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Acidity and Basicity of Metal Oxide Surfaces[1]

II. Determination by Catalytic Decomposition of Isopropanol

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In Part I of this series (Auroux, A., and Gervasini, A., *J. Phys. Chem.* **94**, 6317 (1990)) a microcalorimetric investigation on the acid–base character of a large series of metal oxides was reported. A study concerning the acid–base catalytic properties of the same series of oxides is now reported together with a comparison with the previous results. The decomposition of isopropanol has been chosen as a test reaction to study the acid–base character of the catalytic sites of the oxides. For each oxide employed as catalyst, the rate coefficients as well as the Arrhenius parameters for both the dehydration and the dehydrogenation of isopropanol were determined. A relationship was found between the strength of the acid sites microcalorimetrically evaluated and the activation energy of the dehydration reaction, while the activation energy of the dehydrogenation reaction was independent of the strength of the catalytic sites. On the basis of the dehydration reaction, sets of oxides can be classified in scales of acid strength.

INTRODUCTION

Many catalytic reactions for testing the acidity and the acid strength of catalysts are reported (*2–8*), whereas few test reactions have been employed for the estimation of the basic properties of catalysts (*9*).

Selectivity in the decomposition reaction of isopropanol has long been regarded as one of the typical reactions for investigating the acid–base properties of the catalytic sites of metal oxides (*2, 10–12*). The catalysts can be classified in regard to their propensity toward the dehydration or the dehydrogenation activity to propene or to acetone, respectively.

Ai and co-workers (*11, 13–19*) successfully related the catalytic activity of various mixed oxides for different reactions (oxidation of butene and butadiene, isomerization of butene, and oxidation of acetic acid) to the acid–base character of the active sites of the oxides. This character was determined by means of "indirect" and/or "direct" determinations of acidity and basicity. The indirect determinations consisted of measurements of catalytic activity for the decomposition of isopropanol, and the direct determinations of measurements of the adsorption of acid and basic gaseous molecules. From a mechanistic point of view, Ai *et al.* assumed that the dehydration of isopropanol is catalyzed by an acid site, whereas the dehydrogenation is catalyzed by both acid and basic sites through a concerted mechanism. As a consequence, the dehydration rate (v_p) is regarded as a measure of the acidity of the catalyst, while the ratio of the dehydrogenation rate (v_a) to the dehydration rate as a measure of the basicity. By employing a series of catalysts, i.e., TiO_2–MoO_3, TiO_2–V_2O_5, SnO_2–MoO_3, and SnO_2–P_2O_5 with different composition (*13, 15*), fairly good correlations were found between the acidity measured by the adsorption of ammonia and v_p, and between the basicity measured by the adsorption of carbon dioxide and v_a/v_p.

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[1] Ref. (*1*) is regarded as Part I of this series.

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In our previous paper (*1*) we reported results concerning the characterization of the acidity and basicity of a large series of metal oxides. This included the most common oxides employed in the field of catalysis as supports (Al_2O_3, BeO, CaO, SiO_2, TiO_2, ZnO, and ZrO_2), as active phases (Cr_2O_3, MoO_3, Nb_2O_5, Ta_2O_5, and WO_3), as well as promoters (Ga_2O_3 La_2O_3, Nd_2O_3, Pr_6O_{11}, and ThO_2). The oxides displayed a variety of crystal structures, metal–oxygen bond strengths and acid–base strengths. The number of the acid and basic surface sites was titrated by means of ammonia and carbon dioxide probe molecules, respectively. The acid–base strength of the adsorption sites was determined by direct microcalorimetric measurements.

The aim of the present paper has been to relate our previous results to those obtained by using the decomposition of isopropanol as a test reaction for the determination of the acid–base character of the catalysts. In this way it has been possible to evaluate the soundness of the catalytic test when applied on a widely heterogeneous set of metal oxides.

EXPERIMENTAL

Catalysts

The metal oxides studied are listed in Table 1 together with their BET surface areas after thermal treatment at 673 K. All the catalysts were commercial products with guaranteed degree of purity. In Table 1 are also reported the number of the acid and basic surface sites determined by NH_3 and CO_2 titration (V_{NH_3} and V_{CO_2}), respectively, and the average heats of NH_3 and CO_2 adsorption measured by microcalorimetry ($Q_m(NH_3)$ and $Q_m(CO_2)$. Both the volumetric and calorimetric data derive from the results reported in the previous paper (*1*).

