The Dual-Site Nature of Gamma Alumina Catalysts: Isomerization vs D_2 Exchange Reactions of 1-Butene

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Additional evidence has been obtained to support the contention that there are at least two types of active sites on alumina which catalyze different types of reactions and which are quite independent of each other. Two test reactions were employed: 1-butene isomerization, and the exchange of olefinic H atoms in the butene molecules with D atoms from D_2 gas. Small amounts of adsorbed CO_2 (corresponding to coverages of less than 1.6×10^{13} molecules/cm^2) completely eliminated the exchange reaction but had very little effect on either the absolute rate or the selectivity of the isomerization reaction. When the catalysts were exposed to comparable concentrations of SO_2, HCl, NH_3, or pyridine, at reaction temperature ($\sim 25°C$), there was no signficant effect on the rates of either isomerization or exchange. Speculation about the two types of sites for these reactions are discussed.

INTRODUCTION

Numerous investigations during the past decade have been directed toward elucidating the nature of the active sites on gamma alumina catalysts. The infrared studies of Peri (1, 2) have demonstrated the general acidic character of the alumina surface and have allowed some conclusions to be drawn regarding the nature of the catalytically active sites. Noncyclic olefins have also been extensively employed in various adsorption and test reaction studies (2–6) to obtain further information about the alumina surface. The most common of these test reactions has been the double-bond migration and cis–trans rotation of the n-butenes, relatively simple reactions whose rates are easily measured (4).

One of the more interesting observations to come out of these studies has been that the gamma alumina surface appears to possess at least two different types of active sites, chemically different and quite

independent of each other (1, 7–12). Using their programmed-desorption technique, Cvetanovic and Amenomiya (7) have shown that when trans-2-butene is adsorbed onto gamma alumina, thermal desorption of the olefin occurs from two different types of sites, having unique heats of desorption. The infrared study of Yates and Lucchesi (10) has shown that acetylene and ethylene adsorb on two separate kinds of sites on alumina, and furthermore, that the respective adsorptions occur entirely independently of each other. In addition, previous studies (13–15) of double-bond migration and cis–trans rotation of the n-butenes over alumina have demonstrated that extensive scrambling of the olefinic hydrogen atoms accompanies the isomerization and that this exchange process occurs independently of the isomerization. In the present work, the isomerization and exchange of 1-butene with D_2 were used as test reactions to investigate further the apparent dual-site nature of gamma alumina.

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Experimental Methods

Catalysts

Two gamma alumina catalysts were employed. One was a 0.415-g sample of the GA-48 preparation described previously (15); the other was a 0.250-g quantity of a commercial alumina catalyst manufactured by the American Cyanamid Co. The former had a surface area of 158 m²/g, while the surface area of the latter was 175 m²/g. Both catalysts were in the form of irregular 20/40 mesh particles. Pretreatment of both catalysts prior to each experiment included slow heating in vacuum to 520°C, treatment with oxygen for 2 hr, and overnight evacuation to a pressure of 10^{-6} Torr at the same temperature.

Reactants

The 1-butene was Phillips Research Grade having a purity of 99.9 mole %. It was distilled from −78 to −195°C and outgassed before use. Deuterium was generated electrolytically from D_2O having a minimum isotropic purity of 99.8%; it was passed through a trap at −195°C before use. Carbon dioxide was Matheson Co. bone-dry grade having a purity of 99.8%, and was outgassed before use.

Apparatus

All experiments were performed in a Pyrex, closed-loop recirculation reactor (16) whose volume was 350 ml. The loop consisted of a vertical catalyst tube, a small U-tube trap, an all-glass pulsed recirculation pump, provisions for removing gaseous samples by expansion for gas–liquid chromatography (GLC) analysis, and a spherical mixing vessel which accounted for 85% of the total reactor volume. An important feature of the system was a 2.23 ml bypass doser located immediately upstream from the catalyst, and it was via this doser that pulses of gaseous "poison" molecules could be admitted at any time during the reaction.

The three butene isomers were separated by gas-liquid chromatography using a ⅜ in. × 27 ft propylene carbonate-on-Chromosorb W column maintained at 0°C.

Quantitative analysis involved peak area measurements of signals from a Gow-Mac hot-wire thermal conductivity detector. The separated isomers were collected in traps at −195°C for subsequent mass spectral analysis.

