JOURNAL OF CATALYSIS 57, 1–10 (1979)

Surface Properties of Zirconium Oxide and Its Catalytic Activity for Isomerization of 1-Butene

YASUKO NAKANO, TOKIO IIZUKA, HIDESHI HATTORI, AND KOZO TANABE

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Received February 21, 1978; revised September 7, 1978

Acidic, basic, oxidizing, and reducing properties of ZrO_2 were measured by the ir spectra of adsorbed pyridine, by CO_2 adsorption or the ESR of diphenylnitroxide radical formed from diphenylamine and O_2, by the ESR of adsorbed triphenylamine, and by the ESR of adsorbed nitrobenzene, respectively. The variations of these properties with pretreatment temperature of ZrO_2 were independent of each other. The maximum concentrations of these sites and the pretreatment temperatures at which the maxima were obtained were 3.9×10^{-8} mole/m^2 and 400°C for acidic sites, 1.7×10^{-7} mole/m^2 and 700°C for basic sites measured by diphenylamine, 1.5×10^{-7} mole/m^2 and 700°C for oxidizing sites, and 4.3×10^{-8} mole/m^2 and 500°C for reducing sites. Among these properties, it was the basic property with which the activity for isomerization of 1-butene correlated best. The activity was poisoned not only by CO_2 but also by NH_3 or triethylamine, indicating that the active sites consist of both basic and acidic sites. The results of the coisomerization of 1-butene-d_0/d_8 showed that the reaction involved primarily an intramolecular hydrogen transfer.

INTRODUCTION

Zirconium oxide is known to exhibit characteristic catalytic behavior in dehydration, hydrogenation, and hydrogen exchange reactions. In the dehydration of 2-alkanols, thermodynamically unstable 1-olefins are selectively formed (*1*). In the exchange reaction of 2-propanol-d_8 with surface H atoms, a methyl D is exchanged on ZrO_2 but not on the other oxides such as SiO_2–Al_2O_3, Al_2O_3, or TiO_2 (*2*). These characteristics were considered due to the acid–base bifunctional nature of ZrO_2 surface. In the hydrogenation of 1,3-butadiene, 1,4-addition of H atoms was observed and the molecular identity of H atoms was maintained during the hydrogenation (*3*). However, the surface properties of ZrO_2 have scarcely been studied. In this paper, acid–base and oxidizing–reducing properties of ZrO_2 pretreated at various temperatures were measured, and the nature of active sites for isomerization of 1-butene was discussed on the basis of the observed surface properties and the mechanistic study of the reaction.

EXPERIMENTAL METHODS

Catalysts and Reagents

Zirconium hydroxide was prepared by hydrolysis of $ZrOCl_2$ (Wako Pure Chemicals Ind.) with 28% aqueous ammonia. The precipitate was washed with deionized water until no chloride ions were detected with a silver nitrate test solution and was dried at 100°C for 24 hr. Zirconium oxide was obtained by calcining the hydroxide at various temperatures between 300 and 900°C in air for several hours. The oxide

0021-9517/79/040001-10$02.00/0

was outgassed at the calcination temperatures for 2 hr before use.

Diphenylamine and triphenylamine were briefly degassed at room temperature before use. Pyridine and triethylamine were purified by repeating a freeze–thaw cycle several times followed by passage through a KOH column and 4A molecular sieves, respectively. All these reagents were purchased from Wako Pure Chemicals Ind. 1-Butene (99% purity) was distilled through 4A molecular sieves thermostated at dry ice–acetone temperature.

Measurements of Surface Properties

Acidity. Acidity was measured by the ir spectra of adsorbed pyridine as follows. In order to determine the extinction coefficient of the adsorption band for each sample, a known amount of pyridine (ca. 5×10^{-9} mole) was adsorbed on a self-supported disk sample in an *in situ* cell. The extinction coefficients of the bands at 1605 and 1445 cm^{-1} were obtained from Beer's law.[1] Subsequently, the sample was exposed to 10 Torr of pyridine vapor at 100°C for 30 min and then outgassed at 100°C for 30 to 40 min. In some experiments, pyridine was adsorbed at 200 or 300°C. The ir spectra were recorded at ambient beam temperature (ca. 47°C) with a JASCO DS701G infrared spectrophotometer.

