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Catalytic Behavior and Surface Chemistry of the ZnO/Al_2O_3 System for the Decomposition of 2-Propanol

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Samples of zinc oxide supported on γ-Al_2O_3 (5, 15, 30, and 36 Zn atoms per 100 Al atoms) have been calcined at different temperatures and subjected to oxidation–reduction treatments in order to investigate the type and the extent of the metal–support interaction and the defect state of the surface. The samples were then tested as catalysts in the decomposition of 2-propanol. They were found to give both dehydrogenation and dehydration. The dehydrogenation reaction is due to "free" zinc oxide present on the surface of the support, whereas the dehydration is due to the support. The effect of the calcination temperature on the formation of a "surface spinel" and of the redox pretreatments on the activity and selectivity are also discussed. © 1989 Academic Press, Inc.

INTRODUCTION

In recent years alumina-supported catalysts have attracted considerable interest because of the increasing number and variety of industrial and technological applications. Great interest has been focused on copper-based catalysts, which are widely known as active and selective for methanol synthesis (*1–3*), the water–gas shift reaction (WGS) (*4*), and the hydrogenation of alkenes and ketones (*5–7*).

In particular $CuO/ZnO/Al_2O_3$ catalysts are currently investigated for their special properties in methanol synthesis and the WGS reaction. Major efforts are devoted to the correlation between surface properties and copper content and between Cu/Zn ratio and oxidation state of the copper. The system ZnO/Al_2O_3 constitutes a simplified model for characterizing the more complex ternary system $CuO/ZnO/Al_2O_3$, and, along this line, in our laboratory we have already investigated the CuO/Al_2O_3 system (*8*). On the other hand, ZnO/Al_2O_3 catalysts are also used, per se, for the elimination of hydrochloric acid from 1- and 2-chlorobutenes and for the 1-butene to isobutene isomerization (*9–11*); they also constitute an important component of the ICI catalyst for the WGS reaction (*3*). In the present work, the 2-propanol decomposition has been chosen as a test reaction for investigating activity and selectivity toward dehydration as a function of the zinc concentration, calcination temperature, and redox pretreatments. The first two factors affect the type and the extent of the metal–support interactions, whereas the last factor sheds some light on the role of the defect state of the surface on the activity and selectivity. In addition, it will be shown that the 2-propanol decomposition can be used as a probe reaction for the detection of surface heterogeneity.

EXPERIMENTAL

Samples: Preparation, Characterization, and Conditioning

The ZnO/Al_2O_3 samples are designated AZx, where $x = 5$, 15, 30, and 36 indicates the real number of zinc atoms per 100 atoms of aluminum as determined by atomic absorption analysis. They were obtained by impregnating a given amount of γ-alumina, prepared according to MacIver *et al.* (*12*), with zinc nitrate solution. A calcination at

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773 K in air for 3 h was finally performed. The sample AZ36 was prepared by coprecipitation from nitrate solutions with ammonia at pH 7 and a calcination at 773 K for 24 h in air (*13*). Zinc oxide, ZO, was obtained by thermal decomposition of zinc nitrate in air at 773 K for 4 h. Zinc aluminate, ZA_2, was prepared by spray decomposition from nitrate solutions at 873 K. The sample was successively washed in 2 *M* HNO_3 and then calcined in air for 5 h at 773 K. All chemicals were Carlo Erba reagent grade.

The catalysts were analyzed by atomic absorption for zinc loading. XRD (Cu$K\alpha$ radiation = 1.54178 Å, Ni filtered) at room temperature and reflectance spectra (250–2500 nm, MgO as reference) were used for phase composition and surface investigation, respectively. The surface areas were measured before and after catalysis with a conventional BET apparatus (N_2 as adsorbate).

The sample conditioning consisted of thermal treatments and/or of oxidation–reduction treatments. The thermal treatments simply consisted of a longer calcination time in air at the same preparation temperature and/or of a further calcination at higher temperatures. The catalysts, after the thermal treatments, underwent the following oxidation–reduction procedure. A freshly prepared sample was treated overnight in oxygen (S.I.O. 99.95%) at 693 K, flushed in helium at 693 K for 1 h, and then subjected to catalysis. This sample will be referred to as "oxidized." The oxidized sample, after the catalytic runs, was usually treated in hydrogen (S.I.O. 99.995%) for 0.5 h at 693 K and then flushed in helium at the same temperature for 1 h. On this "reduced" sample catalytic runs were performed. As a further step, a reduced sample, after catalysis, could be retreated in oxygen overnight at 693 K; the subsequent catalytic experiments are then referred to as being conducted on a "reoxidized" sample.