Mass spectral analyses for deuterium content in each isomer were made with a Consolidated Electrodynamics Corp. 21-104 instrument using a low ionizing voltage. Analyses were based on parent-peak heights after correcting for fragmentation and isotopic carbon-13 contributions.

Procedure

With the evacuated catalyst bypassed, the desired pressure of olefin was admitted into the system and frozen into the U-tube trap. A measured pressure of D_2 was then admitted, the system was closed, and the trap was warmed rapidly to room temperature. The gas mixture was homogenized by circulation before being exposed to the pretreated and evacuated catalyst by manipulation of stopcocks which had been used to bypass the catalyst tube. Samples were periodically removed by expanding about 5% of the total reaction mixture into the GLC sampling loop.

Various poisons were added to the reaction when desired by filling the fixed-volume doser to the required pressure with gaseous poison, and then bypassing the circulating gas stream through the doser. In all these poisoning experiments the amount of poison added was 25% in excess of the "lethal dose" $(1.2 \times 10^{13}/\text{cm}^2)$ required to poison completely the exchange of benzene (16) or cyclopentene (17) over the same catalysts at 25°C.

Mathematical Treatment

The extent of the isomerization reaction is described by the first-order equation:

$$\ln \frac{X_e}{X_e - X} = Skt, \qquad (1)$$

where X and X_e are the fractional conversions of 1-butene to 2-butenes at any time t and at equilibrium ($X_e = 0.969$ at 25°C), respectively; S is the total catalyst surface area (m²). While this equation is

strictly valid only for two components involved in first-order reversible reactions, it is a reasonable approximation for the three-component system of n-butenes if the two products are taken together and treated as a single product. The plots obtained by use of Eq. (1) should be linear to at least 80% conversion of 1-butene, and the rate constant k obtained from the slope may be considered a valid measure of the "isomerization activity" of the catalyst for comparison purposes.

The deuterium incorporation was followed by determining changes in the number of D atoms per molecule of butene isomer as a function of time according to the equation

$$D \text{ atoms/molecule} = \sum_{i=0}^{8} i d_i, \quad (2)$$

where d_i is the fraction of all molecules of a particular isomer having i D atoms.

In all poisoning experiments the amount of poison added was normalized to the total catalyst surface area and expressed as poison molecules/cm^2.

RESULTS

The results of all experiments are summarized in Table 1. The isomerization rate constants in columns 6 and 7 have been normalized to 1 m^2 of catalyst surface area to allow a more meaningful comparison since different weights of the two catalysts were used, and each had a different specific surface area.

The isomerization reaction rates were independent of deuterium pressure; i.e., within the limits of catalyst reproducibility (conservatively about ±10%) the rates

TABLE 1

SUMMARY OF 1-BUTENE ISOMERIZATION-EXCHANGE EXPERIMENTS OVER GA-48 AND
CYANAMID ALUMINAS

Expt.	Catalyst	Reactants 1-C$_4$H$_8$:D$_2$ (torr):(torr)	Temp (°C)	Poison	Isomerization rate constant ($\times 10^4$ min^{-1} m^{-2}) Before poison	After poison	Effect of poison on exchange reaction
1-1	GA-48	41:420	20	None	1.93	—	—
1-2	GA-48	41:411	20	None	1.85	—	—
1-3	GA-48	40:402	20	None	1.82	—	—
2-1	Cyanamid	70:288	28	None	0.97	—	—
2-2	Cyanamid	100:408	28	None	0.78	—	—
2-3	Cyanamid	103:398	28	None	0.65	—	—
1-4	GA-48	44:442	20	CO$_2$	1.91	1.87	Exchange poisoned
1-5	GA-48	40:400	20	CO$_2$	1.74	1.71	Exchange poisoned
1-6	GA-48	41:406	20	CO$_2$	2.00	1.68	Exchange poisoned
1-7	GA-48	41:410	20	CO$_2$	1.74	1.68	Exchange poisoned
2-4	Cyanamid	100:423	28	CO$_2$	0.62	0.44	Exchange poisoned
2-5	Cyanamid	101:399	28	CO$_2$	0.81	0.62	Exchange poisoned
1-8	GA-48	42:422	20	Preads. CO$_2$	—	1.35	No exchange obs
1-9	GA-48	41:412	20	Preads. CO$_2$	—	1.59	No exchange obs
1-10	GA-48	41:404	20	Preads. CO$_2$	—	1.64	No exchange obs
1-11	GA-48	42:418	20	Preads. CO$_2$	—	1.78	No exchange obs
2-6	Cyanamid	100:410	29	Preads. CO$_2$	—	0.68	No exchange obs
2-7	Cyanamid	100:399	28	Preads. CO$_2$	—	0.61	No exchange obs
2-8	Cyanamid	100:402	27	SO$_2$	0.69	0.78	No effect[a]
2-9	Cyanamid	100:402	26	NH$_3$	0.52	0.38	No effect
2-10	Cyanamid	100:401	26	Pyridine	0.57	0.53	No effect
2-11	Cyanamid	100:410	27	HCl	0.61	0.59	No effect

