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The Effect of Alumina Structure on Surface Sites for Alcohol Dehydration

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We have studied the effect of alumina form (γ, δ, and α), and impurities, on 2-propanol dehydration activity. In a steady-state flow reactor experiment, α-alumina was approximately 1000 times less reactive (in terms of moles propene formed/s/m^2) than reforming grade γ-alumina. The structure of the transitional alumina (γ vs δ) played a smaller role than Na contamination in determining alcohol dehydration activity. For instance, δ-alumina was $\approx$3–6 times less reactive than reforming grade γ-alumina in its activity for alcohol conversion, while Na-poisoned γ-alumina was $\approx$180 times less reactive. The number of surface sites on these aluminas were determined using temperature-programmed reaction (TPR) of 2-propanol. It was found that $\approx 1–2 \times 10^{18}$ alcohol molecules/m^2 reacted to form propene on all of the aluminas independent of alumina form or impurity concentration. The temperature at which the alcohol reacted to form propene in the TPR experiment correlated inversely with steady-state alcohol dehydration activity. The peak desorption temperature (T_p) during TPR ranged from 440 K for reforming grade γ-alumina to 600 K for α-alumina. These results are discussed in terms of a model for the nature of reactive sites on the surface of alumina.

INTRODUCTION

While transitional alumina is an important catalyst support, active sites on transitional alumina are still poorly characterized. Part of the reason is that the nature of the alumina depends considerably on the precursor from which it is obtained by calcination, the calcination conditions, and the amount of impurities. The dehydration of the precursor (boehmite or bayerite) was studied by Lippens (*1*) and it was shown that calcination at around 623 K leads to formation of γ- or η-alumina, which are commercially important as supports for hydrodesulfurization and reforming reactions (*2*). Dehydration at temperatures above 1023 K produces δ- and θ-alumina, respectively. The transformation from γ- or η-alumina to δ- and θ-alumina is believed to be accompanied by loss of surface hydroxyls and leads to formation of a lower surface area, more crystalline alumina (*2*). Both δ- and θ-alumina eventually transform into α-alumina when heated to temperatures of about 1473 K. The transformation into α alumina also affects the coordination of Al^{3+} which changes from being approximately 75% octahedral in γ-alumina (*3*) to 100% octahedral in α-alumina. The tetrahedrally coordinated aluminum atoms are believed to be responsible for the catalytic reactivity of γ-alumina, and it is generally expected that the higher temperature polymorphs will be less reactive than γ- or η-alumina (*2*). Since alumina supports are often calcined at high temperatures (>1000 K) to provide high-temperature stability, it would be important to know precisely what kinds of sites are lost during the transformation into the higher temperature polymorphs. However, examination of the literature reveals only a few studies where the specific reactivities of aluminas of differing structure have been measured.

One of the earliest studies was that of Pines and Haag (*4*), where the origins of

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the differences in alumina reactivity were explored. Probe reactions such as the skeletal isomerization of cyclohexene and dehydration of *n*-butanol were employed. The differences in reactivity among various aluminas was traced to differing amounts of Na contamination, however, the method of Na incorporation was found to be important. When Na was introduced from an aqueous solution by impregnation, approximately 1×10^{18} atoms of Na/m^2 were sufficient to poison activity of a pure alumina for either of the probe reactions. However, when the Na was incorporated as an impurity during the precipitation and calcination steps that produced the γ-alumina, the results were quite different. On samples where an Na aluminate was used as a precursor, it was found that 8.5×10^{16} Na atoms/m^2 were sufficient to poison the alumina for cyclohexene isomerization, while the alcohol dehydration activity was almost unaffected. Based on these observations, Pines and Haag concluded that the upper limit for the number of acid sites for alcohol dehydration was 1×10^{18} sites/m^2, while that for skeletal isomerization was 8.5×10^{16}/m^2, and that these latter sites were the ones selectively poisoned when Na was incorporated during precipitation. It is not clear why selective poisoning only occurred in the latter case since both sets of samples were eventually calcined at 873 K prior to catalytic testing.

The effect of alumina structure was also studied by Pines and Haag (*4*). Dehydration of the same batch of alumina hydrate at successively higher temperatures ranging from 673–1273 K produced samples of increasing crystallinity. Cyclohexene isomerization activity per unit surface area reached a maximum on the 873 K calcined sample which was primarily η-alumina, and activity declined over 20 times when the calcination temperature exceeded 1073 K, wherein the sample was θ-alumina with a trace of α. It was speculated that if the activity of the 873 K calcined alumina was due to surface strain, the higher temperature annealing would "heal" the strain and lead to lower reactivity. Pines and Haag were able to rule out the hypothesis that the lower activity of the 1073 K calcined samples was due to a lower hydroxyl content, since they found that the hydroxyl content of the two samples did not differ significantly. They also made the important observation that the activity of the 1073 K calcined sample increased after it was subjected to several reaction/regeneration cycles. Subsequent to this work, MacIver *et al.* (*5*) studied the effect of alumina form (γ vs η) on reactivity in double-bond and skeletal isomerization reactions. They found that η-alumina was more reactive than γ-alumina by a factor of 3 after reactivity was normalized to surface area. A more dramatic variation in specific activity was observed by Ponsolle *et al.* (*6*) in the isomerization of cyclohexene. However, while their specific activities varied over two orders of magnitude, they could not obtain a correlation between activity and structure or sodium content.

Since alcohol dehydration requires weaker acid sites than those necessary to catalyze skeletal isomerization, we may expect alcohol dehydration activity to be more closely related to the total number of active sites. Bremer and Glietsch (*7*) found that the specific activity for isopropanol dehydration on θ-alumina was approximately four times lower than on η-alumina. An alternative approach was used by Nortier *et al.* (*8*), who compared transitional aluminas of differing texture (plate-like vs needle-like) by starting from well-defined precursors. Overall, they found their samples were similar in terms of the IR spectra of hydroxyl groups present and adsorbed pyridine. Reactivity for 1-butene isomerization was measured, but since specific reactivities were not reported, it is difficult to draw any conclusions about the role of alumina structure on reactivity.