Except for Cr_2O_3, the metal ions in all of the employed oxides were in the highest degree of oxidation.

Catalysts were calcined in air at 673 K for at least 15 h before the catalytic runs.

Catalytic Runs

The reaction of isopropanol decomposition was carried out under oxidative conditions in a continuous-flow Pyrex microreactor at atmospheric pressure. The feed was a mixture of isopropanol in air obtained by passing the air through liquid isopropanol of purity grade (99.9%) held in a saturator at 288 K, and further by diluting the mixture with air to a partial pressure of isopropanol of 1990 Pa. The total flow rate through the fixed bed of catalyst (70–100 mg) was 0.31 STP ml s^{-1}.

Catalytic runs were carried out for at least 24 h. During the first 8 h, to choose the most suitable temperature range of reaction, we searched for the lowest temperature at which a catalytic activity toward formation of both propene and acetone was detectable. Afterward, the reactor temperature was automatically changed, in a range of about 80 K, in a random manner to prevent a systematic influence of deactivation phenomena. The reaction products were automatically analyzed at 1-h intervals.

The analyses were performed on-line by a gas chromatograph equipped with both FID and TCD detectors by using a stainless-steel column, 2 m long, packed with Porapak Q. The column temperature was programmed from 328 to 428 K.

RESULTS

The catalytic decomposition of isopropanol was carried out under differential conditions ($\leq 10\%$ of conversion). The selectivity to the two main products, propene and acetone, was more than 95% with all the catalysts. Al_2O_3, WO_3, and ZrO_2 also gave traces of isopropyl ether ($<1\%$).

The reaction was performed under oxidative conditions to avoid catalyst deactivation, as the surface metal oxides can lose oxygen under reducing condition.

By measuring the concentration of the reaction products at the outlet of the reactor and taking into account the contact time and

TABLE 1

Physicochemical Properties of the Catalysts[a]

Catalyst	S^{b} (m^2/g)	V_{NH_3} $(\mu mol/m^2)$	$Q_m(NH_3)$ (kJ/mol)	V_{CO_2} $(\mu mol/m^2)$	$Q_m(CO_2)$ (kJ/mol)
Al_2O_3	124.4	1.48	94.6	0.31	61.3
BeO	45.0	3.74	96.3	0.69	40.6
CaO	29.0	3.05	6.9	4.05	118.5
Cr_2O_3	39.5	11.50	87.0	0	0
Ga_2O_3	21.0	5.75	59.1	0.80	17.5
La_2O_3	13.0	6.80	0.6	8.25	95.8
MgO	197.0	0.61	6.9	1.45	89.7
MoO_3	33.5	6.80	6.9	0	0
Nb_2O_5	59.0	3.80	86.8	0.28	6.1
Nd_2O_3	14.1	6.20	4.7	5.05	99.0
Pr_6O_{11}	6.2	9.85	8.2	3.30	71.2
SiO_2	117.6	1.37	2.6	1.37	0
Ta_2O_5	22.0	4.60	39.1	0	0
ThO_2	7.5	7.35	11.4	2.94	85.0
TiO_2	120.0	2.71	110.0	0.31	71.0
WO_3	37.6	4.80	77.1	0	0
ZnO	10.5	9.00	40.0	2.90	103.4
ZrO_2	63.3	5.00	80.0	0.85	56.5

[a] The volumetric (V_{NH_3} and V_{CO_2}) and calorimetric ($Q_m(NH_3)$ and $Q_m(CO_2)$) adsorption data were determined under a final pressure of 66 Pa at 423 K for NH_3 and 296 K for CO_2.

[b] BET surface areas after thermal treatment at 673 K.

the catalyst surface areas, the reaction rates to propene and to acetone were calculated and expressed in mmol · s^{-1} · m^{-2}. The rates can be directly regarded as rate coefficients, as both the reactions are known to be almost of zero-order with respect to the isopropanol concentration (*11, 13–18*).