Basicity. Amounts of basic sites were measured by two methods. One method involved adsorption of CO_2. The pretreated sample (300 mg) was exposed to 20 Torr of CO_2 at 100°C for 30 min and outgassed at this temperature for 30 min. The CO_2 molecules retained on the surface were collected in a liquid N_2 trap by heating the sample at 500°C for 30 min. The collected CO_2 was expanded and its amount was volumetrically measured. In the other method, the diphenylnitroxide radicals formed from diphenylamine adsorbed on basic sites in the presence of O_2 were measured by ESR. A sufficient quantity of diphenylamine for covering one monolayer was adsorbed on the sample at 180°C for 20 hr in an all-glass ESR cell through a breakable seal. The adsorbed diphenylamine was converted to the diphenylnitroxide radical when O_2 was admitted to the system. The number of spins was determined by comparing them with the intensity of Mn^{2+} in CaO whose spin concentration had been calibrated by DPPH solution in benzene. The concentration of DPPH was determined by the uv spectroscopy, in which the extinction coefficient of 1.45×10^4 at 530 nm was used (*4*).

Oxidizing and reducing properties. The number of oxidizing sites was determined by ESR measurement of triphenylamine cation radicals formed from triphenylamine in the presence of O_2. The procedure was the same as in the case of the basicity measurement using diphenylamine.

The number of reducing sites was determined by ESR measurement of nitrobenzene anion radicals formed on the surface when nitrobenzene was adsorbed.

Surface Area

Specific surface area was measured by the BET method using N_2.

Reaction Procedure

Kinetic measurements of the isomerization of 1-butene were carried out in a closed recirculation reactor having a volume of ca. 290 ml. A 60-mg sample of catalyst was used and 100 Torr of 1-butene was reacted at 80 or 100°C. The reaction mixture was periodically withdrawn and analyzed by gas chromatography. Propylene carbonate (30%) on Uniport C was used for the packing in an 8-m chromatographic column of 4-mm-o.d. copper tubing.

In the poisoning experiments, CO_2, NH_3, and triethylamine were used as poisons.

---

[1] Only bands due to pyridine adsorbed on a Lewis acid site were observed.

The catalyst was exposed to about 20 Torr of a poison at 100°C for 30 min. Then the poison was partly desorbed by outgassing at elevated temperatures for 30 to 40 min. The activity was measured as mentioned above.

For the coisomerization of nondeuterio and perdeuterio 1-butene (*5*), a microcatalytic pulse reactor was employed. A mixture containing equal amounts of 1-butene-d_0 and -d_8 (17 μmole) was passed over 60 mg of the catalyst in a He carrier whose flow rate was 133 ml/min. Products were first trapped in a liquid N_2 trap and flash evaporated into a gas chromatographic column. The separated isomers were collected in liquid N_2 and subjected to the mass spectrographic analysis.

The poisoning effects of CO_2 and NH_3 in the coisomerization were examined for ZrO_2 pretreated at 500°C. For the experiments, 890 mg of the catalyst was used. Outgassing temperatures of the poisons were 230°C for CO_2 and 200°C for NH_3. The flow rates of a He carrier were 159 ml/min for the CO_2-poisoned experiment and 41 ml/min for the NH_3-poisoned experiment.

RESULTS

Surface Area

Specific surface areas of ZrO_2 pretreated at different temperatures are given in Table 1. The surface areas decreased monotonously with the rise in pretreatment temperature.

TABLE 1

Specific Surface Areas of ZrO_2 Pretreated at Various Temperatures

Pretreatment temperature (°C)	Surface area (m^2/g)
300	175.5
400	109.0
500	64.5
600	32.1
700	21.4
800	10.8
900	9.9

Acidic Property

Infrared spectra of pyridine adsorbed on ZrO_2 at different temperatures are shown in Fig. 1. Absorption bands at 1600, 1485, and 1440 cm^{-1}, which are attributed to the pyridine coordinately bonded to Lewis acid sites, were observed when adsorbed at 100°C. However, when pyridine was adsorbed at 200 or 300°C, the absorption band at 1550 cm^{-1}, which is assigned to the pyridinium ion, was observed in addition to the bands of coordinately adsorbed pyridine. This implies that the hydroxyl groups on ZrO_2 are too weak to act as Brønsted acid at 100°C but become active at 200 to 300°C.

