

The Isomerization of Butenes over Doped Zinc Oxides

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The isomerization of butenes over cation-doped zinc oxides was investigated in order to elucidate the nature of the active sites and their catalytic behavior in the reaction. The effects of doping of zinc oxide with foreign cations, such as Ga^{3+} , Al^{3+} , and Li^+ , on the catalytic activity and the selectivity were observed. The results were discussed in terms of the acid-base character of $-\text{Zn}-\text{O}-$ pair sites. It may be said conclusively that the nature of the active sites as well as the electronic structures of the semiconductor surface are modified in the presence of the foreign cations so that the relative stabilities of the intermediate complex on these sites are affected.

INTRODUCTION

The isomerization of butenes has been frequently studied as a model reaction over various catalytic systems, such as metals (1) metal oxides (2), metal sulfides (3), metal hydrides (4), metal sulfates (5), and various metal complexes in homogeneous systems (6), as well as in heterogeneous systems like cation-exchanged zeolites (7) and ion-exchanged resins (8).

Using this model reaction, Foster and his co-workers attempted the first systematic approach and found a strong correlation between the catalytic properties and the acid-base character of the solid catalysts (9). They point out that the catalytic selectivities in the reaction are strongly linked to the acid-base properties of the catalysts. They interpreted the results in terms of two typical mechanisms, via the formation of the carbonium ion on acidic sites and that of the carbanion on basic sites. However, many semiconductive oxides, such as zinc oxide and nickel oxides, have been classified into non-acid-base type catalysts which have rather low activity and low selectivity. Subsequently,

many studies have been concerned with the detailed explanations of the catalytic behavior.

The first experimental report on the isomerization over zinc oxide was carried out at very high temperatures of $450 \sim 500^\circ\text{C}$ (2a) where side reactions, e.g., the dehydrogenation, the polymerization, and cracking, may be inevitable due to both the catalytic and the thermal processes. However, the isomerization reaction was recently found to proceed at lower temperatures over commercially available zinc oxide (10) and also over those prepared by the thermal decomposition of basic zinc carbonate in various atmospheres (11).

It has been widely recognized that zinc oxide alters its surface properties as well as the semiconductive properties very sensitively when a small amount of a foreign cation was added or when a gas molecule adsorbed. These findings led to the development of the electronic theory of catalysis (12). As for the structure sensitive behavior and the drastic impurity effect observed in the catalytic reactions, such as H_2 - D_2 exchange (13), CO-oxidation

(14), N₂O-decomposition (14a, 15), and alcohol-decompositions (16), several tentative explanations have been given on the bases of the so-called "valence control theory" (17) and of the participation of the electron or the positive hole in the catalysis.

Recently, Kokes and his co-workers have proposed that the isomerization of butenes over zinc oxide can be described by a π -allyl mechanism from the evidence of ir observations of the intermediate complexes (10, 18). The formation of a similar π -allyl species from propylene was also confirmed by ir evidence (19) and microwave spectroscopy (20). However, the active sites which can abstract the hydrogen atom from the olefins and stabilize the surface complexes have not been well characterized.

In this paper, the catalytic properties of the doped zinc oxides were studied in order to clarify the nature of the active sites over them.

EXPERIMENTAL

Two kinds of zinc oxide catalysts, i.e., ZnO(I) series and ZnO(II) series, were prepared from two different sources, basic zinc carbonate (5ZnO·2CO₃·4H₂O) and a commercially available zinc oxide (Kadox-25), respectively. The carbonate was decomposed by heating at 400°C in a air flow for 5 hr. The resultant oxide and Kadox-25, which was subjected to the same heat treatment, were impregnated with an aqueous solution of metal nitrate which contained a desired amount of the dopant cation. They were dried under an ir lamp and heated for 2 hr in a dry air flow at the melting point or at the decomposition point of the nitrate. Then they were further heated at 500°C for 3 hr. The pure zinc oxide was treated similarly to the modified catalysts using deionized water instead of the nitrate solution.

The catalytic activity of ZnO(I) series was tested in a microcatalytic flow reactor

which was connected to a vacuum system. The fresh catalyst was evacuated at 500°C for 3 hr and cooled down to the reaction temperatures. The reactant gas was diluted with nitrogen carrier gas and the effluent gas was analyzed by gas chromatography.