One problem in studying the effect of alumina form is the difficulty of preparing samples that are phase pure. We have found that a dry process involving vapor phase reactive evaporation of alumina (*9*) yields crystalline particles of an alumina that can be indexed to the δ form (*10*). In a previous study, we reported a comparison of the specific reactivity of this Model nonporous alumina with a commercial γ-alumina (*11*). We found that the nonporous alumina was more reactive than the γ-alumina for dehydration of alcohols such as 1-propanol and t-butanol. These results were surprising since the Model alumina contained single-crystal particles of δ-alumina which would be expected to be less reactive than γ-alumina. We discovered later that the γ-alumina we had used contained significant amounts of Na impurities. To provide a better comparison, we have now studied the reactivity of a larger set of aluminas ranging in structure from γ- to the high-temperature stable α form. These aluminas also contain varying amounts of impurities so that the effects of structure can be contrasted with those due to Na contamination. The results of flow reactor experiments at steady state will be used in conjunction with measurements of alcohol reactivity during temperature programmed reaction (TPR) performed in a thermogravimetric analyzer (TGA). The TPR–TGA method has been shown by us previously to be useful for determining the number of acid sites in zeolites of varying silica/alumina ratios (*12*). In that study, we were able to show that strong acid sites could be quantitatively associated with the number of Al atoms in the framework of the zeolite.

EXPERIMENTAL

The samples used in this study and their compositions obtained from the manufacturers' literature are reported in Table 1. The set includes aluminas that differ in purity (Na concentration up to 3020 ppm) and in structure (γ, δ, and α). The Na impurity content of all these aluminas was measured by Atomic Absorption Spectroscopy (AAS). The X-ray diffraction (XRD) patterns of these aluminas are presented in Fig. 1.

The Engelhard reforming grade alumina (batch 818) has an Na content of 10 ppm (*13*). Rhone Poulenc Spheralite 507 A is made by the flash calcination of gibbsite, which is an alumina trihydrate. It contains significant amounts of Na contamination. La Roche A-201 alumina is prepared by the calcination of alumina trihydrate and contains the largest amount of Na in these samples at 3020 ppm. AlonC is manufactured by the flame hydrolysis of anhydrous $AlCl_3$ and contains significant amounts of Cl impurities. The nonporous alumina was synthesized using the method of Iijima (*9*), which involves collecting the smoke produced by striking an arc between two electrodes of high purity aluminum in an atmosphere of Ar/O_2. The Na content of Model alumina was found to be 170 ppm. One reason for the relatively high impurity content in Model alumina could be that the electrodes are not as pure as stated in the manufacturer's specification. Another possible reason may be due to contamination during collection of the smoke from the reactor.

The assignment of alumina form (γ and δ) is based on XRD powder patterns and transmission electron microscopy (TEM) analysis. Both Engelhard and La Roche show broad diffuse peaks (see Fig. 1) that match those of γ-alumina based on a tetragonally distorted cubic spinel with a lattice parameter of ≈7.9 Å. The most intense peak in both aluminas is the (440) reflection at 1.39 Å, which is consistent with the JCPDS pattern for γ-alumina (card no. 29-1486). Therefore we refer to both of these aluminas as γ-aluminas. In the literature (*14*), δ-alumina is considered to be a more ordered transitional alumina, with a unit cell along the *c*-axis that is three times the spinel cell. The ordering gives rise to superlattic reflections in additions to those due to the spinel structure, but these are typically quite weak and may be missed if the signal/noise ratio is low as is typical of XRD patterns from transitional aluminas. The superlattice reflections are seen most clearly in Model alumina and TEM analysis (*10*) shows that it is composed of single crystal particles, therefore we assign it to be a δ-alumina. In AlonC

TABLE 1

Alumina Samples Used in This Study

Source	Form	Surface area (m^2/gm)	Composition
Engelhard reforming grade (batch 818)	γ	180	Na 10 ppm, $SiO_2 < 45$ ppm, Fe 150 ppm, TiO_2 470 ppm
Rhone Poulenc Spheralite 507 A	γ–δ	66	Na 430 ppm, Ca as CaO 295 ppm, Si as SiO_2 110 ppm, S as $SO_4 < 400$ ppm
La Roche A-201	γ	220	Na 3020 ppm, Fe_2O_3 0.02 wt%, and SiO_2 0.02 wt%
Degussa AlonC	γ–δ	100	Na 65 ppm, Cl 0.5 wt%
Model alumina (arc-evaporation)	δ	55	Prepared from 99.995% Al rods, Na 170 ppm
Sumitomo AKP-50	α	10	Na 39 ppm, Si 8 ppm, Mg 2 ppm, Cu > 1 ppm

Note. Compositions from manufacturers' literature (Na from AAS in our laboratory).

alumina, these superlattice reflections are seen from some regions in TEM micrographs so we assign this alumina to be a mixture of γ- and θ-alumina (*10*). Similarly, in view of the greater crystallinity and lower surface area, we have assigned RP 507A as a γ–δ-alumina. The XRD pattern of the α-alumina matches very well with that reported in the literature. Details of the structural assignments and the refinement of the delta alumina structure will be reported elsewhere (*10*).

Dehydration of 2-propanol was used as a catalytic probe reaction. Approximately 10–30 mg of the alumina was packed in a 1/4″ O.D. quartz U-tube reactor. The reactant stream consisted of 20 sccm of He bubbled through liquid 2-propanol at room temperature. The stainless steel lines in the flow reactor were heated to prevent condensation of the 2-propanol. Reaction products were propene and water with small amounts of dipropyl ether and acetone. These were analyzed in a gas chromatograph (GC) using a 6′ Porapak Q column maintained at 423 K and a thermal conductivity detector. The alumina samples were activated by heating at 773 K in flowing He overnight. The catalyst was cooled to the reaction temperature and the reactant stream was passed over the catalyst for 10 min before injecting the effluent into the GC for analysis. The He was allowed to bypass the bubbler and flow over the catalyst bed for 20 min before the next run. This ensured that reproducible activities were obtained; there was negligible deactivation between runs. The rate was expressed as moles of propene formed per second per m^2 alumina (moles/s/m^2).