The amount of pyridine irreversibly adsorbed at 100°C on a unit surface area basis is shown in Fig. 2 as a function of pretreatment temperature of ZrO_2. The maximum value of 3.9×10^{-8} mole/m^2 (2.4×10^{16} molecules/m^2) was observed when ZrO_2 was pretreated at 400°C.

Formation of Radical from Diphenylamine and Oxygen

When diphenylamine was adsorbed from benzene solution on ZrO_2 followed by introduction of O_2, the sample developed gray coloration and a singlet signal of ESR with $g = 2.002 \pm 0.004$ was observed at room temperature. Addition of a small amount of H_2O to the system resulted in a change in the color of the surface to pinky red and then immediately to beige, accompanied by a red coloration of the benzene solution. When diphenylamine was added to the sample which had already adsorbed a sufficient quantity of triphenylamine (the ionization potential of triphenylamine is lower than that of diphenylamine), the ESR signal intensity increased. When the adsorption of diphenylamine was performed

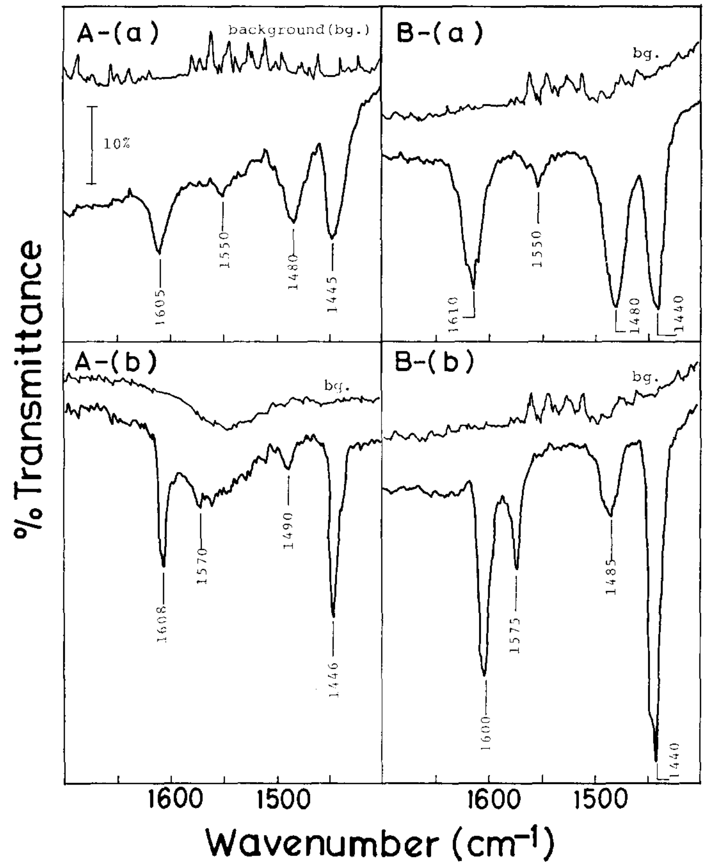


FIG. 1. Infrared spectra of pyridine adsorbed on ZrO_2 pretreated at 300°C (A) and 500°C (B). Adsorption temperature: A-(a), 200°C; B-(a), 300°C; A-(b) and B-(b), 20°C, followed by evacuation at 100°C.

in a vapor phase at 180°C, the same coloration and ESR signal were observed as in the case of the adsorption from solution. Once the radicals were formed in the presence of O_2, the intensity of the ESR signal was not changed by removal of O_2 from a gas phase.

