

## H-D Exchange between Benzene and the OH Groups of Alumina

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H-D exchange of benzene with the OH groups of aluminas was investigated using FTIR spectroscopy. The reactions benzene- $d_6$ -alumina and benzene-alumina- $d$  are of first order with respect to OH and benzene concentrations ( $E_A = 112$  kJ/mol). They mainly take place on centers—probably Lewis acid-base pairs—which are poisoned by  $\text{CO}_2$  adsorbed as carbonate.

## 1. INTRODUCTION

Different exchange reactions on alumina were investigated because of the great importance of aluminas as catalysts. Van Cauwelaert and Hall (1) investigated the exchange between  $\text{H}_2$  and  $\text{D}_2$  over alumina, and observed that but a small part of the surface is catalytically active. Exchange reactions between deuterium and alkenes (2-7) and aromatics (8, 9) take place at room temperature already. Larson *et al.* (7) proposed to use this reaction to prepare perdeuterated alkenes.

Saunders and Hightower (8) observed reactions in the following systems with alumina as a catalyst:  $\text{C}_6\text{H}_6$ - $\text{D}_2$ ,  $\text{C}_6\text{D}_6$ - $\text{H}_2$ ,  $\text{C}_6\text{H}_6$ - $\text{C}_6\text{D}_6$ . The last reaction takes place with about a 10- to 20-fold greater velocity than those of the first two reactions. According to McCosh and Kemball (10), the exchange of  $\text{D}_2$  with aromatic hydrogen is faster than that with aliphatic hydrogen.

Yates and Lucchesi (11, 12) using ethylene and Carter *et al.* (13) using  $\text{D}_2$ , observed that the exchange of OH groups of  $\gamma$ -alumina with a band at  $3585\text{ cm}^{-1}$  is faster than that of the other bands. The same effect—higher reactivity of the OH groups absorbing at the highest wavenumbers—was found by Larson and Hall (14) and Dunken and Fink (15) on  $\gamma\text{-Al}_2\text{O}_3$  too. These observations are in contrast to the results of Peri and Hannan (16), who claim

to have found a higher activity of the OH groups absorbing at the longest wavelengths.

## 2. EXPERIMENTAL

A FTIR spectrometer (Digilab FTS-14) equipped with a globar and a MTC detector was used for the measurements together with a high-temperature measuring cell (17). The oxide samples could be heated to 1000 K in the pretreatment zone; the measuring temperatures could be up to 650 K. Highly purified helium was used as a carrier gas, a part of which was loaded with benzene or benzene- $d_6$  in separate saturators as in former investigations (18, 19). The oxides used are compiled in Table 1. The specific surfaces were determined using the method of Haul and Dümbgen (20).

## 3. RESULTS AND DISCUSSION

## 3.1. Reactions on Pure Oxides

Figure 1 shows the OH and OD bands for increasing degree of deuteration. Evidently there is no difference in the exchange velocities of different OH bands under these conditions ( $T = 621$  K;  $p_{\text{C}_6\text{D}_6} = 48$  mm Hg). The reaction is of first order as is the opposite exchange reaction (benzene- $\text{Al}_2\text{O}_3$ - $d$ ) (Fig. 2), which is considerably faster than the former. The kinetic isotope effect is about 0.7. From Fig. 3, showing the dependence of the velocity constant for the first-order reaction ( $k'$ ) on the benzene