Catalysis: Method and Data Treatment

The catalytic experiments were carried out in a flow system with a 2-propanol partial pressure of about 20 Torr in helium as carrier gas. The total pressure was maintained constant in all the experiments and it was slightly higher than 1 atm. Details on the apparatus and on the GC analysis can be found in Ref. (*8*).

The kinetic treatment used assumes that the two possible reactions due to the decomposition of 2-propanol, i.e., dehydrogenation and dehydration, are parallel and both of the first order

$$\mathrm{A}\begin{array}{l} \xrightarrow{\quad 1 \quad} \mathrm{B} + \mathrm{H_2} \\ \xrightarrow{\quad 2 \quad} \mathrm{C} + \mathrm{H_2O} \end{array}$$

where A = 2-propanol, B = acetone, and C = propene. The mass balance in an element of a flow tubular reactor gives

$$Fd\lambda_1 = r_1 dw = k_1 p_A dw \qquad (1)$$

and

$$Fd\lambda_2 = r_2 dw = k_2 p_A dw, \qquad (2)$$

where F = feed flow (feed mass/time); λ_1, λ_2 = numbers of moles of acetone, propene (mol/feed mass); r_1, r_2 = reaction velocities for dehydrogenation, dehydration (mol/(time × cat. mass)); w = catalyst mass; k_1, k_2 = experimental velocity constants for dehydrogenation, dehydration (mol/(time × cat. mass × pressure)); and p_A = partial pressure of A.

Taking into account that

$$d\lambda_1/d\lambda_2 = k_1/k_2 \qquad (3)$$

the integrated form of Eq. (1) gives

$$\begin{aligned} k_1 + k_2 &= \frac{1}{\tau P}\left((2 + R)a \ln \frac{a}{a - x} - x\right) \\ &= \frac{1}{\tau P}\left(Q \ln \frac{a}{a - x} - x\right) \\ &= \frac{1}{\tau}\left(\frac{Q}{P} \ln \frac{a}{a - x} - \frac{x}{P}\right), \qquad (4) \end{aligned}$$

where τ = contact time = w/F (cat. mass × time/feed mass); a = moles of 2-propanol in the feed/feed mass; R = moles of helium in the feed/moles of A in the feed; $(2 + R)a$ =

Q; and $x = \lambda_1 + \lambda_2$. Taking into account that $P \cong 1$ atm (1 atm = 1.01×10^5 N m^{-2}), $a = 0.0046$ (mol of 2-propanol/feed mass), and that $(2 + R)a = Q \cong 0.2$ (mol/feed mass), it turns out that in Eq. (4) it is possible to neglect x/P with respect to (Q/P) $\ln(a/(a - x))$. In fact, for conversion of 10% the error is about 2.0% and for 50% conversion is 1.8%. The calculated values of k_1 and k_2 are reported as Arrhenius plots under Results.

RESULTS

Catalyst Characterization

The samples of AZx investigated by XRD showed the presence of γ-alumina and zinc aluminate phases only. The peaks at $2\Theta = 34.5°$ and 47.5°, diagnostic in our conditions of the presence of ZnO, were never observed (ASTM Nos. 10-425, 5-0664, 5-0669). However, the optical reflectance spectra showed a significant difference between the more diluted samples AZ5 and AZ15 and the samples AZ30 and AZ36. The latter ones, in fact, exhibited an absorption edge at about 400 nm, typical of the transition valence-conduction band of zinc oxide ($E_g \simeq 3.2$ eV). A mechanical mixture containing only 1% in atoms of zinc with alumina showed that the band at 400 nm was as intense as those presented by AZ30 and AZ36.

The thermal treatments either at the same preparation temperature for a longer time or at higher temperatures had the same qualitative effect on AZx samples. In fact, the XRD spectra envisaged an increase in the intensity of the spinel peaks at $2\Theta = 31°$ and 37°, whereas the reflectance spectra did confirm the presence of zinc oxide on the surface of AZ30 and AZ36.

The ZA_2 sample, before and after the washing in HNO_3, was found to be monophasic (spinel phase). Neither XRD nor reflectance spectra revealed the presence of ZnO.

Finally, the surface areas, S.A., decreased as the zinc content increased and, at a given zinc loading, a longer calcination time and/or a higher calcination temperature provoked a similar decrease. No difference was detected between the values measured before and after catalysis. Table 1 summarizes the main features of the solids.