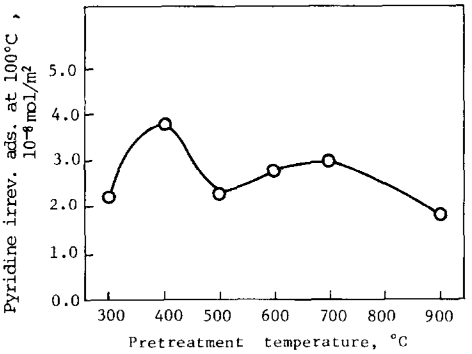


FIG. 2. Amount of pyridine molecules irreversibly adsorbed at 100°C on ZrO_2 pretreated at various temperatures.

In Fig. 3, amount of the radicals formed on the surface when diphenylamine was adsorbed from a vapor phase at 180°C is plotted against pretreatment temperature of ZrO_2. The maximum number of the radicals was formed on ZrO_2 that had been pretreated at 700°C, the number of the radicals being 1.7×10^{-7} mole/m^2 (1.1×10^{17} radicals/m^2).

Adsorption of CO_2

The amounts of CO_2 molecules adsorbed are also shown in Fig. 3. The values were

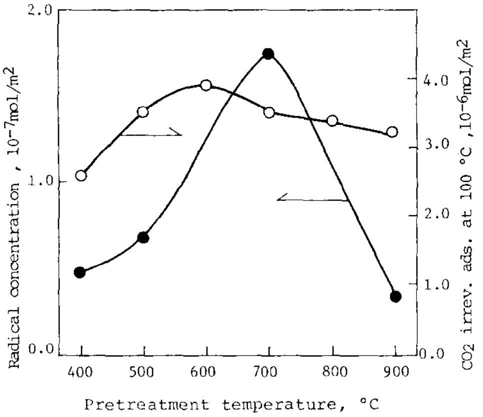


FIG. 3. Amounts of diphenylnitroxide radicals (●) and CO_2 irreversibly adsorbed at 100°C (○) on ZrO_2 pretreated at various temperatures.

much larger than the values of diphenylnitroxide radicals formed on the surface and did not change much with pretreatment temperature of ZrO_2.

Reducing Properties

When ZrO_2 was exposed to nitrobenzene vapor at 20°C, the surface of the oxide turned to a brownish pink; at the same time, an ESR signal appeared. The signal was constituted of three major lines, one central sharp line with $g = 2.003$ and two wings on each side. This signal was assigned to a nitrobenzene anion radical (*6*). After the sample was exposed to nitrobenzene for 24 hr at room temperature, the color became brown and the resolution among the three lines declined. The radical concentration after 48 hr is plotted against pretreatment temperature in Fig. 4. The maximum value was observed when ZrO_2 was pretreated at 500°C, the concentration being 4.3×10^{-8} mole/m^2 (2.6×10^{16} radicals/m^2).

Oxidizing Property

Adsorption of triphenylamine on ZrO_2 did not give any ESR signal, although the ZrO_2 surface developed a light blue color. Subsequent addition of O_2 caused an immediate change in surface color to greenish gray, and a triplet signal with $g = 2.005$ was observed by ESR, and was assigned to the cation radical of triphenylamine. The amplitude of the signal was independent of oxygen pressure. The number of cation radicals as a function of pretreatment temperature of ZrO_2 is shown in Fig. 4. The maximum radical concentration was obtained on ZrO_2 pretreated at 700°C, and its value was 1.5×10^{-7} mole/m^2 (9.3×10^{16} radicals/m^2).

Isomerization of 1-Butene

The variations of the activity and the ratio of *cis*-2-butene to *trans*-2-butene are plotted against pretreatment temperature of ZrO_2 in Fig. 5. Activity is expressed as initial conversion per unit time on a unit surface area basis. The ratio of *cis*-2-butene to *trans*-2-butene was obtained by extrapolation to zero conversion. The activity of ZrO_2 appeared on pretreatment at 400°C and reached the maximum on pretreatment at 800°C and then rapidly decreased on pretreatment at 900°C. The ratio of *cis*-2-butene to *trans*-2-butene gradually decreased as the pretreatment temperature was raised.