By employing the rate coefficients obtained at different temperatures, the Arrhenius parameters for both the reactions were calculated. Table 2 collects the kinetic parameters together with the temperature range in which each catalyst was active. In order to give an indication of the fair accuracy of the parameters, both the estimated standard error of the activation energy (E) and the correlation coefficients are reported in Table 2. The low correlation coefficient (0.85) obtained for acetone formation with BeO can be ascribed to the low slope of the line, more than to the dispersion of the points.

In general, the values of E for the formation of propene (E_p) were found to be much higher than the ones for the formation of acetone (E_a). It can be deduced that the latter reaction requires less selective sites than the former. In fact, all the catalysts gave acetone, including oxides as inactive as SiO_2.

To facilitate the comparison between the catalytic behavior of the different oxides, the Arrhenius plot for the two reactions is drawn in Figs. 1 and 2. The lines are calculated by means of the parameters of Table 2 in the experimental temperature ranges.

An inspection of Fig. 1 reveals that the oxides more active for the dehydration reaction were MoO_3 and WO_3, which gave propene in the temperature range 400–430 K. In the temperature range 430–490 K were active Al_2O_3, Nb_2O_5, Ta_2O_5, TiO_2 and ZrO_2. The catalysts generally regarded as basic oxides (CaO, MgO, Pr_6O_{11}, and ThO_2) con-

TABLE 2

Arrhenius Parameters for Isopropanol Decomposition

Catalyst	Temperature range (K)	Reaction to propene			Reaction to acetone		
		ln A^a	E (kJ/mol)	r^b	ln A^a	E (kJ/mol)	r^b
Al_2O_3	493–495	13.873	132.0 ± 2.5^c	0.999	−4.819	74.1 ± 5.6^c	0.984
BeO	460–508	20.956	179.2 ± 0.7	>0.999	−14.584	21.7 ± 5.9	0.853
CaO	492–532	10.483	141.7 ± 20.7	0.989	−4.683	71.3 ± 10.8	0.968
Cr_2O_3	396–449	—	—	—	4.689	81.7 ± 5.3	0.992
Ga_2O_3	451–501	13.990	146.5 ± 41.7	0.962	−4.240	65.7 ± 9.6	0.969
La_2O_3	457–500	—	—	—	3.771	95.5 ± 11.5	0.979
MgO	477–529	2.425	98.4 ± 7.8	0.991	−4.724	70.8 ± 5.4	0.991
MoO_3	396–445	8.760	95.5 ± 12.3	0.976	2.875	83.7 ± 9.5	0.981
Nb_2O_5	438–489	16.837	145.1 ± 2.9	0.999	−13.917	31.7 ± 5.0	0.953
Nd_2O_3	478–531	—	—	—	−2.040	66.8 ± 1.9	0.999
Pr_6O_{11}	482–534	17.951	165.7 ± 11.4	0.995	−1.750	67.3 ± 5.5	0.987
SiO_2	426–489	—	—	—	−7.077	60.5 ± 2.5	0.996
Ta_2O_5	447–498	7.787	105.2 ± 1.7	0.999	−13.652	37.8 ± 7.7	0.925
ThO_2	470–523	1.280	95.3 ± 13.3	0.955	−3.759	66.0 ± 6.8	0.969
TiO_2	437–477	14.092	130.4 ± 3.0	0.999	3.318	98.1 ± 6.3	0.990
WO_3	400–442	11.513	104.5 ± 8.1	0.988	1.282	81.1 ± 3.1	0.997
ZnO	435–486	11.758	130.9 ± 48.3	0.938	16.926	141.4 ± 14.5	0.985
ZrO_2	455–499	10.230	112.4 ± 5.7	0.995	−2.645	64.7 ± 5.8	0.984

[a] A expressed in mmol s^{-1} m^{-2}.

[b] Linear correlation coefficient.

[c] Standard error.