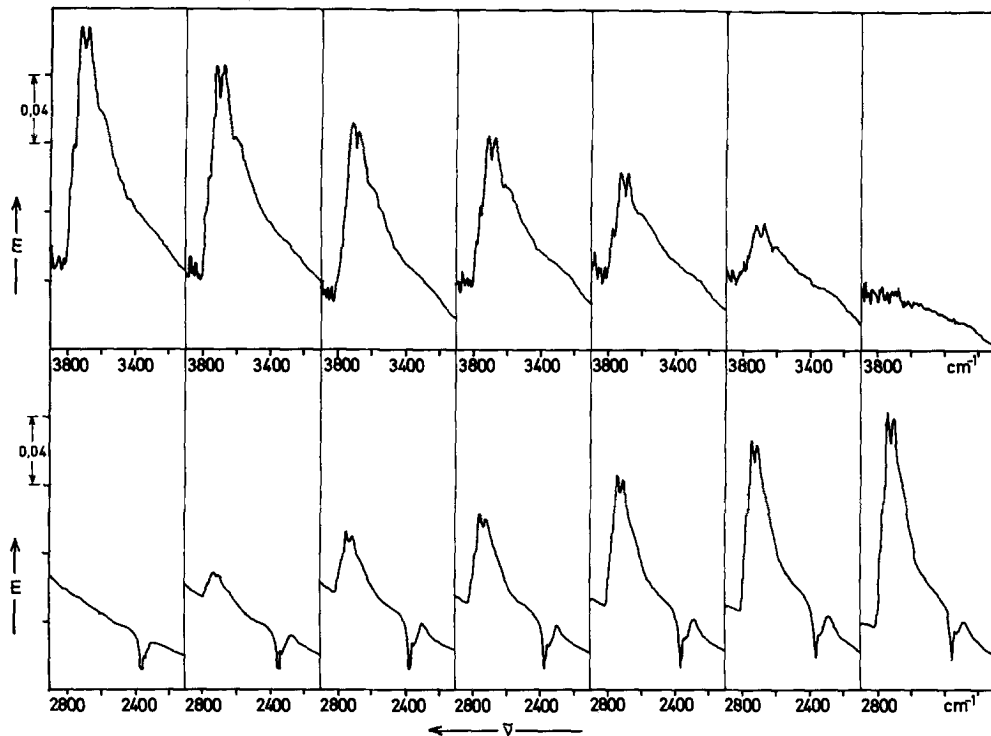


FIG. 1. Changes in ir spectra of  $\gamma$ - $\text{Al}_2\text{O}_3$  (Type C) during H-D exchange with benzene- $d_6$ . ( $\theta = 348^\circ\text{C}$ ,  $p_{\text{C}_6\text{D}_6} = 45$  mm Hg.)

partial pressure, it follows that the reaction is also of first order with respect to the benzene partial pressure. Thus the exchange may be described by

$$\frac{dE_{\text{OD}}}{dt} = -kE_{\text{OD}}p_{\text{C}_6\text{H}_6}$$

Figure 4 shows an Arrhenius plot, leading to an activation energy of 112 kJ/mol. All

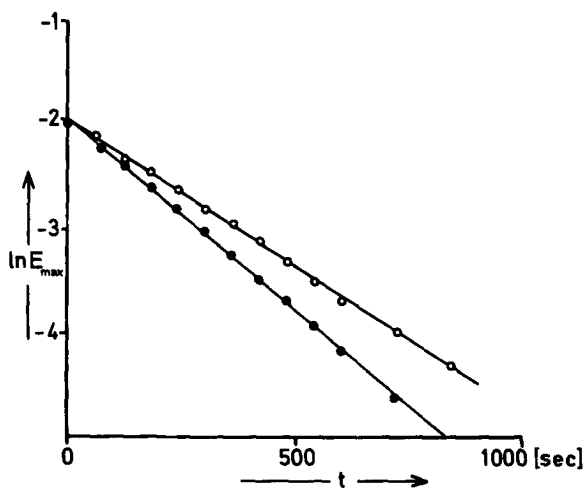


FIG. 2. Kinetics of H-D exchange. ( $\theta = 348^\circ\text{C}$ ;  $p_{\text{Hydrocarbon}} = 45$  mm Hg.) (●) Benzene- $\text{Al}_2\text{O}_3$ - $d$ ; (○) benzene- $d_6$ - $\text{Al}_2\text{O}_3$ .