[a] "No effect" was used whenever the "poisoned" exchange reaction rate was within 10% of the unpoisoned rate.
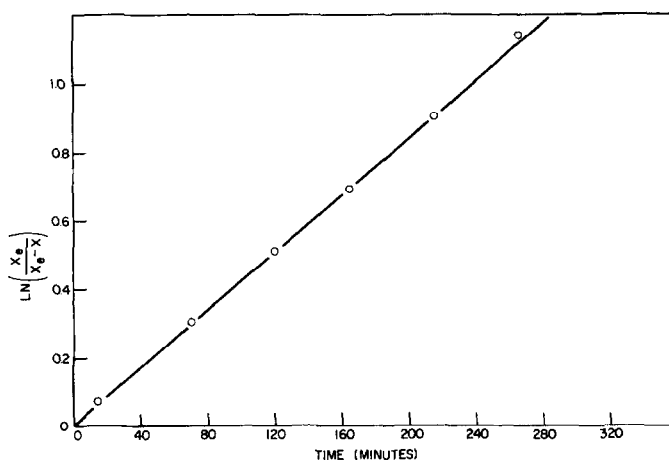
FIG. 1. 1-Butene isomerization rate of a 1-butene: D_2 = 70:288 Torr mixture over 0.250 g of Cyanamid alumina at 28°C (Expt. 2-1).

were the same with, or without, H_2 or D_2. A standard error analysis indicated that the uncertainty in the isomerization rate constants is the order of ±5–10%; hence changes in the rate constant of 10% or less (after poison addition, *vida infra*) were considered negligible.

1-Butene + D_2

Both *n*-butene isomerization (without skeletal rearrangement nor observable polymerization) and deuterium incorporation into the olefins (without saturation to butane) occurred simultaneously. Results of a typical experiment (No. 2-1) over the Cyanamid catalyst with no poison added

are shown in Figs. 1 and 2. Figure 1 depicts the extent of the isomerization reaction as plotted according to Eq. (1), while Fig. 2 shows the deuterium incorporation as calculated from Eq. (2). The first-order isomerization curve is linear up to 80% conversion of the 1-butene, which indicates that there was no significant poisoning during the reaction. Even the isomerization rate constant k was within a factor of two for the two catalysts at the same temperature and for the same reaction mixture.

At all times the reactant 1-butene contained more D-atoms per molecule than either of the 2-butenes, whose deuterium content decreased in the order *cis* > *trans*
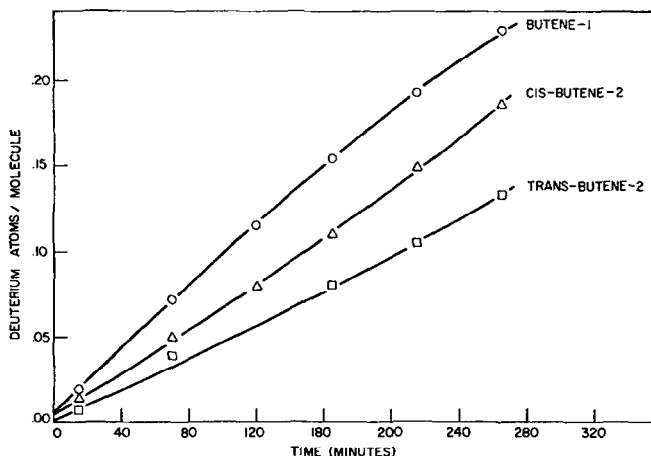

