wt% potassium doped zirconia

> 0.8 wt% sulfated-zirconia > silica–alumina

> silica.

All the tests, except methylene cyclohexane isomerization on ZrO_2 and CO_2 chemisorption on CeO_2 , are well-adapted for characterizing the acidity and the basicity of the oxides. Contrary to what was observed with isopropanol, the dehydrogenation of cyclohexanol implies the basic sites and, apparently, not the redox sites of the solid.

In the case of the 33DMB1 isomerization, the Brønsted acidity of the oxides can be determined in the presence of supported metals. On reduced alumina catalysts the acidity is the same as that of the bare alumina. On ceria modified alumina the presence of the noble metals increases the acidity of the modified oxide. This change in the oxide acidity depends on the catalyst pretreatment and follows the different states (oxidized or partially reduced) of the ceria supported on alumina. On zirconia, the weak Brønsted acidity is totally removed after the metal impregnation. There is apparently a preferential impregnation of the metal salts on these Brønsted acid sites of zirconia.

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