The experimental procedure and equipment used for the TPR–TGA experiments was similar to that described previously (*12*). A Cahn microbalance was mounted within a high vacuum chamber whose base pressure was below 1×10^{-7} Torr. The sample weight could be continuously monitored using the microbalance, and desorption was carried out *in vacuo* so that desorbing species could be directly monitored using a Spectramass mass spectrometer. The spectrometer was interfaced with a microcomputer to allow several mass peaks to be simultaneously monitored during a TPR experiment. A thermocouple placed near the sample was used for temperature measurement, and the heating rate during desorption was maintained at 10 K/min by a feedback controller. The sample consisted

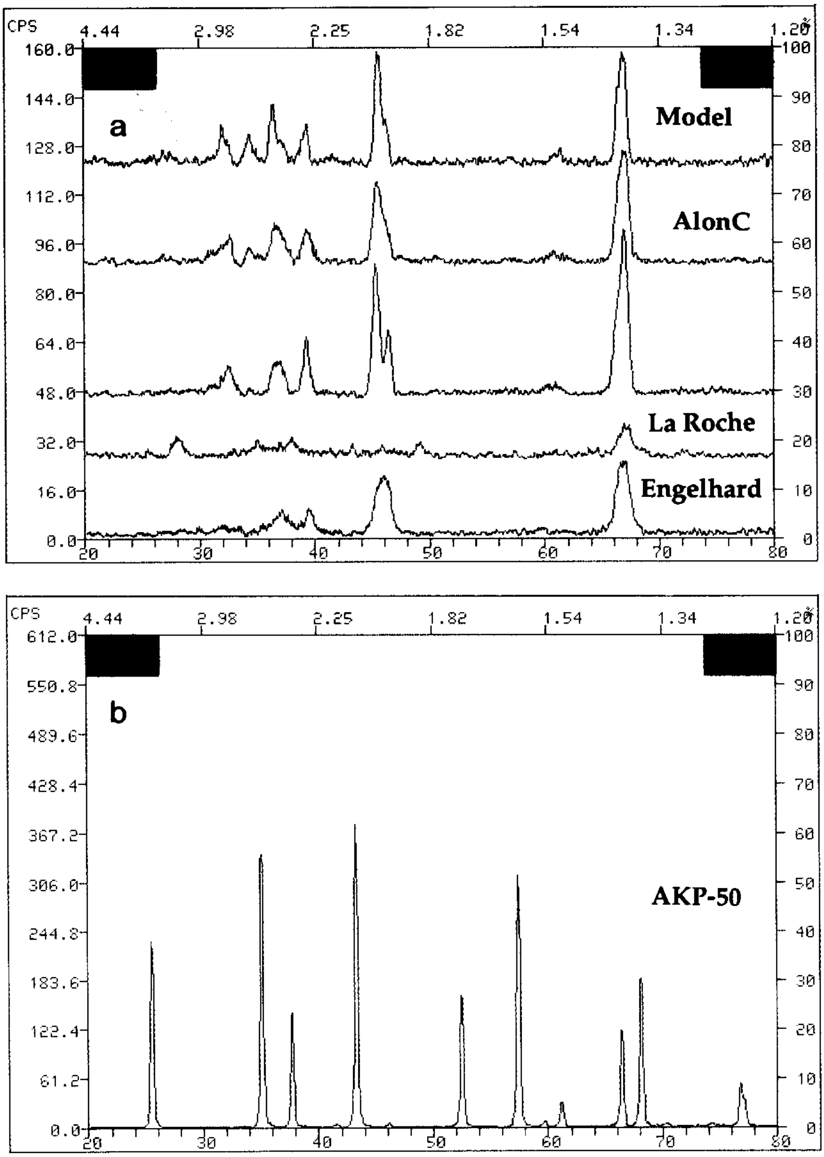

FIG. 1. (a) XRD patterns of the transitional aluminas studied. (b) XRD pattern of AKP-50 α-alumina.

of between 30–40 mg of alumina spread over a flat pan to avoid bed effects (*15*).

RESULTS

The reactivity of the alumina samples after 773 K treatment in flowing He is reported in the form of an Arrhenius plot for propene formation and total consumption of 2-propanol in Figs. 2 and 3, respectively. Reaction periods of 10 min were alternated with 20 min of flow of He over the catalyst bed at reaction temperature. No deactivation of the catalyst was observed. For some samples, an overnight calcination in 10% O_2 in He was also used but had no effect on the activity of alumina. Propene and dipropylether were the major reaction products along with water and traces of acetone. As temperature was increased past 475 K, dipropyl ether formation showed a pro-

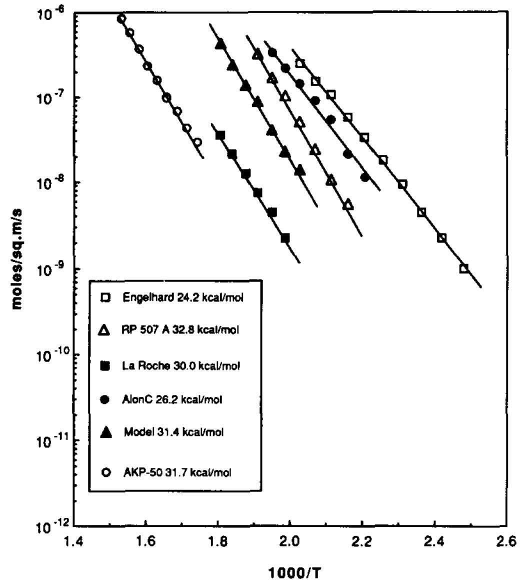

FIG. 2. Arrhenius plot for propene formation (moles/s/m^2) during 2-PrOH dehydration by different aluminas.

nounced non-Arrhenius behavior and the reaction rate decreased with increasing temperature. This is caused by the decreasing surface coverage of reactant alcohol which affects the bimolecular reaction to ether formation much more strongly than the unimolecular reaction leading to propene. Negligible amounts of dipropyl ether were detected from α-alumina, therefore the rate of propene formation in Fig. 2 is equal to that of 2-propanol consumption reported in Fig. 3. Dehydration was the favored reaction on all aluminas with the exception of Model alumina where dehydrogenation to acetone was favored. The selectivity of Model alumina did appear to change when the alumina was used on succesive days for alcohol conversion leading to a small degree of irreproducibility. Generally, the selectivity towards propene increased with time on stream, approaching the behavior of the other transitional aluminas where propene was the dominant product.