TABLE 1

Samples and Their Features

Sample	Calcination		Phases detected by XRD	S.A. (m^2 g^{-1})	S_{H_2O}
	T (K)	Time (h)			
AZ5	773	3	A, ZA_2	180	0.9 (490 K)
AZ15	773	3	A, ZA_2	160	0.8 (489 K)
AZ15	773	27	A, ZA_2	133	1 (487 K)
AZ30	773	3	A, ZA_2, ZO[a]	166	0.1 (483 K)
AZ30	773	27	A, ZA_2, ZO[a]	109	0.6 (482 K)
AZ30	873	24	A, ZA_2, ZO[a]	95	0.9 (483 K)
AZ36	773	24	A, ZA_2, ZO[a]	145	0.1 (487 K)
AZ36	873	22	A, ZA_2, ZO[a]	90	0.5 (474 K)
ZO	773	4	ZO	10	—
ZA_2	773	5	ZA_2	140	Inactive

Note. A, γ-alumina; ZO, ZnO; ZA_2, zinc aluminate.

[a] As detected by reflectance spectra.

Catalysis

γ-Alumina and zinc aluminate. γ-Al_2O_3 was studied previously (*8*) and in the following, when needed, its activity level will be given as reference. Here it is sufficient to recall that in the T range 433–523 K γ-Al_2O_3 gave only propene as a result of the 2-propanol decomposition and both its activity and E_a were unaffected by oxidizing or reducing treatments, the latter quantity being 170 ± 10 kJ/mol (*8*). The ZA_2 catalyst treated either in hydrogen or in oxygen did not show any appreciable activity below 600 K. If, however, the experiment was performed at 600 K and higher temperatures a low dehydration activity appears.

Zinc oxide. Several portions of the same ZnO batch were investigated in the T range 490–560 K. Dehydrogenation was the only reaction observed in stationary conditions, while traces of propene were observed during the first minutes on stream. The results were highly reproducible on different portions of ZnO and a linear relationship $\ln(a/(a - x))$ vs W/F was satisfactorily

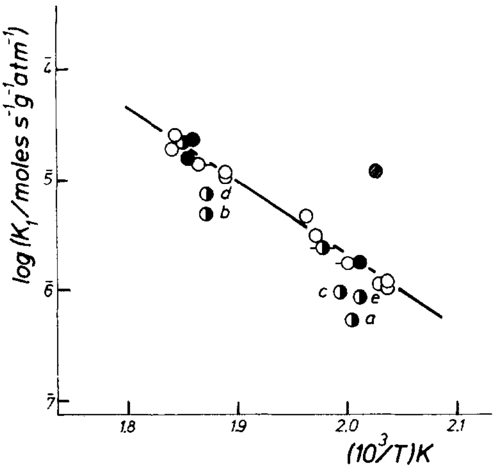

FIG. 1. Arrhenius plot for 2-propanol dehydrogenation on zinc oxide. ○, Oxidized; ●, reduced; -○-, reoxidized; ▨, reduced, initial activity; ◑, reduced and poisoned with acetone (see text); -◑-, reduced, poisoned with acetone, and flushed in He, 24 h (see text).

obeyed at 500 and 530 K. The E_a value found was 126 ± 10 kJ/mol. It is worthy of note that the dehydrogenation activity of an oxidized sample was practically constant after 1 h on stream and then remained constant for times as long as 172 h. The effect of reduction, as described in the conditioning section, had a very pronounced effect on the activity. In fact, the initial dehydrogenating activity of a ZO reduced in hydrogen is well above that of an oxidized one. However, the activity tended to decay slowly and, in a time of 24 h, reduced to that of the oxidized sample. No further decay was then observed. Due to the rapidity of the decay, it was not possible to monitor substantial differences in initial dehydrating activity of reduced ZnO with respect to oxidized ZnO.

In order to investigate the effects of the reoxidation procedure and of water or acetone preadsorption on the activity of ZO, the sample was reoxidized and checked for its activity which turned out to be equal to that of the oxidized sample. Then two experiments of selective poisoning were performed with either water or acetone. The procedure consisted of (i) reduction in hydrogen; (ii) flushing in helium at 693 K, 1 h; (iii) flushing in helium containing water (P = 24 Torr) or acetone (P = 250 Torr) at 530 K, 0.5 h; (iv) flushing in helium at 693 K for 1 h. The treatment with water suppressed the initial dehydration activity but did not produce any change in either the activity or the E_a with respect to the oxidized sample for dehydrogenation. By contrast the presence of acetone had a pronounced effect on the dehydrogenation activity. The catalyst showed an activity less than that of the oxidized sample, but it tended to increase while on stream. The phenomenon is clearly shown in Fig. 1 where initial activity of the reduced ZO and activities of the ZO oxidized, reoxidized, and reduced are reported together with the results of the poisoning test. It must be added that after about 50 h on stream, the activity of the catalyst treated in acetone is still below that of the oxidized sample; however, the process of approaching the activity level of the oxidized sample can be accelerated if after step (iii) the catalyst is flushed in He at 693 K but for a longer time, typically 24 h. The increase in flushing time in He over 24 h, after which the catalyst reached the activity of the oxidized sample, did not have any further effect on the activity level in stationary conditions.