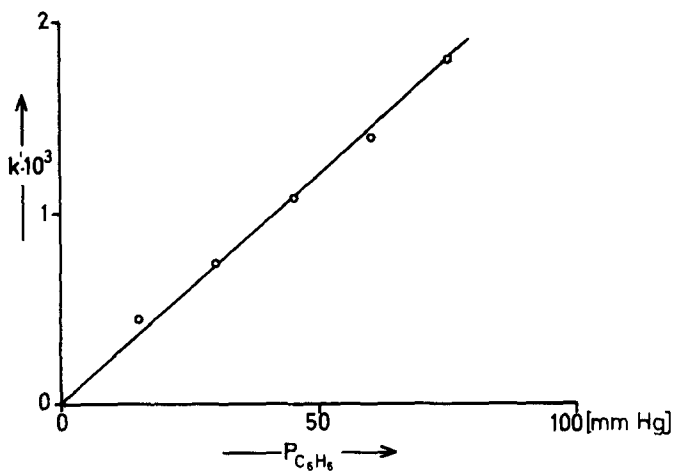


FIG. 3. Dependence of velocity constant on benzene partial pressure ( $\theta = 300^\circ C$ ).

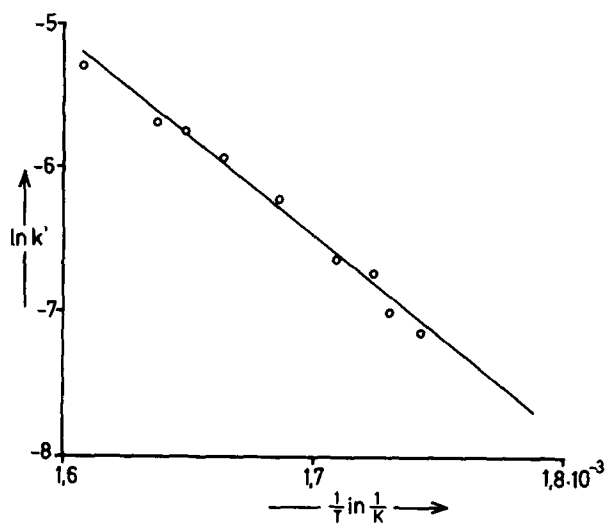


FIG. 4. Arrhenius plot for reaction of benzene with  $Al_2O_3-d$  ( $p_{C_6H_6} = 75$  mm Hg).

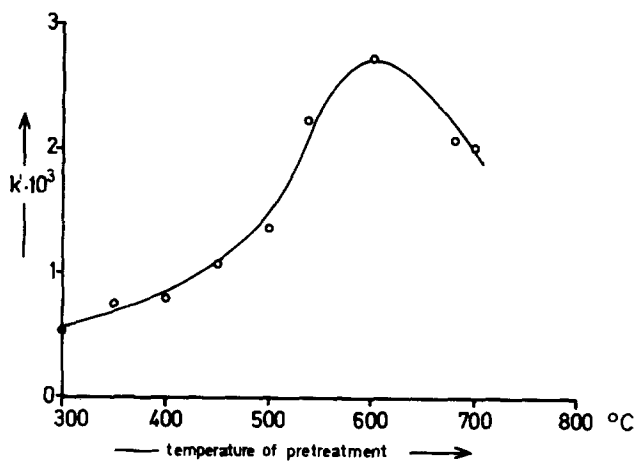


FIG. 5. Dependence of velocity constant on temperature of pretreatment ( $\theta = 310^\circ C$ ,  $p_{C_6H_6} = 75$  mm Hg).

TABLE 1

Oxides Used in These Investigations		
Oxide	Source	Spec. surf. (m <sup>2</sup> /g)
1. $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Degussa Type C	99.3
2. $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Merck	79.4
3. $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Prepared from Bomite	250.9
4. $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Prepared from Al(NO <sub>3</sub> ) <sub>3</sub>	151.6
5. $\eta$ -Al <sub>2</sub> O <sub>3</sub>	Prepared from Bayerite	316.6

these experiments were made with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Type C, preheated at 803 K (530°C). The reactivity of the oxide strongly depends on the pretreatment temperature. The activity increases up to about 600°C, Fig. 5. This is in good agreement with investigations (21) about the reactivity for alkene isomerization and cyclization, which show that reactive centers are formed during preparation of the oxide (calcination). The centers are poisoned by adsorbed water, which may be removed by heating as seen in Fig. 5. Calcination or preheating at above 600°C diminishes the number of centers probably by the annealing of defects.