The reactivity of the various alumina samples for conversion of 2-propanol to propene, dipropyl ether and acetone is compared in Table 2. The data is reported in terms of moles 2-propanol converted per second per m^2 (moles/s/m^2) at 513 K. For α-alumina and Engelhard reforming grade γ-alumina, the data in Table 2 represent an extrapolation from the measured values at 593 and 493 K, respectively. Both the initial activity and the activity of the aged Model alumina are presented in Table 2. The amounts of ether and acetone formed for each alumina, and the total consumption of 2-propanol are also reported. The activation energies for propene formation and total consumption of 2-propanol are also presented. It can be seen from this data that the reforming grade γ-alumina is almost 1000 times more reactive than α-alumina. Among the γ-aluminas, Na poisoning appears to play a major role with alcohol dehydration activity declining from 10×10^{-7} moles/s/m^2 for Engelhard with an Na content of 10 ppm to 4.8×10^{-9} moles/s/m^2 on La Roche that contains 3020 ppm of Na. The more crystalline aluminas have reactivities com-

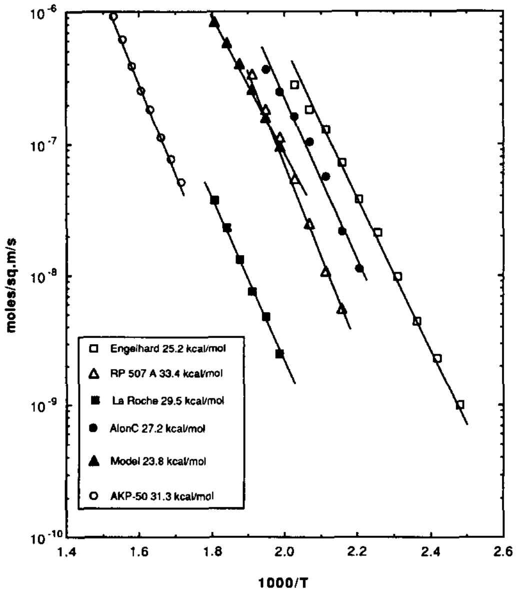

FIG. 3. Arrhenius plot for total conversion (moles/s/m^2) during 2-PrOH dehydration by different aluminas.

TABLE 2

Summary of Kinetic Parameters for 2-PrOH Dehydration

Sample	Reaction rate at 513 K (moles/s/m^2 × 10^9)				Activation energies kcal/mol (±3 kcal/mol)	
	Propanol converted to propene	Propanol converted to acetone	Propanol converted to ether	Total propanol conversion	Propene formation	Total propanol conversion
Engelhard γ-alumina	800[a]	0	50	1000	24.2	25.2
RP507A (1) γ–δ-alumina	167.5	0	15.3	182.8	32.8	33.4
RP507A (2) γ–δ-alumina	404.1	0	27.1	431.2	27.2	27.5
La Roche γ-alumina	4.4	0.4[b]	<0.1	4.8	30.0	29.5
AlonC γ–δ-alumina	336.2	0	29.1	365.3	26.2	27.2
Model[c] δ-alumina	40.4 545.8	117.1 72.1	<0.1[a]	157.5 617.9	31.4	23.8
AKP-50 α-alumina	0.8[a]	<0.1[a]	0	0.9	31.7	31.3

[a] Extrapolated from Arrhenius plots.

[b] Almost constant at all temperatures.

[c] Rate for fresh catalyst and rate after 1 day on stream.

parable to each other when consumption of 2-propanol is considered: 1.57×10^{-7} moles/s/m^2 for Model alumina, 1.82×10^{-7} moles/s/m^2 for RP507A and 3.65×10^{-7} moles/s/m^2 for AlonC. In contrast, the value for Engelhard γ-alumina is 10×10^{-7} moles/s/m^2.

This shows that γ-alumina is between three and five times more reactive than the more crystalline transitional aluminas. However, the lower initial propene selectivity of Model δ-alumina makes it about 20 times less reactive than Engelhard γ-alumina when reactivity for propene formation is considered. The formation of acetone was favored over propene on fresh Model alumina, but with increasing time on stream the selectivity approached that of the other transitional aluminas. The activity of the aged Model alumina sample is also reported in Table 2. Ether formation is seen to be a minor product on all of the aluminas, since it is a bimolecular reaction favored at lower temperatures where surface coverage of the reactants is greatest. On AKP-50 α-alumina, since the reaction was carried out at elevated temperatures, no dipropyl ether was detected, and only traces of acetone was found. As seen from Table 2, the activation energies for both propene formation and total consumption of 2-propanol range from 24–27 kcal/mol for the γ-aluminas to about 31 kcal/mol for the higher temperature polymorphs. Two sets of values are quoted for Rhone Poulenc: the activation energy was ≈27 kcal/mol on most aliquots but one of the aliquots gave a value of 32.8 kcal/mol. In the case of Model alumina there is a large difference of about 7 kcal/mol between the activation energy for propene formation and that for consumption of 2-propanol due to the lower activation energy for acetone formation, the major product on the fresh Model alumina. In all these measurements, the error in activation energy is estimated to be about ±2–3 kcal/mol.

The order of reaction was determined by studying the variation in reactivity with in-

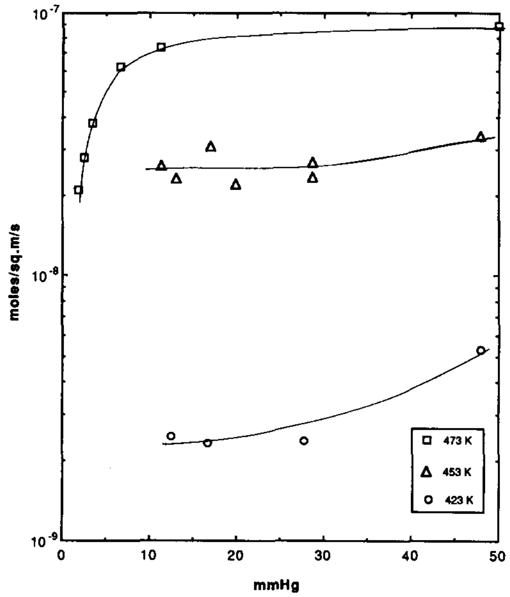

FIG. 4. Plot of propene formed (moles/s/m^2) during 2-PrOH dehydration by Engelhard alumina vs partial pressure of 2-PrOH in the gas phase at different temperatures.

creasing partial pressure of 2-propanol. Figure 4 shows a plot of propene formed as a function of 2-propanol partial pressure at three different temperatures. We have shown the data for Engelhard γ-alumina, which is the most reactive amongst the aluminas studied. While there is negligible change in reactivity with pressure at 423 and 453 K, the reactivity is more sensitive to partial pressures at 473 K, with a sharp fall off as pressure is lowered below 10 Torr. Reactivity data at pressures lower than 10 Torr for the 423- and 453-K cases showed a lot of scatter and have not been presented here. But in the normal operating regime of 45–50 Torr (vapor pressure of 2-propanol at room temperature), it is seen that the reaction is essentially zero order with respect to 2-propanol concentration.