FIG. 2. Deuterium concentration in butene isomers during reaction of a 1-butene: D_2 = 70:288 Torr mixture over 0.250 g of Cyanamid alumina at 28°C (Expt. 2-1).
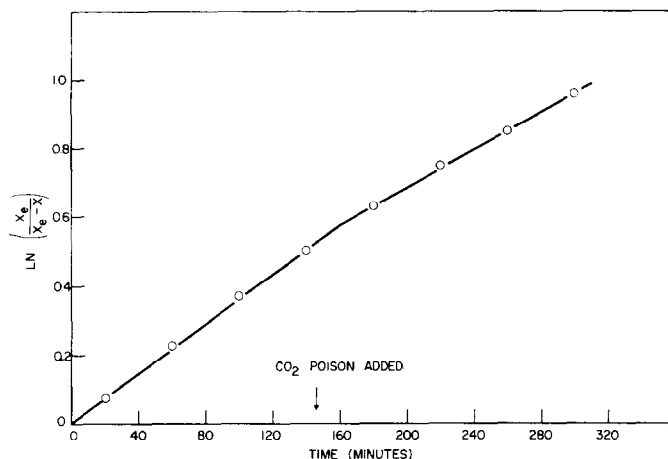
FIG. 3. 1-Butene isomerization rate of a 1-butene:D_2 = 101:399 Torr mixture over 0.250 g of Cyanimid alumina at 28°C with addition of CO_2 poison (Expt. 2-5).

at any given time. Essentially identical results were obtained with the GA-48 catalyst (13).

1-Butene + D_2 + CO_2

The effect of carbon dioxide addition during the reaction is illustrated for the Cyanamid catalyst (Expt. 2-5) in Figs. 3 and 4. As shown, the isomerization reaction (Fig. 3) is not greatly affected by the poison, but the exchange reaction is completely poisoned. Addition of a second quantity of carbon dioxide equal to the first produced no further effect on either reaction. Parallel results were obtained with the GA-48 catalyst.

The slopes for the exchange curves for both 2-butenes in Fig. 4 are nonzero after poison addition simply because of the continued formation of these products from the 1-butene which itself contains a high D concentration. In other words, these positive slopes represent a redistribution of D atoms through isomerization within the butene molecules and do *not* indicate further exchange with D_2.

1-Butene + D_2 + Preadsorbed CO_2

When a quantity of carbon dioxide identical to that used in the preceding experiments was preadsorbed onto either catalyst prior to starting the reaction, the isomeri-
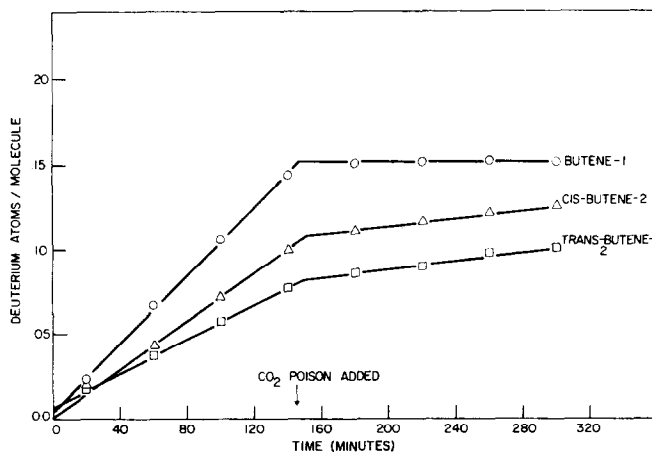

FIG. 4. Deuterium concentration in butene isomers during reaction of a 1-butene:D_2 = 101:399 Torr mixture over 0.250 g of Cyanamid alumina at 28°C with addition of CO_2 poison (Expt. 2-5).

zation reaction again proceeded normally, but no deuterium exchange whatever could be detected into any of the three butene isomers. Addition of a quantity of carbon dioxide during the reaction had no further effect.

Other Poisons

Experiments were performed over the Cyanamid catalyst using amounts of sulfur dioxide, hydrogen chloride, ammonia, and pyridine poisons equal to the amount of carbon dioxide used in the preceding experiments. In all four cases, only very small effects were observed on either the isomerization or the exchange reaction rates (see Table 1).