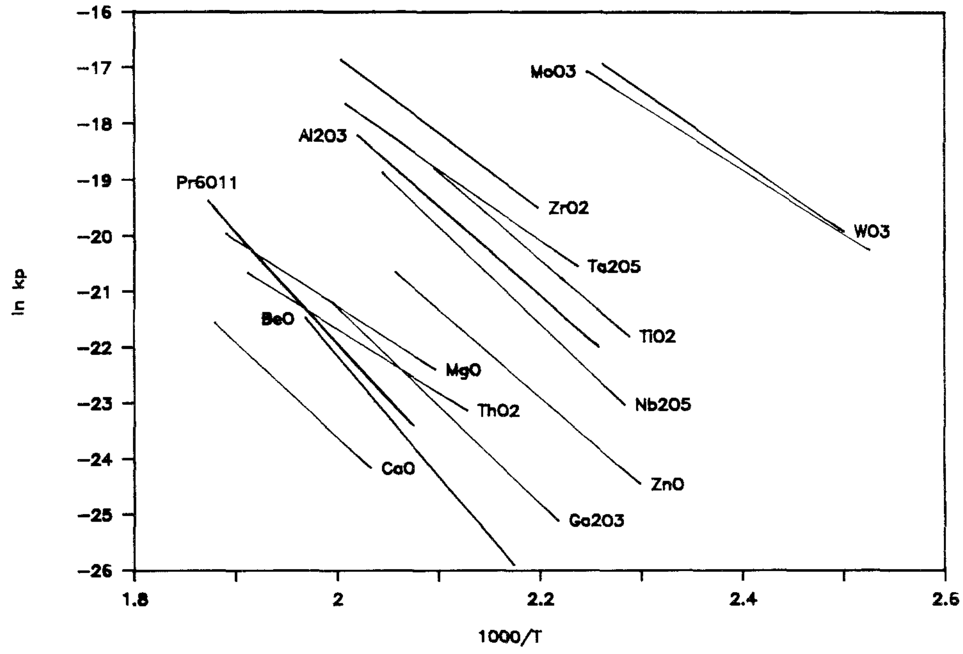

FIG. 1. Arrhenius plots for the decomposition of isopropanol to propene.

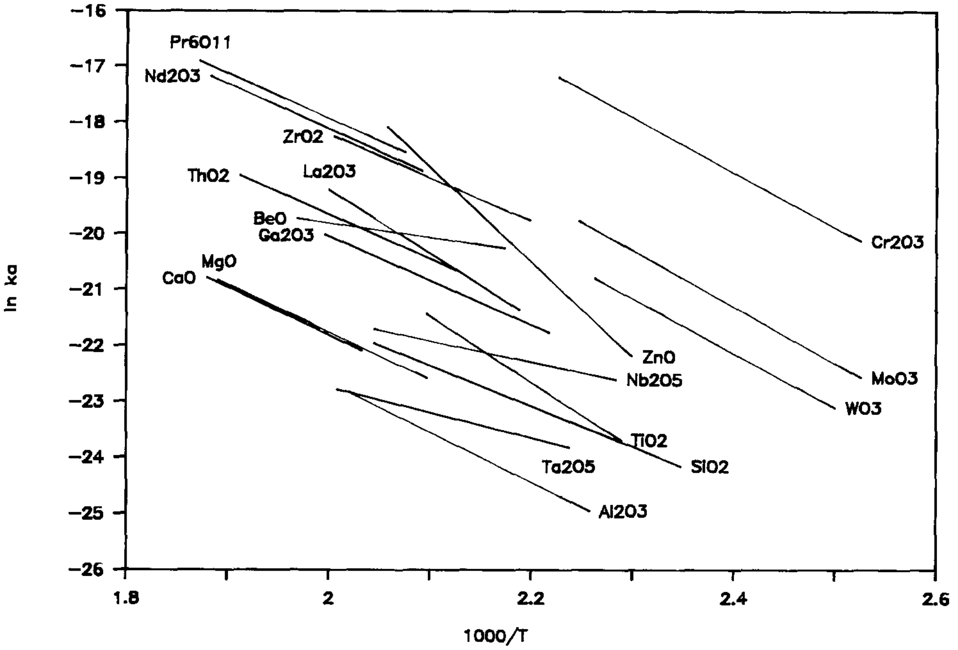

FIG. 2. Arrhenius plots for the decomposition of isopropanol to acetone.

verted isopropanol to propene at the highest temperatures. Cr_2O_3, La_2O_3, Nd_2O_3, and SiO_2 did not show any dehydration activity in the investigated range of temperature.