Zinc oxide/alumina. Several portions of catalysts with different zinc content were investigated in the T range 450–540 K, although the upper limit of this range was seldom reached. They were both dehydrating and dehydrogenating. That the assumptions made in the Data Treatment section were correct was proved by plotting the experimental data at 450 and 530 K according to Eq. (4). Good straight lines were obtained for AZ30 and AZ5, both oxidized. Both reactions are a complex function of (i) zinc content and (ii) thermal treatments. With respect to the dehydration reaction, the samples AZ5, AZ15, and AZ30 all calcined at 773 K for 3 h showed a decreasing activity as the zinc content increases. Given that the E_a's for all the samples agree well with that of the pure alumina (broken lines in Figs. 2a and 3a), the activities, taking as a

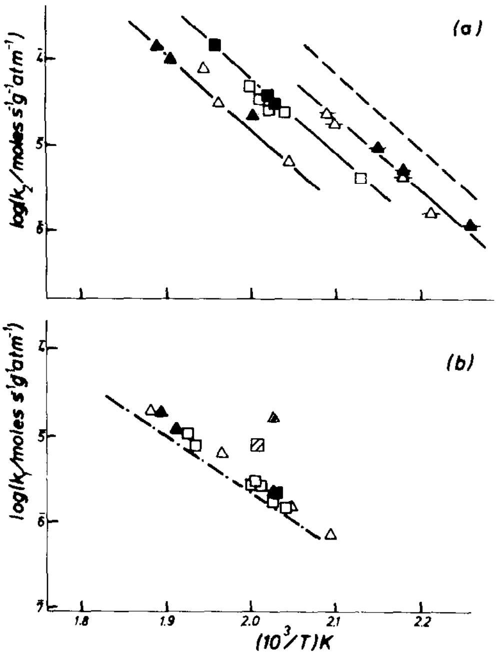

FIG. 2. Arrhenius plots for 2-propanol decomposition on AZ5 and AZ15. (a) Dehydration, --- γ-alumina from Ref. (*8*), and (b) dehydrogenation, —·—ZnO from Fig. 1. □, AZ5 oxidized; ■, AZ5 reduced; △, AZ15 oxidized; ▲, AZ15 reduced; -△-, AZ15, 773 K, 27 h, oxidized; -▲-, AZ15, 773 K, 27 h, reduced; ▨, AZ5, reduced, initial activity; ◮, AZ15, reduced, initial activity.

reference that of AZ5, are in the ratios 1 (AZ5), 0.25 (AZ15), 0.025 (AZ36), and 0.008 (AZ30). As a consequence the selectivity toward dehydration, S_{H_2O}, defined as the ratio between the conversion to propene and the total conversion, passes from 0.9 for AZ5, 773 K for 3 h, to about 0.1 for AZ30, 773 K for 3 h (see Table 1).

The Arrhenius plots are reported in Figs 2a and 3a. In the latter the activity of coprecipitated AZ36 is also shown. It may be noted that it is only slightly more active than AZ30.

The pretreatments in hydrogen did not modify the dehydration activity in stationary conditions. In Figs. 2a and 3a the points relative to those experiments are well in line with the activity levels of oxidized and reoxidized samples.

The effects of thermal treatments, as described in the Conditioning section and as summarized in Table 1, are very pronounced. AZ15, AZ30, and AZ36, when calcined at 773 K for a longer time or at 873 K for 22–24 h (see Table 1), increase their dehydration activity to such an extent that S_{H_2O} for AZ30 passes from about 0.1 (773 K for 3 h) to 0.9 (873 K for 24 h) and for AZ15 from 0.8 (773 K for 3 h) to about unity (773 K for 27 h). The different quantitative effect of the thermal treatment on AZ30 and AZ36 should be noted. This can be thought of as a consequence of the different preparation method.