The steady state flow reactor measurements provide information on the reactivity per unit surface area, but the number of active sites cannot be inferred from this data. For this purpose, we studied the dehydration of alcohols in a single turnover experiment. The alumina was pretreated in vacuum at 773 K for 2 hr and the sample weight recorded before the sample was exposed to $\approx$10 Torr of 2-propanol at room temperature. When the weight of the sample reached a steady value, the alcohol was evacuated and the sample weight recorded. The increase in weight after room temperature adsorption at 10 Torr and subsequent evacuation provides information on the number of alcohol molecules adsorbed/m^2. This weight change could also include physisorbed alcohol molecules as well as any water that adsorbs during the cooling of the alumina sample before alcohol is introduced into the system. Therefore this number is not considered a reliable indicator of the number of reactive molecules on the surface. To determine the number of reactive molecules, the sample temperature was linearly ramped at 10 K/min and the products detected with a mass spectrometer. Figures 5–10 show results from these experiments. In each of these figures, the mass of the sample is plotted in (a) and the mass spectrometer signal in (b), both as a function of temperature. The weight change that occurs when the product molecules desorb corresponds to the molecules of alcohol that react to form propene and water. Under the conditions of this experiment, no ether was detected. Based on data such as that reported in Figs. 5–10, the number of reactive molecules per unit surface area can be determined. These results are summarized in Table 3. The results in Table 3 show that all aluminas have between 1 and 2 $\times$ 10^{18} reactive alcohol molecules/m^2. When a similar experiment was performed with a silica sample, all of the 2-propanol desorbed without reacting to form propene. The peak desorption temperature for 2-propanol ranges from 440–600 K and correlates inversely with the reactivity of the alumina during steady state flow reactor experiments.

Using the activation energies obtained from kinetic measurements and the TPR peak temperatures, a pre-exponential factor

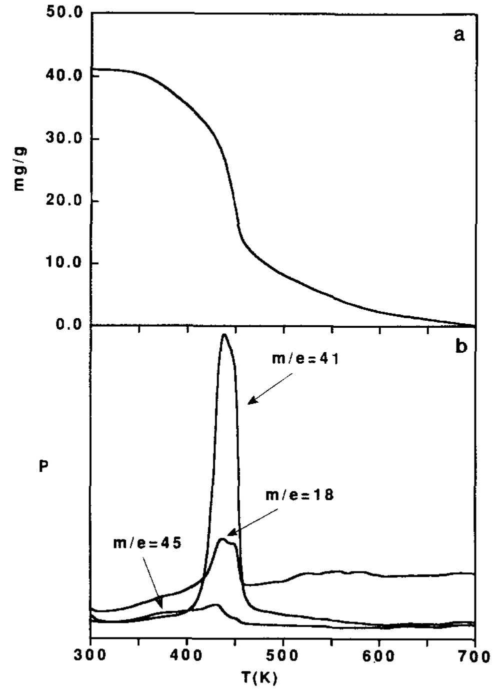

FIG. 5. TPR of 2-PrOH from Englehard (γ) alumina: (a) weight change per g catalyst as a function of temperature and (b) mass spectrometer signal as a function of temperature.

A for the surface reaction can be derived. Equation (1) is based on the method of analysis proposed by Redhead (*16*):

$$A = \frac{\beta E_a}{R (T_p)^2} \exp\left(\frac{E_a}{R T_p}\right). \tag{1}$$

In this equation, E_a is the activation energy, β is the heating rate, T_p is the peak desorption temperature, and R is the gas constant. Alternatively, the pre-exponential factor can be calculated directly from the kinetic data which was presented in the form of an Arrhenius plot in Fig. 2. The assumption made here is that the surface concentration of 2-propanol is $\approx 1 \times 10^{18}$ molecules/m^2 on all aluminas and this number is invariant with temperature. The pre-exponential factor obtained using these alternate approaches is presented in Table 4. Two sets of numbers are reported for RP507A based on kinetic analysis. These correspond to the two aliquots that gave widely differing activation energies (see Table 2). The calculated pre-exponential factor for RP507A based on Redhead's analysis was based on E_a of 27.2 kcal/mol which was the activation energy for most aliquots of this sample. In the case of Model alumina, the TPR spectra exhibited a broad band for propene formation with a shoulder at 510 K. This suggests that there are two kinds of sites present on the surface of Model alumina. There is close agreement between the pre-exponential factor obtained kinetically and the same calculated by Redhead's analysis using a T_p of 510 K (Table 4). This leads us to believe that the sites with a T_p of 510 K are the ones responsible for the steady state reactivity of Model alumina. For most of the aluminas, the pre-exponential factors are of the order of 10^{10} s^{-1}, which is consistent with a unimolecular decomposition reaction based on

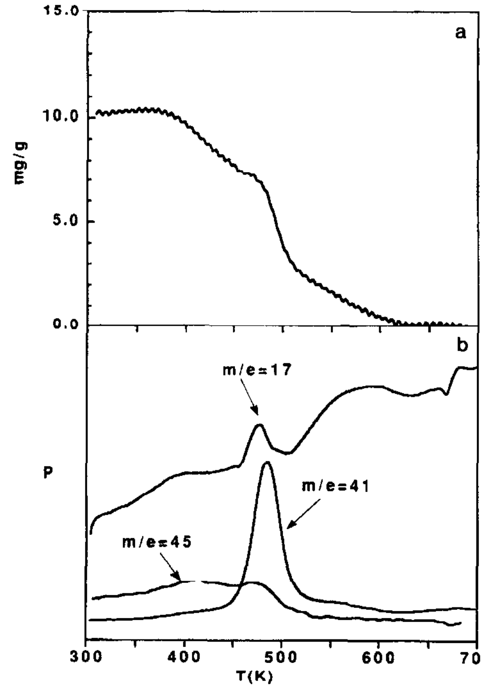

FIG. 6. TPR of 2-PrOH from RP507A (γ–δ) alumina: (a) weight change per g catalyst as a function of temperature and (b) mass spectrometer signal as a function of temperature.