Figures 6 and 7 show the recovery of activity with an increase in outgassing

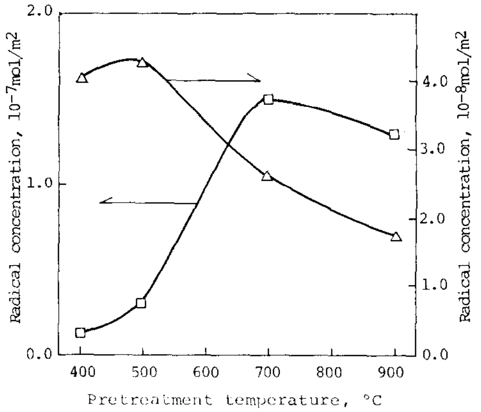


FIG. 4. Amounts of triphenylamine cation radicals (□) and nitrobenzene anion radicals (△) on ZrO_2 pretreated at various temperatures.

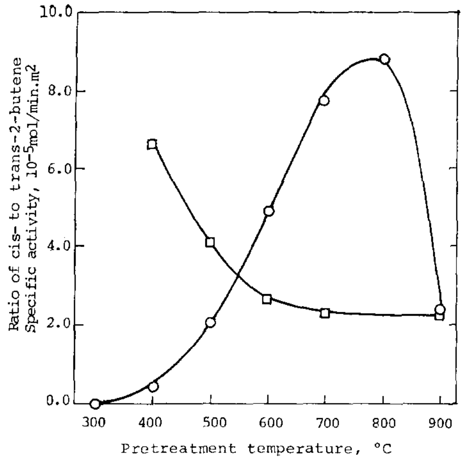


FIG. 5. Changes in the activity for isomerization of 1-butene (○) and in the ratio of *cis*-2-butene to *trans*-2-butene (□) with pretreatment temperature of ZrO_2.

temperature of poisons adsorbed on ZrO_2 pretreated at 500 and 700°C in the poisoning experiments. The reaction was completely retarded by all poisons irreversibly adsorbed at 100°C for both catalysts. In the poisoning experiments with NH_3 or triethylamine, the activity was recovered by outgassing at much lower temperature for ZrO_2 pretreated at 500°C than for ZrO_2 pretreated at 700°C. On the other hand, the reverse results were obtained in the case of the poisoning with CO_2. The temperatures at which the activities recovered to 90% their original values by outgassing after poisoning with CO_2 were about 410°C for ZrO_2 pretreated at 500°C and 330°C for ZrO_2 pretreated at 700°C.

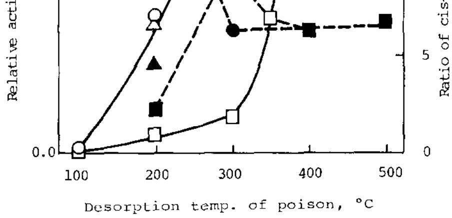


FIG. 6. Recovery of the activity and the ratio of *cis*-2-butene to *trans*-2-butene for isomerization of 1-butene over ZrO_2 pretreated at 500°C by desorption of preadsorbed NH_3 (○, ●), triethylamine (△, ▲) and CO_2 (□, ■). Open symbols represent activity, solid symbols represent *cis*-/*trans*- ratio. Reaction temperature: 100°C for triethylamine poisoning, 80°C for NH_3 and CO_2 poisoning.

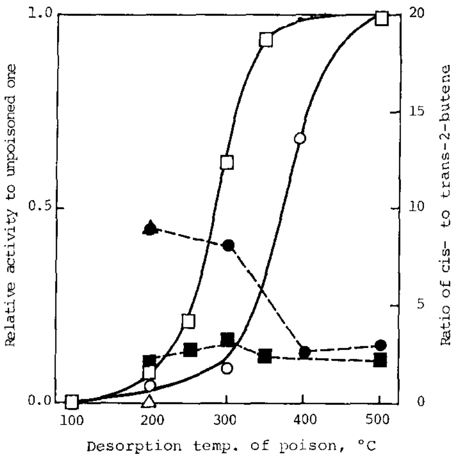


FIG. 7. Recovery of activity and the ratio of *cis*-2-butene to *trans*-2-butene for isomerization of 1-butene over ZrO_2 pretreated at 700°C by desorption of preadsorbed NH_3, triethylamine, and CO_2 adsorbed at 100°C. Symbols are explained in legend to Fig. 6. Reaction temperature: 100°C in all cases.