As far as the dehydrogenation is concerned, the reducing treatments had a transitory effect giving rise to an initial dehydrogenating activity higher than the one found in stationary conditions for all the samples. The behavior is quite similar to

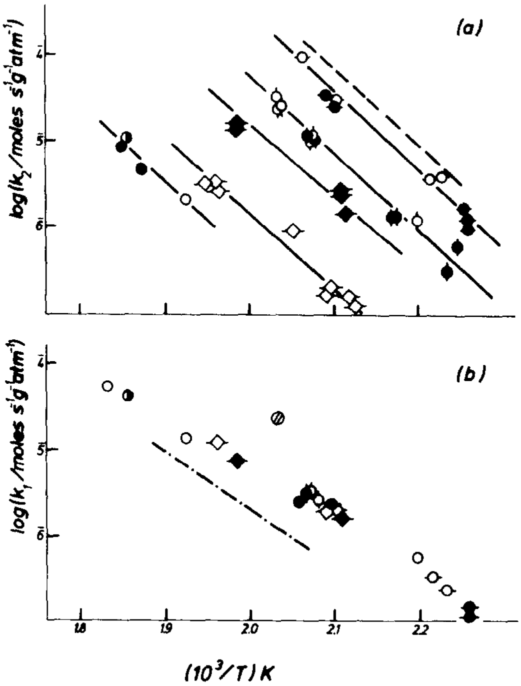

FIG. 3. Arrhenius plots for 2-propanol decomposition on AZ30 and AZ36. (a) Dehydration, --- γ-alumina from Ref. (*8*), and (b) dehydrogenation, —·—ZnO from Fig. 1. ○, AZ30, oxidized; ●, AZ30, reduced; ◑, AZ30, reoxidized; ⧲, AZ30, 773 K, 27 h, oxidized; ⧳, AZ30, 773 K, 27 h, reduced; -○-, AZ30, 873 K, 24 h, oxidized; -●-, AZ30, 873 K, 24 h, reduced; ◇, AZ36, 773 K, 24 h, oxidized; -◆-, AZ36, 873 K, 22 h, oxidized; ◍, AZ30, reduced, initial activity.

that of pure ZnO. At the same time, the E_a values are well in agreement with that found on ZnO. The Arrhenius plots in Figs. 2b and 3b do not show dramatic variations in activity in spite of the different zinc content and/or of the thermal treatment. It must be stressed, however, that the ratio in dehydrogenation activity, expressed as moles of acetone produced per gram of catalyst per second, between AZ15, 773 K for 3 h, and AZ15, 773 K for 27 h, is 4.4, whereas it is 1.3 between AZ30, 773 K for 3 h, and AZ30, 773 K for 27 h.

DISCUSSION

Zinc Oxide, γ-Alumina, and Zinc Aluminate

Zinc oxide is known for its dehydrogenation activity even though a limited dehydration ability is frequently reported. In recent years there has been detailed work, mainly by temperature-programmed techniques, on the kinetics and mechanism of primary and secondary alcohol decompositions on zinc oxide (*14–17*). Two different mechanisms have been proposed for the 2-propanol decomposition. The first (*15*) suggests that acetone formation proceeds via elimination of the α-hydrogen from an adsorbed isopropoxy species, whereas the dehydration occurs via a reaction between an adsorbed isopropanol and a surface hydroxyl group leading to an adsorbed isopropoxy species, water and an oxygen vacancy. The second mechanism (*18*) proposes that dehydrogenation takes place via hydrogen β-elimination leading to a surface enolate (*19*), whereas the dehydration proceeds via a reaction between an adsorbed isopropoxy species and a surface hydroxyl group leading to a surface enolate, water, and an oxygen vacancy.

The former mechanism for dehydrogenation is substantiated by the results of decomposition of deuterated 2-propanol (*20*) and, as rds, the α-elimination was proposed (*16*). The latter is based on experiments of acetone adsorption–desorption (*17*), which showed the evolution of both acetone and propene as a result of the presence of a common surface intermediate, i.e., a surface enolate. The β-elimination was proposed as the rds for the dehydrogenation (*17*).

Whatever the mechanism, the 2-propanol decomposition is found to be a reaction which is "nonfacile" or "structure dependent." Bowker *et al.* (*14*) proposed that the dehydrogenation sites are possibly $\underline{Zn}^+$ ions, on polar (0001) planes, whereas $(000\bar{1})$ and prism planes would be responsible for dehydration. Cheng *et al.* (*21*) suggested that the (0001) surface possesses the highest dehydrogenation activity in methanol dehydrogenation. By contrast, Chadwick and O'Malley (*17*) found that only propene is formed in a significant amount on (0001) planes and that acetone is produced on $(10\bar{1}0)$ nonpolar faces only. The present results obey a first-order kinetic law in agreement with both the rds proposed above. Also the present value of E_a are in accord with previous findings (*22*). In addition the following facts need to be given a reasonable rationalization: (i) the disappearance of a dehydration activity after a few minutes on stream; (ii) the time needed for having a constant acetone conversion on oxidized samples; (iii) the high initial dehydrogenation activity of reduced samples; and (iv) the poisoning effect of preadsorbed water on dehydration.