A greater number of experiments with a constant benzene or benzene-*d*<sub>6</sub> partial pressure of 75 mm Hg were made at different measuring temperatures with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Type C, and  $\eta$ -Al<sub>2</sub>O<sub>3</sub>. The degree of dehydration was varied during these measurements by changing the pretreatment

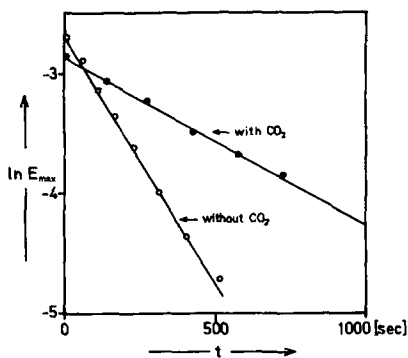


FIG. 6. Influence of poisoning with CO<sub>2</sub> (benzene-*d*<sub>6</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:  $\theta = 330^\circ\text{C}$ ,  $p_{\text{C}_6\text{D}_6} = 75$  mm Hg,  $p_{\text{CO}_2} = 9.5$  mm Hg).

TABLE 2

Constants for the Arrhenius Equation of $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (Type C) and $\eta$ -Al <sub>2</sub> O <sub>3</sub>		
Const.	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\eta$ -Al <sub>2</sub> O <sub>3</sub>
<i>a</i>	$7.77 \cdot 10^6$	$1.66 \cdot 10^7$
<i>b</i>	$-3.28 \cdot 10^9$	$-9.81 \cdot 10^{10}$
<i>c</i>	$4.36 \cdot 10^{13}$	$1.80 \cdot 10^{14}$
<i>d</i>	0.827	0.793
<i>e</i>	$-1.00 \cdot 10^2$	-3.07
<i>f</i>	$9.31 \cdot 10^4$	$8.79 \cdot 10^4$
<i>g</i>	$2.20 \cdot 10^7$	$3.59 \cdot 10^7$

temperature. The integral absorbance of a formal single Al<sub>2</sub>O<sub>3</sub> surface after complete deuteration

$$E'_{\text{OD}} = 10^{-4}(E_{\text{OD}} F_p / m_p F_s),$$

$E_{\text{OD}}$  : integral absorbance of OD bands,

$F_p$  : area of the wafer (3.80 cm<sup>2</sup>),

$m_p$  : weight of the wafer (g),

$F_s$  : specific surface of oxide (m<sup>2</sup>/g),

was used to characterize the degree of

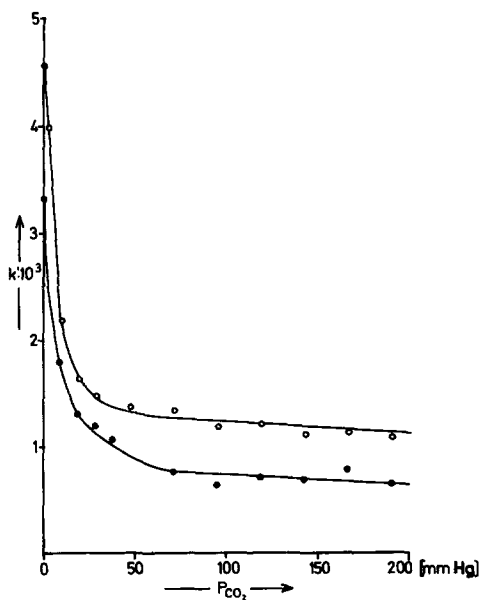


FIG. 7. Reactivity and CO<sub>2</sub> partial pressure ( $\theta = 330^\circ\text{C}$ ,  $p_{\text{Hydrocarbon}} = 75$  mm Hg). (○) Benzene-Al<sub>2</sub>O<sub>3</sub>-*d*; (●) benzene-*d*<sub>6</sub>-Al<sub>2</sub>O<sub>3</sub>.