The catalytic behavior of ZnO(II) series were also studied in a closed circulation system. The catalyst was evacuated at 450°C and treated with oxygen at 100 Torr, and then it was evacuated again at 500°C for 3 hr.

RESULTS

(1) The Isomerization of *cis*-2-Butene over ZnO(I) Series

The kinetic behavior of the isomerization reaction followed in the circulation system was found to be described by a first order rate equation, which will be described in section (2), though a simple adequate rate expression applicable over the whole range of conversion could not be found. Thus, it was assumed that a measure of the catalytic activity of a sample catalyst can be tentatively approximated by the rate constant of first order rate equation applied for the flow system, viz.,

$$\ln \frac{1}{1 - \alpha} = (W/F)k' = (S/F)k, \quad (1)$$

where α denotes the conversion of the reactant in the flow reactor, W (g) denotes the weight of the catalyst, S (m²) denotes the surface area of the catalyst, and k' (min⁻¹ ml g⁻¹) and k (min⁻¹ ml m⁻²) denote the rate constants, respectively. The flow rate, F (ml min⁻¹), was fixed in this experiment. The relative catalytic activity per unit surface area can be represented by k . The initial selectivity of the catalyst between the *cis-trans* isomerization and the double-bond migration was defined by the initial ratio of the two product isomers (*trans*-/1-)₀ = (₀*S*₁^t)₀, obtained by the extrapolation of the isomer-ratio to time zero.

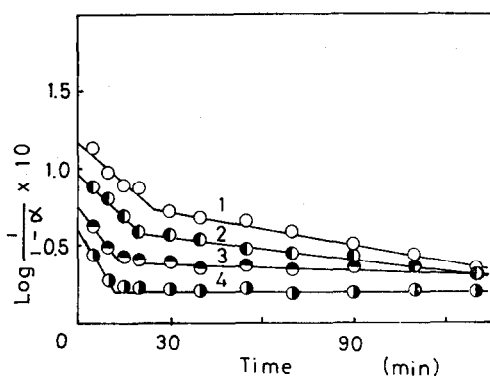


FIG. 1. Change in the catalytic activity during a run (flow system). Catalyst: ZnO(I)-Ga-02 200 mg. *cis*-2-Butene: 1 ml (NTP)/min. N₂: 10 ml (NTP)/min. Temperature: (1) 350°C; (2) 335°C; (3) 320°C; (4) 300°C.

Figure 1 shows the activity change during the constant flow experiment. The activities of ZnO(I) series catalyst which were prepared in the air flow usually decreased rapidly in the early stage of the reaction and then either decreased slowly or reached a constant level. Similar features of the two-stage decrease in the deactivation curve were observed over zinc oxide prepared in a nitrogen flow (11) and reported with zinc sulfide (3*b*, 3*c*) and with silica-alumina (21). However, when zinc oxide was prepared in a CO₂ flow or under

a vacuum from the carbonate, the initially decreased activity was restored during the reaction continued (11*a*).

Since the plots of $\log 1/(1-a)$ vs t seem to be approximated by the two straight lines as shown in Fig. 1, the two tentative values for the initial activity, $(k_T)_0$ and $(k_{II})_0$, can be obtained by extrapolating both sections of the curves to time zero. Another initial value $(k_I)_0$ can be evaluated as follows:

$$(k_I)_0 = (k_T)_0 - (k_{II})_0 \quad (2)$$

It may be assumed that the initial activity $(k_I)_0$ represents the catalytic activity due to the site which may be active but easily poisoned in the early stage of a run, and another value $(k_{II})_0$ represents the activity ascribed to another site which may be less active but rather poison-resistant. The total apparent activity can be given by $(k_T)_0$. The catalytic selectivity indicated by the ratio (*trans*-/*l*-) = (S_1^t) changed monotonously with conversion. The initial selectivity $(S_1^t)_0$ also was determined by the extrapolation of (S_1^t) to time zero. These kinetic values are listed in Table 1.