The disappearance of the dehydration activity could be due to a surface defect state equilibration of zinc oxide and/or to reconstruction of polar planes. In fact, in both the schemes proposed above, the dehydration occurs via a reaction involving an oxygen vacancy and water formation. Waugh *et al.* (*16*) claimed that water is dissociated into adsorbed oxygen and hydrogen on zinc oxide when 2-propanol is preadsorbed on it and that the defect state of the ZnO surface depends on the reaction atmosphere, thermal treatments, and/or redox pretreatments. Cheng *et al.* observed by LEED that, due to the high surface energy of the (0001) polar surface of ZnO, a reconstruction into well-ordered surfaces may occur

(*21*). These indications suggest that the oxygen vacancies may be destroyed either by surface reoxidation or by surface reconstruction in the first minutes of reaction, so that the dehydration reaction is suppressed.

As regards the stabilization of the dehydrogenation activity, the surface defect state of nonpolar planes such as $(10\bar{1}0)$ has been related to the activity in methanol decomposition (*21*). The $(10\bar{1}0)$ planes, when reduced, are more active than the stoichiometric ones. The slow increase in dehydrogenation presently observed is an indication that the defectivity of nonpolar planes (i.e., the amount of Zn^+) is increasing, due to a reducing medium such as 2-propanol. Accordingly a surface heavily reduced at 693 K in hydrogen would be expected to show a high initial dehydrogenation activity (Fig. 1). Due to the rapidity of the decay, it was not possible to monitor differences in initial dehydration activity.

As to the experiments with preadsorbed water, we found complete suppression of the transient dehydration activity and no influence on the dehydrogenation. Coadsorption of 2-propanol and water gave rise to TPD spectra where the acetone peak was unaffected and propene was selectively displaced by hydroxyl groups (*17*). In addition, the presence of a higher hydroxyl coverage increased the amount of water desorbed at a high temperature (around 700 K). An IR study (*23*) assigned the most stable hydroxyl adsorption states to polar planes; it turns out that propene is mainly formed on (0001) polar planes and acetone on nonpolar planes as suggested by Chadwick and O'Malley (*17*). Their results did not exclude that propene could be formed on nonpolar planes even in a lesser amount with respect to polar planes. The present results show that, in stationary conditions, the fraction of sites active for dehydration, located on nonpolar planes is not effective possibly because of a fast self-poisoning due to the strongly held water.

Finally, the effect of acetone preadsorption can be discussed. A study of acetone adsorption on ZnO by Chadwick and O'Malley (*17*) yielded a TPD spectrum containing a CO_2 desorption peak at 750 K. Given that the CO_2 desorption from carbonate decomposition or from CO_2 adsorption takes place at 580 K (*24*) it was inferred that the evolution of CO_2 at 750 K derived from the decomposition of a carboxylate complex produced by oxidation of a surface enol (*17*).

The long time required in the present case to recover a stationary activity after acetone adsorption could be a result of the carboxylate decomposition and/or of the highly activated oxidation of possible carbonaceous residues by surface hydroxyl species.

As far as γ-alumina is concerned, the mechanism and the kinetic parameters of secondary alcohol dehydration have been extensively reviewed in the past and the results reported here have been presented elsewhere in connection with a study of the CuO/Al_2O_3 system (*8*). With regard to the inactivity of zinc aluminate in the temperature range presently explored, this finding agrees quite well with the classical work by Alsop and Dowden (*25*). They clearly showed that on stoichiometric zinc aluminate no activity was present below 573 K and that in the system ZnO/Al_2O_3 the dehydrogenation reaction, when present, was due to zinc oxide finely dispersed on the surface.

Zinc Oxide/Alumina

Turning now to the ZnO/Al_2O_3 system calcined at 773 K for 3 h, we recall that it shows both dehydration and dehydrogenation activities. The dehydration activity appears to depend on zinc content, time, and temperature of calcination, whereas the dehydrogenation activity shows minor variations.