hydratization. Assuming a linear (or quadratic) dependence of the constants of the Arrhenius equation on  $E'_{OD}$  one gets

$$k' = k'_0 \cdot f_i \cdot e^{-E_A/RT},$$

with

$$\begin{aligned} k'_0 &= a + b \cdot E_{OD} + cE_{OD}^2, \\ f_i &= d + e \cdot E_{OD} \quad (\text{isotopic factor}), \\ E_A &= f + g \cdot E_{OD}. \end{aligned}$$

The constants  $a-g$  were determined using the optimization method of Nelder and Mead (22). The results are given in Table 2. According to these measurements both the number of centers ( $k'_0$ ) and the activation energy ( $E_A$ ) depend on the degree of hydratization in a way to be expected for centers with a distribution of energy:  $k_0$  decreases and  $E_A$  increases with  $E'_{OD}$  (varying from  $2.8$  to  $10 \cdot 10^{-4} \text{ cm}^{-1}$ ). The higher reactivity of  $\eta\text{-Al}_2\text{O}_3$  is mainly caused by the greater number of centers.

The velocity constants for different oxides under the same conditions are given in Table 3. Within the limits of error there are no differences between  $\gamma$ -aluminas pre-

TABLE 3

Velocity Constants of the H-D Exchange between Benzene, Benzene- $d$ , and OD or OH Groups of Different Aluminas<sup>a</sup>

Oxide	Velocity constants (sec <sup>-1</sup> )	
	Al <sub>2</sub> O <sub>3</sub> - $h$ -benzene- $d_6$	Al <sub>2</sub> O <sub>3</sub> - $d$ -benzene
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> , Type C (Degussa)	$1.59 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (Merck)	$1.53 \cdot 10^{-3}$	$2.10 \cdot 10^{-3}$
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (from Bomite)	$1.69 \cdot 10^{-3}$	$2.42 \cdot 10^{-3}$
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (from Al(NO <sub>3</sub> ) <sub>3</sub> )	$1.48 \cdot 10^{-3}$	$2.31 \cdot 10^{-3}$
$\eta$ -Al <sub>2</sub> O <sub>3</sub> (from Bayerite)	$3.56 \cdot 10^{-3}$	$4.35 \cdot 10^{-3}$

<sup>a</sup>  $p_{\text{C}_6\text{H}_6, \text{C}_6\text{D}_6} = 75 \text{ mm Hg}$ ,  $\theta = 310^\circ\text{C}$ .

pared in a different way.  $\eta$ -Alumina is markedly more active.

### 3.2. Poisoning Experiments with CO<sub>2</sub>

It is well known that CO<sub>2</sub> may be a poison for H-D exchange reactions (1, 2, 4, 6, 8). Figure 6 shows the effect of CO<sub>2</sub> (9.5 mm Hg) on the exchange reaction: The