The results of the coisomerization of 1-butene-d_0/d_8 are summarized in Table 2. Over the unpoisoned catalyst, the amounts of exchanged products were small, though a slight increase in the exchanged products was observed as the pretreatment temperature was lowered. The low values of the number of H (or D) atoms exchanged per molecule (AEM value) indicate that the reaction involves primarily an intramolecular H transfer. The isotope effects were about 3 in all the cases of unpoisoned catalysts.

Poisoning with NH_3 gave rise to an increase in the isotope effect, but did not

TABLE 2

Isotopic Distribution of Product Isomers in Coisomerization of 1-Butene-d_0/d_8 over ZrO_2

Pretreatment temperature (°C)	Reaction temperature (°C)	Ratio of *cis-/trans-*	Product	Amount of each product (%)	Isotopic distribution (%)								AEM[a]	IE[b]
					d_0	d_1	d_2	d_3,d_4	d_5	d_6	d_7	d_8		
400	98	1.58	*trans*	7.3	64.4	6.9	1.1	0	0.4	1.8	7.3	18.1	0.212	2.6
			cis	11.5	67.1	2.9	0.5	0	0	1.3	6.8	21.4	0.133	2.7
			1	81.2	41.9	0.3	0	0	0	0.4	6.3	51.1	0.074	0.73
700	99	1.39	*trans*	4.9	71.8	1.9	0.2	0	0	0.4	4.3	21.4	0.074	2.9
			cis	6.9	74.5	1.2	0.1	0	0	0.4	3.8	20.0	0.060	3.3
			1	88.2	43.6	0	0	0	0	0.4	5.9	50.2	0.067	0.78
900	99	1.38	*trans*	3.7	72.8	2.5	0.3	0	0	0	3.3	21.1	0.064	3.0
			cis	5.2	78.0	0	0	0	0	0	2.9	19.1	0.029	3.5
			1	91.1	46.6	0	0	0	0	0.4	5.6	47.4	0.064	0.85
500 (Poisoned by CO_2)	100	2.9	*trans*	7.4	50.8	9.9	4.6	0	0	6.4	7.1	21.2	0.390	1.9
			cis	21.0	48.8	13.3	3.8	0	0	3.4	9.9	20.8	0.376	1.9
			1	71.6	42.0	6.9	1.7	0	0	1.1	9.9	38.4	0.224	1.0
500 (Poisoned by NH_3)	100	7.6	*trans*	2.0	75.5	4.9	1.7	0	0	1.5	4.3	12.1	0.156	4.6
			cis	15.3	74.4	7.2	0.5	0	0	0	4.3	13.6	0.125	4.6
			1	82.7	40.0	1.0	0.6	0	0	1.1	8.0	49.3	0.124	0.71
Reactant					51.2	0.04	0	0	0	0	4.7	44.0	0.047	1.05

[a] Calculated from $\sum_{i=0}^{4} i \cdot N_i + \sum_{i=5}^{8} (8 - i) \cdot N_i$.

[b] Calculated from $(\sum_{i=0}^{3} N_i + 0.5N_4)/(\sum_{i=5}^{8} N_i + 0.5N_4)$, where N_i represents a fraction of the isomer containing i D atoms in a molecule.

TABLE 3

Comparison of the Activity for Isomerization of 1-Butene and Surface Properties of ZrO_2 Pretreated at 700°C before and after Treatment with $CHCl_3$

	Before treatment (BT)	After treatment (AT)	(AT)/(BT)
Activity	7.2×10^{-5} mole/m^2/min	0.43×10^{-5} mole/m^2/min	0.06
Basicity by diphenylamine	1.7×10^{-7} mole/m^2	0.051×10^{-7} mole/m^2	0.03
Basicity by CO_2	3.5×10^{-6} mole/m^2	1.8×10^{-7} mole/m^2	0.05
Oxidizing property	1.5×10^{-7} mole/m^2	3.7×10^{-7} mole/m^2	2.5

affect the AEM value much. On the contrary, poisoning with CO_2 resulted in an increase in the AEM value and a decrease in the isotope effect.