The picture can be rationalized by considering the surface chemistry of the ZnO/Al_2O_3 system calcined at 773 K in air. It is generally accepted that various oxides supported on γ-alumina give rise to a surface spinel (*26–28*). In particular, Zn^{2+} ions diffuse into the T_d vacant sites of the γ-alumina (*29*). Strohmeier and Hercules (*30*) calculated that saturation of the surface of γ-alumina of 195 m^2/g occurs at a metal content of approximately 21%. They also found that, as the calcination temperature increases, a greater percentage of zinc ions can diffuse into the γ-alumina lattice and that the percentage of metal ions in the spinel form is the greatest at low metal loading. However, they also claimed that once all the available surface sites are saturated, further addition of zinc can be accommodated by segregation of a separate ZnO phase (*30*).

The present results add more details to this picture. In fact, even at the lowest zinc contents (i.e., AZ5 and AZ15), a well-developed dehydrogenation activity is present. Because the E_a values resemble in all cases that of the pure ZnO, first-order kinetics are obeyed as for ZnO, and, finally, the behavior of reduced samples is quite similar to that of ZnO, is is reasonable to attribute the dehydrogenating activity to a ZnO phase. At the same time, the E_a values found for the dehydration are in good agreement with the value found for pure γ-alumina. Given that pure zinc aluminate is completely inactive it is reasonable to attribute the dehydration activity to the γ-alumina surface. Thus, the 2-propanol decomposition appears to occur on two different sites belonging to pure γ-alumina and pure ZnO, respectively, and any role of the interface between zinc oxide and zinc aluminate may be disregarded (*31, 32*).

The presence of a ZnO phase on the γ-alumina, even at low zinc content, deserves further attention. The free energy of formation of bulk zinc aluminate from Al_2O_3 and ZnO in the range of 1060–1317 K is given by

$$\Delta G^\circ = -59{,}022 + 4.89T \text{ J/mole } (33).$$

However, the preparation of a bulk spinel is still incomplete after a calcination at 1173 K for 72 h (*30*).

Even though the surface reaction between zinc oxide and γ-alumina, as opposite to bulk reaction, may require much milder conditions, the present results clearly show that, in addition to surface zinc aluminate, some zinc oxide is still present on the surface in a form unable to give observable coherent diffraction. It may be noted that, according to Strohmeier and Hercules (*30*), the specimens AZ5 and AZ15 have a zinc content insufficient to give a monolayer of a surface spinel. The valuable results of these authors (*30*) may then be complemented by the present catalytic results and it is possible to evaluate the amount of the "free" zinc oxide present on the surfaces. By neglecting, as a very rough approximation, any difference in parameters such as crystallinity, crystal size, defectivity, and, in general, morphology and texture between pure zinc oxide and free zinc oxide, the upper limits of surface coverages of the free zinc oxide calculated simply by the moles of acetone evolved per gram of catalyst per second in stationary conditions are 2.4, 5.2, and 16.6%, respectively, for AZ5, AZ15, and AZ30 (Table 2).

Finally, the trend of the dehydration activity may be discussed as a function of the thermal treatments. The catalysts results show that the dehydration activity increased as the samples AZ15, AZ30, and AZ36 underwent more severe thermal treatments. From the kinetic parameters it appears that the γ-alumina is responsible for the dehydration and an increasing number of sites on it are active when the time and/or the temperature of calcination is increased. In fact, by increasing the time and/

TABLE 2

ZnO Coverages on AZ*x* Samples (773 K, 3 h)

Sample	T (K)	Acetone (mol × $10^7/g_{cat}$)	Φ^a (cm^3/s)	ZnO (m^2/g_{cat})
Z0	518	2.62	0.387	10.0
AZ5	519	0.85	0.530	4.4
AZ15	514	2.15	0.395	8.4
AZ30	519	6.70	0.415	27.5

[a] Flow rate of effluent gas.

or the calcination temperature, a greater percentage of zinc ions can diffuse into the γ-alumina lattice. As a result the Zn/Al ratios, measured by ESCA, decreased when the calcination temperature was increased from 673 to 873 K (*30*). In addition, the ISS spectra, due to the shorter sampling depth, indicate that the uppermost layers are depleted to a greater extent than the outer ones seen by ESCA (5–10 atomic layers) (*30*). The present AZ15 sample (773 K for 27 h) exhibited a dehydration activity slightly less than that of pure alumina, and the calculated zinc oxide coverage diminished from 5.2 to 1.4%. Similarly, the thermal treatments on AZ30 and AZ36 decreased the percentage of ZnO coverages, and the dehydration activity was enhanced almost to the level of that of the pure alumina. It appears that, in spite of the lesser quantity of ZnO present on AZ15 with respect to AZ30 and AZ36, the complete dissolution of it is never realized. In addition, the increase in dehydration and an easily measurable dehydrogenation would suggest that zinc migration from the surface zinc aluminate into the alumina lattice is faster than the surface reaction between free zinc oxide and γ-alumina.