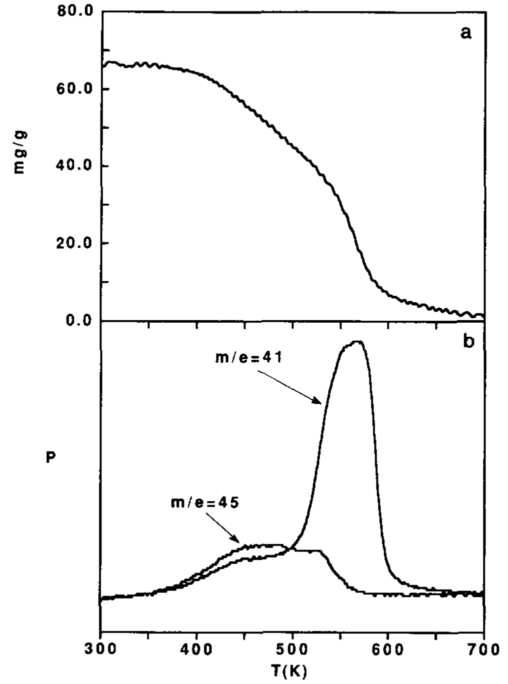

FIG. 7. TPR of 2-PrOH from La Roche (γ) alumina: (a) weight change per g catalyst as a function of temperature and (b) mass spectrometer signal as a function of temperature.

transition state theory. The pre-exponential factor calculated from the kinetic data appears to increase when the activation energy increases. This suggests a possible compensation effect which can be verified by plotting log (A) vs E_a, as shown in Fig. 11. The data for all of the aluminas (including the two aliquots of RP507A), with the exception of the two least reactive ones, appear to fall very nicely on a straight line.

From the kinetic data for 2-propanol dehydration, and assuming that there are approximately 1×10^{18} sites/m^2, we can derive an experimental value for the turnover frequency (TOF). We can also calculate the TOF using

$$\mathrm{TOF} = A \exp\left(-\frac{E_a}{RT_p}\right), \tag{2}$$

since we know the pre-exponential factor (col. 5, Table 4) and the activation energy for propene formation. It is assumed here that the surface reaction leading to formation of water and propene from adsorbed 2-propanol represents the rate-limiting step. The assumption is justified since the reaction is effectively zero order in 2-propanol gas phase concentration under the experimental conditions implying that the surface is covered with alcohol. The calculated and the measured TOFs are listed in Table 5. The data are reported at the peak desorption temperature for 2-propanol which ranges from 440–600 K over the alcohols studied. We would expect that the TOF calculated by Redhead's analysis at T_p would be rather insensitive to E_a, and this is borne out in column 4 of Table 5. We find that the experimental TOFs are quite comparable to the calculated values with significant discrepancies only in the case of Model alumina and AKP-50 α-alumina.

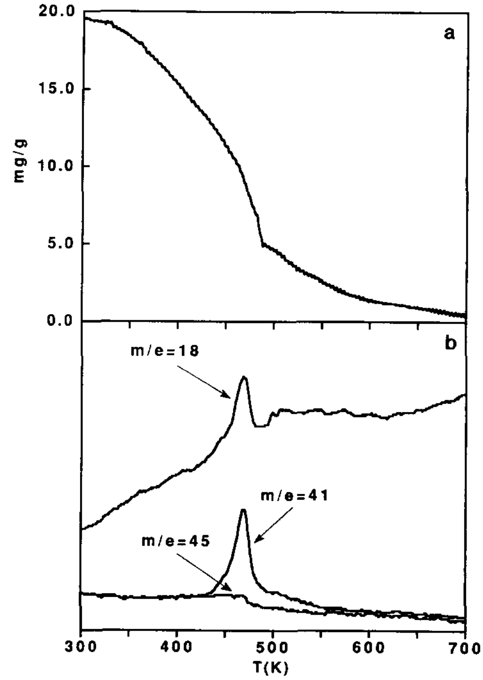

FIG. 8. TPR of 2-PrOH from AlonC (γ–δ) alumina: (a) weight change per g catalyst as a function of temperature and (b) mass spectrometer signal as a function of temperature.

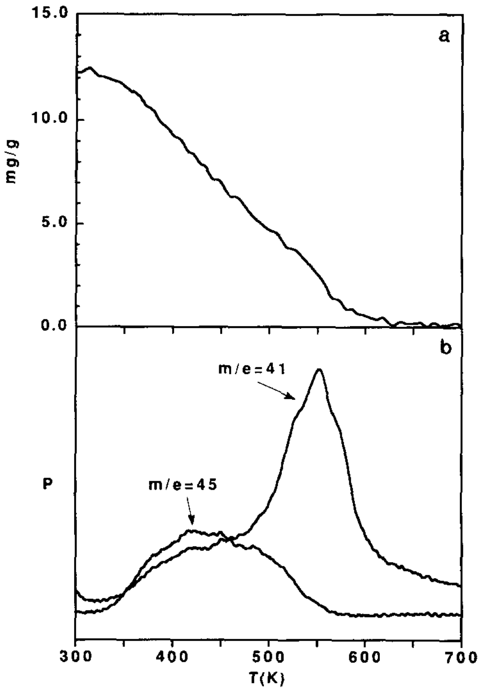

FIG. 9. TPR of 2-PrOH from Model (δ) alumina: (a) weight change per g catalyst as a function of temperature and (b) mass spectrometer signal as a function of temperature.

DISCUSSION

The steady-state flow reactor measurements of alcohol dehydration activity confirm the findings of Pines and Haag (*4*) that Na contamination plays a major role in influencing the reactivity of γ-alumina. In our experiments, the Na was not introduced by impregnation but was present in the sample as a consequence of the commercial preparation procedure. Our results show that Na poisoned γ-alumina is only 0.005 times as reactive as reforming grade γ-alumina, while the crystalline transitional alumina (δ) is approximately 0.2–0.33 times as reactive. This difference between γ and δ is comparable to that observed previously by MacIver *et al.* (*5*) between η- and γ-alumina, both of which are considered to be reactive aluminas. The reactivity of θ-alumina was also previously reported to be almost 20 times lower than that of γ-alumina (*4*). These results would then suggest that Model δ-alumina should be considered to be closer to γ-alumina than the other higher temperature polymorphs such as θ- or α-alumina. We have also shown previously that the hydroxyl bands on the δ-alumina are comparable to those on γ-alumina (*17*). The X-ray diffraction powder pattern of δ-alumina shows that the strong spinel reflections in γ-alumina are preserved in δ-alumina, and solid state NMR spectra show that the fraction of tetrahedral aluminum in Model δ-alumina is actually greater than that in γ-alumina (*17*). This is in contrast to the structure of θ-alumina where the lattice has transformed completely from the cubic spinel-related lattice of γ- and δ-alumina into a monoclinic lattice.