In Table 3 the effects of the treatment with chloroform on the activity and surface properties are given. Upon treatment the activity and the number of the radicals formed from diphenylamine decreased, while the number of oxidizing sites increased.

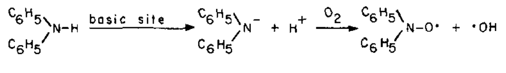
DISCUSSION

The Process of Formation of the Radical from Diphenylamine and O_2

The processes of forming radicals from diphenylamine and O_2 on some oxides were studied in detail (*7*). In the case of Al_2O_3, a singlet ESR signal was observed, accompanied by gray coloration of the Al_2O_3 surface. The radical species generated on the surface could be transferred from the surface into benzene by addition of polar liquid such as H_2O. The dissolved paramagnetic species in benzene gave a red coloration. The radical species formed on Al_2O_3 were determined to be diphenylnitroxide radicals. The formation of diphenylamine cation radical is also possible and this occurred on SiO_2–Al_2O_3 under the comparable condition. In this case the color of the oxide surface was greenish black and the material dissolved into benzene caused a blue fluorescence (*7*).

In the case of ZrO_2, the color developed on the surface was gray and its benzene solution became red upon addition of H_2O. This indicates that diphenylnitroxide radicals were produced on ZrO_2 from diphenylamine and O_2.

An increase in the signal amplitude of the ESR was observed when diphenylamine was added to the ZrO_2 that had adsorbed triphenylamine followed by admission of O_2. This suggests that the sites for the formation of diphenylnitroxide radicals were different from the sites for the formation of triphenylamine cation radicals, because the ionization potential of triphenylamine is lower than that of diphenylamine. Therefore, it is considered that the diphenylnitroxide radicals were formed on ZrO_2 by an action of basic sites as follows.



$$(C_6H_5)_2N\text{-}H \xrightarrow{\text{basic site}} (C_6H_5)_2N^- + H^+ \xrightarrow{O_2} (C_6H_5)_2N\text{-}O\cdot + \cdot OH$$

The concentration of diphenylnitroxide radicals was taken as the concentration of basic sites, since the radicals could not desorb from the sites unless a polar molecule was added. Since the pK_a value of diphenylamine is 23, only strong basic sites could be measured by this method. Actually the numbers of basic sites measured by this method were one order of magnitude lower than those measured by CO_2 adsorption.

Relation between Surface Properties and the Activity for Isomerization of 1-Butene

Since the variations of the surface properties with pretreatment temperature were independent of each other, it is considered that there are different types of sites on ZrO_2. Among these sites, basic sites measured by the adsorption of diphenylamine correlated best with the activity for isomerization of 1-butene. Besides the correlation, the activity and basicity decreased upon treatment with chloroform, while the number of oxidizing sites increased. It is likely that the basic sites participate in the isomerization of 1-butene. However, strong poisoning effects of both the basic molecules (NH_3 and triethylamine) and the acidic molecule (CO_2) suggest that acidic sites as well as basic sites are involved in the active sites for the reaction. The idea that the active site on ZrO_2 is an acid–base pair site and that each site is cooperative in a reaction was proposed for interpretation of the selective formation of 1-olefins in the dehydration of 2-alkanols (*1*).