DISCUSSION

These results demonstrate rather conclusively that at least two types of catalytically active sites exist on the surface of gamma alumina. One group of sites catalyzes the double-bond migration and *cis-trans* rotation of 1-butene, while the other promotes exchange of the olefinic hydrogen atoms with deuterium. Furthermore, the catalytic activities of these two types of sites are apparently quite independent of each other since one of the reactions can be selectively poisoned with virtually no effect on the other. That this dual-site nature is an inherent property of gamma alumina surfaces in general is attested to by the fact that identical results were obtained over two different alumina samples. One of these (GA-48) is a special laboratory preparation, while the other (Cyanamid sample) is a commercially-used alumina catalyst, prepared under considerably less stringent conditions.

It is impossible to draw any completely unambiguous conclusions about the exact nature of these two sites. However, a few general comments can be made about the sites on which the exchange occurs. These are apparently the same sites which catalyze the exchange of D_2 with benzene and cyclopentene, since all exchange reactions are poisoned completely by addition of approximately the same amount of CO_2. As shown previously by quantitative titra-

tion (*16, 17*), the site concentration (based on the assumption of a 1-to-1 stoichiometry between adsorbed CO_2 molecules and active sites) is probably in the range of 6–12×10^{12} exchange sites/cm². Furthermore, earlier work with $^{14}CO_2$ (*16, 17*) has shown that all the added CO_2 is adsorbed and that, even in the presence of the hydrocarbons, the catalyst has the capacity to adsorb up to twice the amount of CO_2 necessary to poison all the exchange sites. This suggests that the CO_2 is being selectively adsorbed on the active sites.

In their temperature programmed desorption studies, Cvetanovic and Amenomiya (*7*) designated the two types of active sites on alumina as Type I, which catalyzed ethylene hydrogenation, and Type II, which prompted ethylene polymerization. It appears unlikely that either of these types of sites corresponds to those evidenced in our work, since we observed neither saturation nor polymerization of the *n*-butenes. However, the existence of more than two types of sites is not improbable, since Maatman and Vande Griend (*12*), in a recent study of *n*-butanol decomposition on alumina, have found evidence for at least *four* types of active sites, each presumably having a unique nature. The two types of sites found in our work may correspond with two of these four or they may be additional types of sites which still remain unclassified.

The apparent complexity of the alumina surface casts some doubt on the general applicability of the low site density calculations of Maatman (*18*) based on absolute rate theory and a single reacting species. In these exchange reactions, obviously at least two reacting species are involved.

Perhaps the exchange sites may have basic character in the Lewis sense, as the reactions are readily poisoned by the acidic CO_2 but are unaffected by addition of Lewis bases such as NH_3 or pyridine. On the other hand, this argument seems inconsistent with the observation that SO_2 and HCl, compounds having an even stronger Lewis acid nature than CO_2, do not poison the reaction. This may have

occurred simply because the SO_2, HCl, NH_3, and pyridine molecules were either not adsorbed at all or were adsorbed nonselectively on other sites as well as on the exchange sites; no evidence to test either hypothesis was obtained.

Parkyns (19) has characterized the complex IR spectra observed when CO_2 is adsorbed on alumina. Only one of the adsorption types he described (a band at 1780 cm^{-1} which was neither pressure sensitive nor time dependent) correlates with the rapid, irreversible poisoning observed at the reaction temperature, and this adsorption apparently occurs on an exposed Al^{3+} ion. Perhaps it is these sites which catalyze the exchange reaction.

Little new light can be shed on the nature of the isomerization sites as a result of these studies, since none of the added poison molecules had any significant effect on the isomerization reaction. Previous work (14, 17) indicates that these reactions proceed via an essentially intramolecular mechanism and may take place on isolated oxygen ions on the surface. Additional studies are underway which hopefully will help elucidate the nature and concentration of these isomerization sites.

CONCLUSIONS

The existence of at least two different and independent types of sites has been demonstrated on the surface of gamma alumina. One type catalyzes exchange of olefinic and aromatic hydrogen atoms with D_2, and these sites occur on the average at a concentration of about one site per each 1000 $Å^2$ of surface as indicated by CO_2 poisoning. The other sites which catalyze the isomerization and cis–trans rotation of 1-butene are not subject to poisoning by CO_2, NH_3, SO_2, HCl, or pyridine added at the reaction temperature of about 25°C.

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