In conclusion, for all the Zn loadings, the surface of the ZnO/Al_2O_3 system, calcined at 773 K, appears to be constituted by dispersed zinc oxide, surface zinc aluminate, and pure γ-alumina. The relative coverages are a function of the zinc loading and of the thermal treatments, but, in the conditions experimentally used, a complete dissolution of ZnO into γ-alumina has never been observed Thus, the 2-propanol decomposition can be used as a probe reaction for detecting surface heterogeneity not always observable by means of other surface techniques.

REFERENCES

1. Kung, H. H., *Catal. Rev. Sci. Eng.* **22,** 235 (1980).

2. Klier, K., *Adv. Catal.* **31,** 243 (1982).

3. Andrew, S. P. S., "Postcongress Symp. 7th Congress on Catalysis, Osaka July 1980," Paper 12.

4. van Herwijnen, T., and De Jong, W. A., *J. Catal.* **63,** 83 (1980).

5. Phillipson, J. J., Wells, P. B., and Gray, D. W., "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 1250. North Holland, Amsterdam, 1965.

6. Jenk, J., Germain, J. E., *J. Catal.* **65,** 133 (1980).

7. Jenk, J., Germain, J. E., *J. Catal.* **65,** 141 (1980).

8. Pepe, F., Angeletti, C., De Rossi, S., and Lo Jacono, M., *J. Catal.* **91,** 69 (1985).

9. Vinek, H., Noller, H., Ebel, M., and Schwartz, K., *J. Chem. Soc. Faraday Trans. 1* **73,** 734 (1977).

10. Vinek, H., and Noller, H., *Z. Phys. Chem.* **102,** 247 (1976).

11. Vinek, H., and Noller, H., *Z. Phys. Chem.* **102,** 255 (1976).

12. MacIver, D. S., Tobin, H. H., and Barth, R. T., *J. Catal.* **2,** 485 (1963).

13. Falcone, M., Thesis, University of Rome, 1983.

14. Bowker, M., Petts, R. W., and Waugh, K. C., *J. Catal.* **99,** 53 (1986).

15. Bowker, M., Petts, R. W., and Waugh, K. C., *J. Chem. Soc. Faraday Trans. 1* **81,** 3073 (1985).

16. Waugh, K. C., Bowker, M., Petts, R. W. Vandervell, H. D., and O'Malley, J., *Appl. Catal.* **25,** 121 (1986).

17. Chadwick, D., and O'Malley, P. J., *J. Chem. Soc. Faraday Trans. 1* **83,** 2227 (1987).

18. Mazanec. T. J., *J. Catal.* **98,** 115 (1986).

19. Koga, O., Onishi, T., and Tamaru, K., *J. Chem. Soc. Faraday Trans. 1* **76,** 19 (1980).

20. Akiba, E., Soma, M., Onishi, T., and Tamaru, K., *Z. Phys. Chem.* **119,** 103 (1980).

21. Cheng, W. H., Akhter, S., and Kung, H. H., *J. Catal.* **82,** 341 (1983).

22. Jover, B., Juhasz, J., and Szabo, Z. G., *Z. Phys. Chem.* **111,** 239 (1978).

23. Atherton, K., Newbold, G., and Hockey, J. A., *Discuss. Faraday Soc.* **52,** 33 (1971).

24. Bowker, M., Houghton, H., and Waugh, C. K., *J. Chem. Soc. Faraday Trans. 1* **77,** 3023 (1981).

25. Alsop, B. C., and Dowden, D. A., *J. Chem. Phys.* **51,** 678 (1954).

26. Lo Jacono, M., and Schiavello, M., "Preparation of Catalysts," p. 474. Elsevier, Amsterdam, 1976.

27. Wu, M., and Hercules, D. M., *J. Phys. Chem.* **83,** 2003 (1979).

28. Chin, R. L., and Hercules, D. M., *J. Phys. Chem.* **86,** 360 (1982).

29. Navrotsky, A., and Kleppa, O. J., *J. Inorg. Nucl. Chem.* **30,** 479 (1968).

30. Strohmeier, B. R., and Hercules, D. M., *J. Catal.* **86,** 266 (1984).

31. Uma, R., and Kuriacose, J. C., *Indian J. Chem.* **12,** 1314 (1974).

32. Udrea, I., and Crisan, D., *Rev. Roum. Chim.* **20**(2), 217 (1975).

33. Gilbert, I. G. F., and Kitchener, J. A., *J. Chem. Soc.* **761,** 3922 (1956).