For the dehydrogenation reaction, the catalysts can hardly be separated into distinct groups (Fig. 2). However, a group of oxides which gave acetone at low temperatures (Cr_2O_3, MoO_3, and WO_3, usually employed as active phases in various oxidation reactions) can be discerned.

DISCUSSION

The catalytic decomposition of isopropanol was employed with the aim to classify the metal oxides in terms of their acidity and basicity.

Following the Ai approach (*11*) the acidity was related to the rate coefficients of dehydration (k_p), while the basicity was related to the rate-coefficient ratios of dehydrogenation to dehydration ($r = k_a/k_p$). The acidity of each catalyst was evaluated with respect to the acidity of alumina taken as reference by calculating the ratio $[k_p/k_p(Al_2O_3)]$. Analogously the basicity was referred to magnesia by calculating the ratio $[r/r(MgO)]$. In the absence of even a partial field of overlap for all the ranges of reaction temperature, a comparison among the catalyst activities was performed at three temperatures: one in the field of the low temperatures (423 K), one in the field of the high temperatures (523 K), and one intermediate (473 K). The rate coefficients were calculated by either interpolation or extrapolation using the Arrhenius parameters of Table 2. The extrapolations were justified by the good linearity of the experimental points. The values of $[k_p/k_p(Al_2O_3)]$ and $[r/r(MgO)]$ calculated for each catalyst are collected in Table 3. An inspection of Table 3 shows that unique scales of acidity and basicity cannot be obtained because both the values and the order of $[k_p/k_p(Al_2O_3)]$ and $[r/r(MgO)]$ are strongly affected by the temperature. This behavior is due to the great variety of the E values together with a great variety of the frequency factors (A) (Table 2).

By contrast with the relations observed

TABLE 3

Acidity and Basicity of the Oxides Evaluated through the Catalytic Decomposition of Isopropanol

Catalyst	$k_p/k_p(Al_2O_3)$[a]			$r/r(MgO)$[b]		
	423 K	473 K	523 K	423 K	473 K	523 K
Al_2O_3	1	1	1	0.053	0.021	0.010
BeO	0.0018	0.0073	0.023	5150	104	4.42
CaO	0.0021	0.0029	0.0036	64.6	17.8	6.29
Cr_2O_3	0	0	0	—	—	—
Ga_2O_3	0.018	0.028	0.039	57.7	11.7	3.20
La_2O_3	0	0	0	—	—	—
MgO	0.149	0.054	0.024	1	1	1
MoO_3	192	64.1	26.4	0.040	0.064	0.093
Nb_2O_5	0.463	0.687	0.945	2.25	0.171	0.021
Nd_2O_3	0	0	0	—	—	—
Pr_6O_{11}	0.0041	0.011	0.025	1950	233	41.7
SiO_2	0	0	0	—	—	—
Ta_2O_5	4.523	2.027	1.059	0.053	0.016	0.0061
ThO_2	0.112	0.037	0.015	13.6	12.9	12.4
TiO_2	1.96	1.87	1.80	0.102	0.088	0.079
WO_3	234	102	52.5	0.014	0.016	0.018
ZnO	0.162	0.157	0.153	4.49	14.1	35.5
ZrO_2	6.86	3.81	2.36	0.988	0.540	0.331

[a] Acidity referred to alumina, see text.

[b] Basicity referred to magnesia, see text.

by Ai for homogeneous series of oxides (*13*, *15*), the "indirect" acidity and basicity measures of Table 3 could not be related in any way to the "direct" measures of the number of the acid and basic sites expressed as V_{NH_3} and V_{CO_2}, respectively (Table 1). On the other hand, simple relations with the strength of the sites expressed as $Q_m(NH_3)$ and $Q_m(CO_2)$ (Table 1) were not found either. Probably the wide heterogeneity of our series of oxides, in terms of number, nature (Brønsted or Lewis), and strength of the acid–base sites (*1*), prevents simple relations from being diagnosed.