The initiation of the isomerization reaction could be either abstraction of an allylic H from 1-butene by basic sites or addition of an H^+ from acidic sites. Dominant intramolecular H transfer in the coisomerization reveals that the reaction is mainly initiated by the abstraction of an H^+ by basic sites. Perhaps, Lewis acid sites assist the abstraction of the H^+ by polarizing the butene molecule or stabilizing the resulting carbanion. However, intermolecular H transfer is involved in the reaction to some extent over the catalyst pretreated at a low temperature. The contribution of the intermolecular H transfer became more enhanced when the catalyst was partly poisoned by CO_2. The active sites unblocked by partial poisoning with CO_2 are not single acid sites but are acid–base pair sites whose basic strength is weak, because the further addition of CO_2 could completely block all active sites. Since the main reaction involves intramolecular H transfer, the effect of NH_3 poisoning is not so large. Nevertheless, the changes in the isotope effect and probably in the AEM value caused by NH_3 poisoning were opposite to those caused by CO_2 poisoning. The characteristics of base-catalyzed isomerization were pronounced by the partial poisoning with NH_3. Therefore, it is suggested that there is more than one kind of acid–base pair site which is different in the strength of acidic and basic properties.

The strength of acidic and basic properties of the active sites is dependent on pretreatment temperature of ZrO_2. Most of the adsorbed NH_3 on ZrO_2 pretreated at 500°C was removed by evacuation at 300°C, while most of the adsorbed NH_3 on ZrO_2 pretreated at 700°C could be removed only by evacuation at 500°C. On the other hand, CO_2 is adsorbed more strongly on the active sites of ZrO_2 pretreated at 500°C than on those of ZrO_2 pretreated at 700°C. Therefore, the basic property is more pronounced for ZrO_2 pretreated at 500°C than for ZrO_2 pretreated at 700°C, whereas the acidic property is just the reverse.

The acid–base pair sites are probably exposed zirconium ions with adjacent O^{2-} ions which are generated by removal of H_2O molecules from neighboring OH groups, as was proposed for crystalline aluminosilicate (*8*) and Al_2O_3 (*9*). The OH groups on ZrO_2, like those on Al_2O_3, are not capable of protonating the butene molecule.

The number of CO_2 molecules removed from the surface of ZrO_2 pretreated at 500°C is 2.7×10^{-7} mole/m^2 (1.6×10^{17} molecules/m^2) after evacuation at 300°C, with which most of the active sites were blocked. Therefore, the number of active sites on ZrO_2 pretreated at 500°C is about 1.6×10^{17} sites/m^2. Based on this value and the rate (3.7×10^{-7} mole/m^2/sec at 100°C), the turnover frequency for isomerization is calculated to be 1.4 molecules/site/sec. The value of 2.1×10^{-2} molecules/site/sec was estimated for the reaction temperature of 28°C using the activation energy of

14 kcal/mole which was obtained for ZrO_2 evacuated at 500°C. This value is about the same order as those observed at 28°C on Al_2O_3 (*10*) but much smaller than that found with La_2O_3 (52 molecules/site/sec at 0°C) (*11*).

Since the active sites are only about 2% in surface coverage, all the acid–base pair sites do not serve as active sites. Only those pair sites whose polarizing strength exceeds a certain strength may be able to act as the active site.

REFERENCES

1. Yamaguchi, T., Sasaki, H., and Tanabe, K., *Chem. Lett.* 1017 (1973).

2. Yamaguchi, T., Nakano, Y., Iizuka, T., and Tanabe, K., *Chem. Lett.* 677 (1976).

3. Yamaguchi, T., and Hightower, J. W., *J. Amer. Chem. Soc.* **99**, 4201 (1977).

4. Poirier, R. H., Kahler, E. J., and Benington, F., *J. Org. Chem.* **17**, 1437 (1952).

5. Hightower, J. W., and Hall, W. K. *Chem. Eng. Progr. Symp. Ser.* **63**, 122 (1967).

6. Tench, A. J., and Nelson, R. L., *Trans. Faraday Soc.* **63**, 2254 (1967).

7. Flockhart, B. D., Mollan, P. A. F., and Pink, R. C., *J. Chem. Soc. Faraday Trans. 1* **71**, 1192 (1975).

8. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69**, 2117 (1965).

9. Peri, J. B., *J. Phys. Chem.* **69**, 211, 220, 231 (1965).

10. Lunsford, J. H., Zingery, L. W., and Rosynek, M. P., *J. Catal.* **38**, 179 (1975).

11. Rosynek, M. P., and Fox, J. S., *J. Catal.* **49**, 285 (1977).