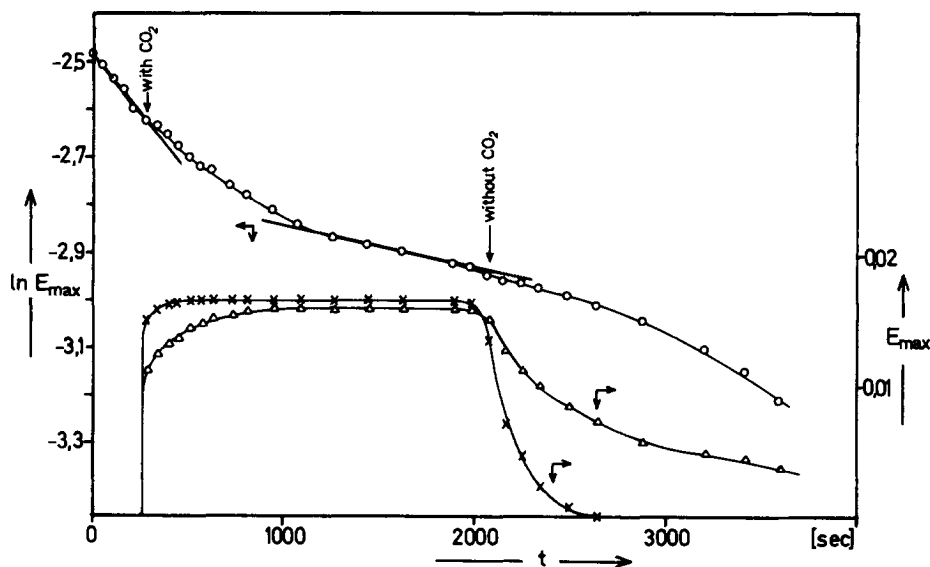


FIG. 8. Exchange reactivity and adsorbed CO<sub>2</sub> species. (O) Kinetic data; benzene-Al<sub>2</sub>O<sub>3</sub>- $d$ :  $\theta = 270^\circ\text{C}$ ,  $p_{\text{C}_6\text{H}_6} = 75 \text{ mm Hg}$ ,  $p_{\text{CO}_2} = 9.5 \text{ mm Hg}$ ; (x) formation of hydrogen carbonate ( $E_{\text{max}}$  of band at  $1647 \text{ cm}^{-1}$ ); ( $\Delta$ ) formation of carbonate species ( $E_{\text{max}}$  of band at  $1520 \text{ cm}^{-1}$ ).

reaction is partially poisoned, but the order of the reaction is not influenced. The dependence of reactivity on  $\text{CO}_2$  partial pressure is shown in Fig. 7. Obviously one may distinguish two parallel exchange reactions; the centers for the more important of these reactions are poisoned by  $\text{CO}_2$ . The centers for the other reaction are not influenced by this poison.

From spectroscopic investigations (23–31) it is known that  $\text{CO}_2$  is adsorbed in different forms: physisorbed  $\text{CO}_2$ , hydrogen-carbonate, and carbonate forms. By comparing the adsorption isotherms (23) for hydrogen-carbonate and carbonate species with Fig. 7, one may conclude that the reactive centers are poisoned by formation of carbonate. This conclusion is confirmed by kinetic experiments shown in Fig. 8. The exchange reaction ( $\ln E_{\max}$ ) is compared with the amount of hydrogen-carbonate and carbonate species formed after addition of  $\text{CO}_2$  and that remaining on the surface after stopping  $\text{CO}_2$  addition. The reactivity clearly correlates with the amount of carbonate species. From (23) it is known that three different carbonate species are formed with adsorption bands at 1580, 1520, and  $1455\text{ cm}^{-1}$ . The sum of carbonate-forming centers was determined to be  $5.8 \cdot 10^{11}$  per square centimeter for  $\gamma\text{-Al}_2\text{O}_3$  and  $12.2 \cdot 10^{11}$  per square centimeter for  $\eta\text{-Al}_2\text{O}_3$ , which is in good agreement with the relative exchange activities. By comparing the relative absorbances of the carbonate species on  $\eta$ - and  $\gamma\text{-Al}_2\text{O}_3$  (2.0 (1580), 2.1 (1520), and 1.4 ( $1455\text{ cm}^{-1}$ )) with the relative reactivity for H–D exchange one may conclude that either the band at  $1580\text{ cm}^{-1}$  or the one at  $1520\text{ cm}^{-1}$  is formed by  $\text{CO}_2$  adsorption on the reactive centers.

The most probable assumption for the structure of the reactive centers seems to be Lewis acid–base pairs formed by aluminum and oxide ions on sites with extremely high energy. The number of sites would agree with the number of corners of oxide crystallites, but the fact that the exchange velocity does not depend on the specific

surface (Table 3) as it should for sites on corners seems to rule out this assumption.

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