Considering that the number and the nature of the sites should mainly affect the Arrhenius parameter A while the strength of the sites should mainly affect E, we approached the comparison of the acidity/basicity of the catalysts in a different way. First, the value of A of the reaction of formation of propene was divided by the number of the acid sites (V_{NH_3}) and, always in the framework of Ai's approach, the value of A of the reaction to acetone by the sum of the acid and basic sites ($V_{NH_3} + V_{CO_2}$). The so calculated "specific frequency factors per site" (A'_p, in s^{-1} for dehydration, and A'_a, in $m^2 \cdot mmol^{-1} \cdot s^{-1}$ for dehydrogenation) are reported in Table 4 as logarithms.

An inspection of Table 4 shows that several oxides display roughly similar values of $\ln A'_p$ and $\ln A'_a$. In the reaction of propene formation CaO, WO_3, ZnO, and ZrO_2 have $\ln A'_p$ values in the range 15.5–16.9, and Al_2O_3, Ga_2O_3, Nb_2O_5, Pr_6O_{11}, and TiO_2 in the range 19.1–22.6. For the acetone formation, Al_2O_3, CaO, Ga_2O_3, MgO, Nd_2O_3, Pr_6O_{11}, SiO_2, ThO_2, and ZrO_2 have $\ln A'_a$ values in the range 6.1–9.8. Frequency factors of the same order, corresponding to similar activation entropies, should reflect similar structures of the activated complexes. Looking for a relation between the activation energy and the strength of the sites (expressed as $Q_m(NH_3)$ and $Q_m(CO_2)$),

TABLE 4

Specific Parameters per Site for the Catalytic Decomposition of Isopropanol

Catalyst	ln $A_p'^a$	ln $A_p'^b$	$k_p'/k_p'(Al_2O_3)^c$ (473 K)
Al_2O_3	20.388	9.776	1
BeO	26.545	−1.717	0.0029
CaO	16.275	6.619	0.0014
Cr_2O_3	—	—	0
Ga_2O_3	19.149	8.050	0.0071
La_2O_3	—	13.559	0
MgO	9.827	9.214	0.132
MoO_3	13.751	—	13.9
Nb_2O_5	22.410	−0.164	0.267
Nd_2O_3	—	8.331	0
Pr_6O_{11}	22.572	8.584	0.0017
SiO_2	—	6.109	0
Ta_2O_5	13.168	—	0.652
ThO_2	6.193	6.983	0.0075
TiO_2	20.003	17.308	1.02
WO_3	16.852	—	31.6
ZnO	16.468	27.480	0.026
ZrO_2	15.528	9.724	1.13

[a] A_p' expressed in s^{-1}.

[b] A_a' expressed in $m^2\ mmol^{-1}\ s^{-1}$.

[c] Acidity referred to alumina, see text.

sound comparisons must be made within sets of catalysts having similar specific frequency factors per site.

Linear dependences of E_p vs $Q_m(NH_3)$ were observed for groups of catalysts with similar ln A_p' (Fig. 3). This shows that the catalytic activity in the dehydration reaction is markedly influenced by the acid strength of the sites. Catalysts having stronger acid sites display a higher activity because of the major lowering of E_p. Hence within the set of catalysts having ln A_p' in the range 19.1–22.6 the acid strength order

$$TiO_2 \geq Al_2O_3 > Nb_2O_5 > Ga_2O_3 > Pr_6O_{11}$$

corresponds to the catalytic activity order. Such an activity order is evaluated on the basis of the ratio $k_p'/k_p'(Al_2O_3)$, where k_p' is the rate coefficient per site of the reaction to propene calculated as k_p/V_{NH_3} (Table 4). The same behavior is shown by the catalysts with ln A_p' in the range 15.5–16.9:

$$WO_3 > ZrO_2 > ZnO > CaO.$$

For the reaction to acetone, reporting E_a vs $Q_m(CO_2)$, the catalysts are still grouped according to their ln A_a'. However, in this case, E_a and $Q_m(CO_2)$ are not correlated (Fig. 4). The same absence of correlation has been observed also reporting E_a either vs $Q_m(NH_3)$ or vs $(Q_m(CO_2) + Q_m(NH_3)$ to fully test the influence of both the acid and basic sites operating in the concerted mechanism of the reaction. These observations suggest that the dehydrogenation of isopropanol to acetone is not influenced by the strength of either the acid or the basic sites.