When the Arrhenius plots for alcohol dehydration are examined, we find that increase in activation energy is accompanied

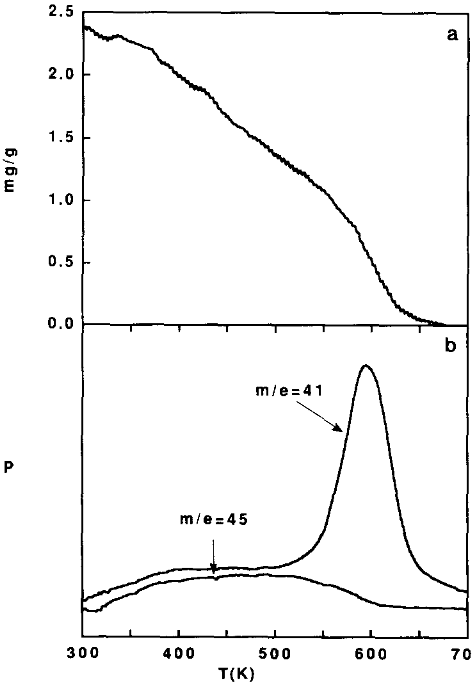

FIG. 10. TPR of 2-PrOH from AKP-50 (α) alumina: (a) weight change per g catalyst as a function of temperature and (b) mass spectrometer signal as a function of temperature.

TABLE 3

Summary of TPR Results for 2-PrOH Dehydration

Sample	Molecules adsorbed[a] ($\times 10^{18}/m^2$)	Molecules Reacted[b] ($\times 10^{18}/m^2$)	Propene desorption temp. T_p (K)
Engelhard (γ-alumina)	2.3	1.9	440
RP507A (γ–δ-alumina)	1.2	1.0	490
La Roche (γ-alumina)	3.7	2.0	560
AlonC (γ–δ-alumina)	1.7	1.0	468
Model alumina (δ-alumina)	2.2	1.3	552[c]
AKP-50 (α-alumina)	2.4	1.2	600

[a] Determined using alcohol molecules remaining after evacuation.
[b] Determined using weight loss during propene formation.
[c] Broad peak.

by an increase in pre-exponential factor. For most of the aluminas, there seems to be a linear relationship between log (A) and E_a suggesting these aluminas exhibit a simple compensation effect. The two aliquots of RP507A alumina also fall nicely on the compensation plot. Bond *et al.* (*18*) have suggested that any family of catalysts exhibiting a simple compensation effect must have active centers which are similar in their geometric and electronic properties. The exceptions are La Roche γ-alumina and AKP-50 α-alumina. It should be pointed out that these are also the least reactive among the aluminas studied here. La Roche γ-alumina is inactive due to the presence of 3020 ppm

TABLE 4

Comparison of Pre-exponential Factors

Sample	Activation energy for propene formation	Propene desorption temperature (T_p)	Pre-exponential (from kinetic analysis)	Pre-exponential (from Redhead analysis)
	(kcal/mol)	(K)	1/s (10^{10})	1/s (10^{10})
Engelhard	24.2	440	0.94	1.1
RP507A	32.8	490	1000	1.2[a]
	27.2		9.1	
La Roche	30.0	560	1.6	0.43
AlonC	26.2	468	3.5	1.7
Model	31.4	510[b]	64	29
AKP-50	31.7	600	1.9	0.26

[a] Pre-exponential factor calculated using E_a = 27.2 kcal/mole and T_p = 490 K.
[b] Pre-exponential factors calculated at 510 K.

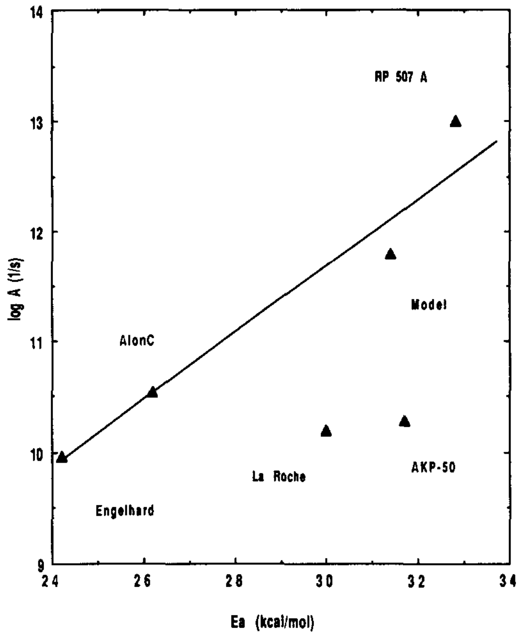

FIG. 11. Compensation plot for pre-exponential factor A vs activation energy E_a for propene formation during 2-PrOH dehydration by different aluminas.

of Na and AKP-50 is unreactive because it is an α-alumina, having a very different structure from the other transitional aluminas. While the oxygen atoms are nearly close packed in all of the aluminas, in α-alumina they resemble hexagonal close packing (repeat of ababa . .), whereas γ and δ have cubic closed packing (repeat of abcabc . .). The coordination of the aluminums is also fundamentally different with all Al^{+3} being located in octahedral sites in α-alumina, but Al^{+3} are located in tetrahedral as well as octahedral sites in the transitional aluminas.

While the flow reactor measurements do show that α-alumina and Na-poisoned γ-alumina are the least reactive samples, it is not clear whether the difference is caused by a smaller number of active sites, or by sites that are uniformly less active. To investigate this aspect further, we studied temperature programmed reaction of 2-propanol. The results from the TPR of 2-propanol show the alcohol is irreversibly adsorbed at room temperature. The number of alcohol molecules adsorbed ranges from 1.7–3.7 × 10^{18} molecules/m^2. These numbers are comparable to those observed previously on other oxides. For instance Kim *et al.* (*19*) reported that ≈2.5 × 10^{18} molecules of 2-propanol were irreversibly adsorbed per m^2 on titania, while Bowker *et al.* (*20*) on ZnO found 2.2 × 10^{18} molecules irreversibly adsorbed per m^2. When the sample is heated, some of the adsorbed alcohol desorbs unreacted at lower temperatures (<400 K) along with some water that may have adsorbed on the sample after its thermal pretreatment. At higher temperatures, one sees very little de-

TABLE 5

Turnover Frequency Calculations

Sample	Activation energy for propene formation	Propene desorption temperature (T_p)	Turnover frequency at T_p by Redhead's analysis	Observed turnover frequency at T_p
	(kcal/mol)	(K)	(1/s)	(1/s)
Engelhard	24.2	440	0.0105	0.0057
RP507A	32.8	490	0.0114	0.0240
La Roche	30.0	560	0.0080	0.0135
AlonC	26.2	468	0.0100	0.0360
Model	31.4	510	0.0099	0.0240
AKP-50	31.7	600	0.0073	0.0451

sorption of the parent alcohol. The number of product molecules desorbing in this temperature range would then correspond to the number of reactive alcohol molecules on the surface. Bowker *et al.* have reported this number to be 1.4×10^{18} molecules/m^2 and the reaction products included propene and acetone. However, in our study, propene was the only reaction product detected. The number of reactive alcohol molecules on the alumina surface as reported in Table 3 are consistent with previous estimates: notably 1×10^{18}/m^2 postulated by Pines and Haag (*4*) as the upper limit for the number of reactive sites. However, it is indeed surprising to find that α-alumina which is 0.001 times as reactive as reforming grade γ-alumina (see Table 2), has only 50% less reactive alcohol molecules/m^2 as measured by TPR. Also, Na poisoned γ-alumina, which is only 0.005 times as reactive as reforming grade γ-alumina, has almost the same number of reactive alcohol molecules/m^2 during the single turnover experiment.