It is noteworthy that the catalysts did not group in an analogous way by dividing the frequency factor of the reaction to acetone by the number of the basic sites instead of the sum of both the acid and basic sites. This is in accord with the hypothesis that the dehydrogenation of isopropanol proceeds through a concerted mechanism.

CONCLUSION

In the dehydration of isopropanol to propene catalyzed by metal oxides, the number, the nature and the strength of the acid sites affect the catalytic activity. The number and the nature influence mainly the entropic activation parameter (i.e., the frequency factor), while the strength influences the activation energy. To present evidence for the relationship between the acid strength and the activation energy, a set of catalysts with similar specific frequency factor per site must be compared.

In the dehydrogenation of isopropanol to acetone, the activity of the catalysts takes place through a concerted mechanism involving both acid and basic sites. Also in this case the number and the nature of the sites influence mainly the entropic term, but the activation energy is independent of the strength of both the acid and the basic sites.

The catalytic decomposition of isopropanol is a good test to compare metal oxides in terms of the strength of their acid sites, but it must be employed with care in investi-

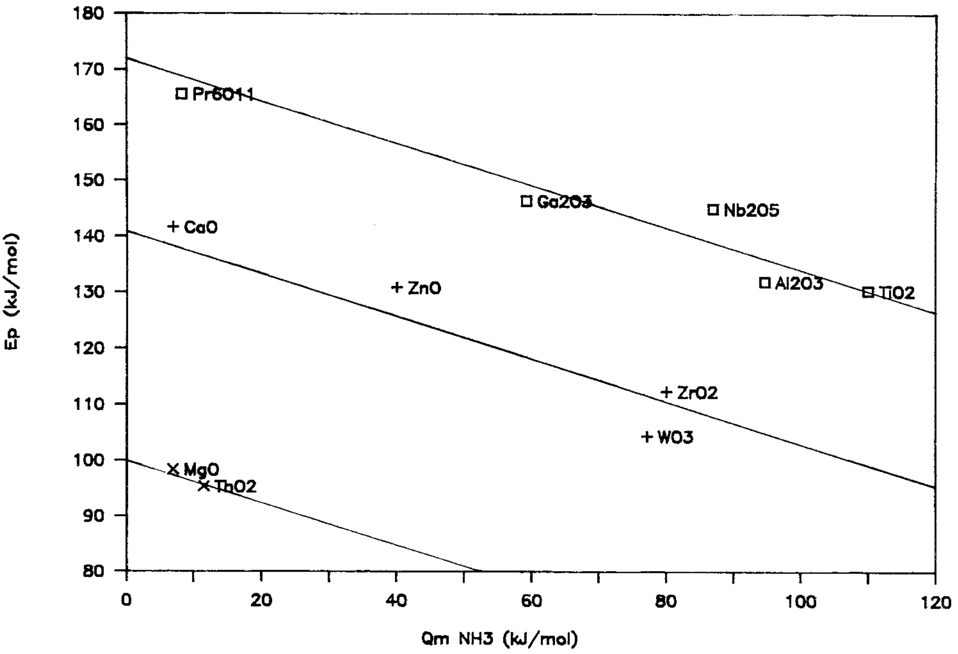

FIG. 3. Relation between the activation energy of the decomposition of isopropanol to propene and the strength of the acid sites. ×, ln A'_p: 6.2–9.8; +, ln A'_p: 15.5–16.9; □, ln A'_p: 19.1–22.6.