On La Roche γ-alumina, the amount of Na (3020 ppm) would correspond to 3.59×10^{17} atoms of Na/m^2, assuming all of the Na was present on the surface of the alumina. If one assumes that alumina possesses 1×10^{18} sites/m^2 reactive for alcohol dehydration, only 36% of these sites would be poisoned by Na. Since the reactivity of the La Roche γ-alumina at 473 K is only 0.005 times that of Engelhard γ-alumina, it would appear that one atom of Na poisons more than three surface sites on the alumina surface. It is difficult to visualize how this may occur and one must consider alternate explanations for the data reported here.

The first question that arises is whether the number of reactive alcohol molecules measured by TPR corresponds to the number of active sites that catalyze the reaction during the steady-state flow reactor experiments. The calculated and measured turnover frequencies (Table 4) are in good agreement for all the aluminas, the differences being within experimental error. This would suggest that all the sites measured by TPR (1×10^{18}/m^2) are uniformly active and the change in the peak desorption temperature for the various aluminas is due to the differences in activation energy of these sites. This would be consistent with the observed variation in peak desorption temperature as one goes from the more reactive to the less reactive aluminas. The only exception is Model alumina, where the desorption peak for propene is rather broad, suggesting a distribution of active sites. However, the model presented above (that of uniformly active sites) is at odds with the observation that in Na-poisoned aluminas, 0.36 atoms of Na per surface site are sufficient to reduce steady-state reactivity by 200 times.

Another scenario could be considered here. The adsorbed alcohol molecule could be very strongly bound to surface sites that are present on all aluminas. The concentration of between 1 and 2×10^{18}/m^2 would almost correspond to a monolayer of alcohol molecules on the surface. However, for the reaction to take place, the presence of some defect sites may be required, and it is possible the products can desorb only from these sites. Such a model is depicted below where the molecule S has to first transform to S* which represents the molecule adsorbed on the reactive or defect site. Such an assumption would be similar to the case of desorption occurring with a precursor state as treated previously by Gorte and Schmidt (*21*):

$$S \overset{K}{\rightleftharpoons} S^* \xrightarrow{k_2} \text{product}. \qquad (3)$$

We can assume that the adsorbed molecule S and the precursor state S* are in fast equilibrium. The rate limiting step is the surface reaction step having rate constant k_2. The number of such defect sites could differ markedly on the aluminas studied and could also could account for the differences in their steady-state reactivity. From the TPR data, we obtain an estimate of the number of adsorption sites (1×10^{18}/m^2, which may

TABLE 6

Pre-exponential Factors Calculated Assuming an Activation Energy of 24.2 kcal/mol

Sample	Propene desorption temperature (T_p) (K)	Pre-exponential factor (1/s (10^{10}))
Engelhard	440	1.1000
RP507A	490	0.0520
La Roche	560	0.0018
AlonC	468	0.1857
Model	510	0.0183
AKP-50	600	0.0003

indeed be constant on all aluminas including α-alumina. This model also could explain the observed differences in activation energies since the apparent activation energy for steady-state reaction would be (ΔH + E_a), where ΔH is the heat effect for the step S→S*. The observed activation energy depends on both the energy barrier for reaction which may be assumed to be 24 kcal/mole and the barrier for adsorption onto a defect site from the initial adsorbed state (which could be 3–7 kcal/mole). The differences in ΔH, which depends on the structure of the alumina and the heat of adsorption of the alcohol, could account for the observed variation in activation energy. If we assume that the activation energy of reaction for the most reactive alumina to represent the true value of the barrier between the precursor state and the desorbed gas phase product molecule, a different set of pre-exponential factors can be calculated for all of the aluminas. The results are shown in Table 6. It can be clearly seen that the pre-exponential factor for Engelhard γ-alumina is still reasonable ($\approx 1.1 \times 10^{10}$ s^{-1}), while those for other aluminas are much smaller (ranging from 0.18–0.0003 × 10^{10} s^{-1}). During the TPR experiment, if we assume a fast exchange between S and S*, the process we observed will be that of S* going to products. Since the concentration of S* on the surface will directly appear in the pre-exponential factor, we would expect a smooth variation in peak desorption temperature (but no change in the number of reactive alcohol molecules/m^2) as we go from the more reactive to the less reactive aluminas. We therefore feel that this model adequately accounts for the shift in the peak desorption temperatures observed in the TPR experiments. More work is underway to explain the nature of these defect sites and the effect of Na doping in these aluminas.

CONCLUSIONS

We have studied the role of structure and impurities on the activity of alumina for 2-propanol dehydration. We find that transitional aluminas such as γ and δ differ in reactivity by less than a factor of 3–5 when normalized to surface area, however, α-alumina is 1000 times less active than reforming grade γ-alumina. Na poisoning appears to play a major role in affecting the reactivity of γ-alumina. In the samples studied here, Na was present in the precursors used to prepare the alumina and did not affect the number of alcohol molecules that reacted per m^2 of alumina surface in a single turnover experiment. All aluminas (including α-alumina) possess $\approx 1 \times 10^{18}$ sites/m^2 capable of adsorbing 2-propanol. In a temperature-programmed reaction experiment, these alcohol molecules transform to propene, but the reaction temperature varies from 440 K on the most reactive alumina to 600 K on the least reactive α-alumina. All of the transitional aluminas (except the Na-poisoned γ) fall nicely on a simple compensation plot, suggesting they have similar sites in terms of electronic or geometric structure. We interpret our TPR data in terms of a model where there are 1×10^{18} sites/m^2 on all aluminas but only a few defect sites that catalyze the conversion of the alcohol. The less reactive aluminas have fewer defect sites and therefore exhibit a higher T_p during TPR of 2-propanol and lower steady-state reactivity during 2-propanol dehydration.

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