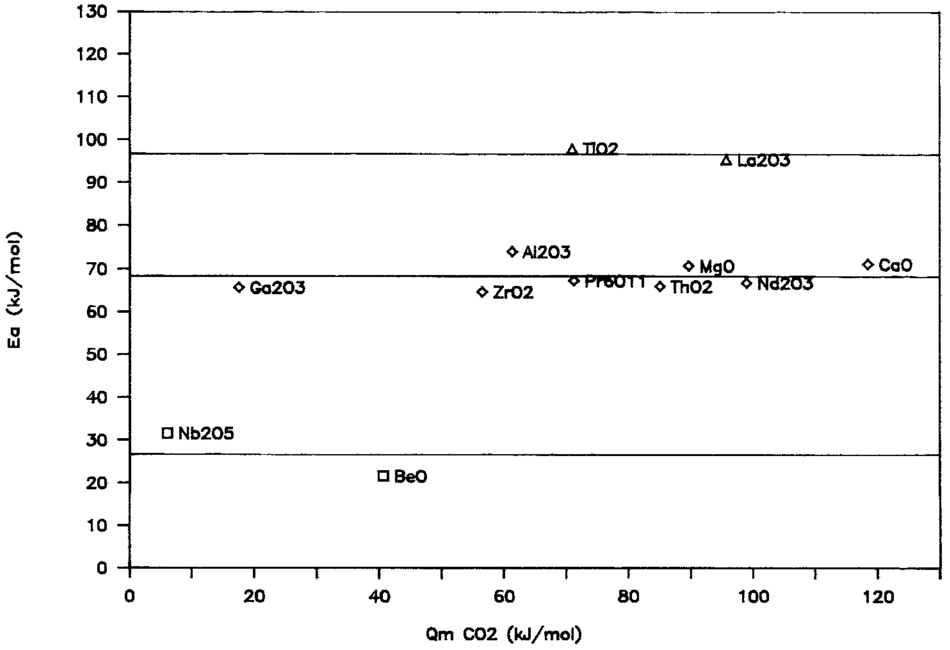

FIG. 4. Relation between the activation energy of the decomposition of isopropanol to acetone and the strength of the basic sites. □, ln A'_a: -1.7–-0.2; ◇, ln A'_a: 6.1–9.8; △, ln A'_a: 13.6–17.3.

gating the basic character of the catalysts. In fact, the activity of the acid sites in the concerted mechanism is evaluated on the basis of the parallel reaction to propene. However, this evaluation could not be sound because the kinetics of the reaction to acetone depends only on the number of the sites, but does not depend on their strength, in contrast with the formation of propene.

REFERENCES

1. Auroux, A., and Gervasini, A., *J. Phys. Chem.* **94,** 6317 (1990).
2. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., *in* "New Solid Acids and Bases, Their Catalytic Properties" (B. Belmon and J. T. Yates, Eds.), Vol. 51. Elsevier, Amsterdam, 1989.
3. Guisnet, M., *in* "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), Stud. Surf. Sci. Catal. Series, Vol. 20, p. 283. Elsevier, Amsterdam, 1985, and references therein.
4. Grzybowska-Swierkosz, B., *in* "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), Stud. Surf. Sci. Catal. Series, Vol. 20, p. 45. Elsevier, Amsterdam, 1985.
5. Barthomeuf, D., and Figueras, F., *in* "Chemical and Physical Aspects of Catalytic Oxidation" (J. L. Portefaix and F. Figueras, Eds.), p. 241. Editions du CNRS, 1980.
6. Hattori, H., Maruyama, K., and Tanabe, K., *Bull. Chem. Soc. Jpn.* **50,** 2181 (1977).
7. Hattori, H., Asada, N., and Tanabe, K., *Bull. Chem. Soc. Jpn.* **51,** 1704 (1978).
8. Tanabe, K., Hattori, H., *Chem. Lett.,* 625 (1976).
9. Fukuda, Y., Hattori, H., and Tanabe, K., *Bull. Chem. Soc. Jpn.* **51,** 3150 (1978).
10. Cunningham, J., Hodnett, B. K., Ilyas, M., Leahy, E. L., and Fierro, J. L. G., *Faraday Disc USS. Chem. Soc.* **72,** 283 (1981).
11. Ai, M., *Bull. Chem. Soc. Jpn.* 50, 2579 (1977).
12. Nollery, H., and Ritter, G., *J. Chem. Soc. Faraday Trans. 1* **80,** 275 (1984).
13. Ai, M., *Bull. Chem. Soc. Jpn.* **49,** 1328 (1976).
14. Ai, M., *J. Catal.* **40,** 318 (1975).
15. Ai, M., *J. Catal.* **40,** 327 (1975).
16. Ai, M., and Ikawa, T., *J. Catal.* **40,** 203 (1975).
17. Ai, M., and Suzuki, S., *Bull. Chem. Soc. Jpn.* **47,** 3074 (1974).
18. Ai, M., and Suzuki, S., *J. Catal.* **30,** 362 (1973).
19. Ai, M., *Bull. Chem. Soc. Jpn.* **50,** 355 (1977).