It is obvious from Table 1 and Fig. 2 that the catalytic activity for the isomerization increased by the doping with the

TABLE 1

Kinetic Parameters for the Isomerization of *cis*-2-Butene over ZnO(I) Series (Flow System)

Catalyst ^a	Surface area (m ² /g)	Rate constant ^b × 10 ² (ml min ⁻¹ m ⁻²)			Selectivity ^b (S_1^t) ₀	Activation energy ^c (kcal/mol)		
		$(k_T)_0$	$(k_I)_0$	$(k_{II})_0$		E_T	E_I	E_{II}
ZnO-pure	11.3	4.98	2.02	2.96	2.8	24.7	30.5	23.2
ZnO-Ga-02	15.9	5.07	2.45	2.62	3.2	12.8	7.3	18.6
ZnO-Ga-10	19.9	8.22	4.05	4.17	3.2	21.5	16.3	24.7
ZnO-Al-02	12.5	5.89	2.39	3.60	3.0	13.7	15.6	11.7
ZnO-Al-10	13.2	7.58	3.89	3.69	3.2	15.6	15.2	14.8
ZnO-Li-02	13.1	2.98	1.68	1.32	1.8	24.3	—	20.5
ZnO-Li-10	13.1	0.97	0.25	0.72	1.2	45.7	—	30.4

^a ZnO-Ga-10 indicates the catalyst doped with 10 atom% of Ga³⁺ and similarly with others.

^b The values for the reaction temperature at 320°C.

^c The range of the reaction temperature, 300 ~ 350°C.

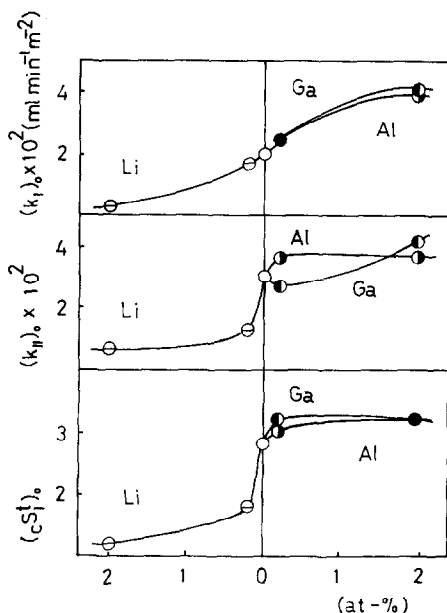


FIG. 2. Effect of doping on the catalytic activity and the selectivity over ZnO(I) series (flow system). Reaction: 320°C.

trivalent cation, Ga^{3+} or Al^{3+} , while it decreased by the doping with the monovalent one. The apparent energy of activation was also affected by these dopings. The initial selectivity also showed a tendency of an increase by the doping with the trivalent cations and of a decrease by the doping with the monovalent one. The value of the activation energy for pure zinc oxide obtained in the range 300 ~ 350°C deviated from a reported value of 18 kcal/mol (10). This discrepancy might be attributed to the difference in the catalyst preparation and/or the reaction temperature. Figure 3 shows the plots of $\log A$ vs E_{II} for the more stable sites corresponding to $(k_{\text{II}})_0$. It is apparent that a compensation effect is observed over these modified zinc oxide catalysts.

(2) The Isomerization of Butenes over ZnO(II) Series

The initial rate of the isomerization of *cis*-2-butene observed in the circulation system seemed to depend slightly on the

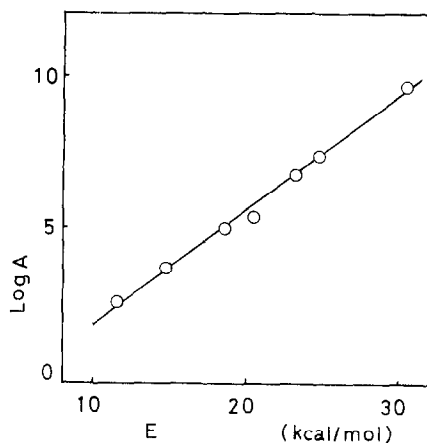


FIG. 3. Correlation between $\log A$ and E_{II} for the isomerization of *cis*-2-butene over ZnO(I) series.

initial pressure, but at the later stage, the rate showed a pressure-dependent behavior. The order of the reaction appeared to be about 0.25 ~ 0.3 with respect to the reactant. A similar feature was also reported by Kokes (10). These facts suggest that some of adsorbed species may retard the reaction. However, in this case, a Langmuir type rate expression was found to be inapplicable. As shown in Fig. 4, the kinetic behavior could be approximately described

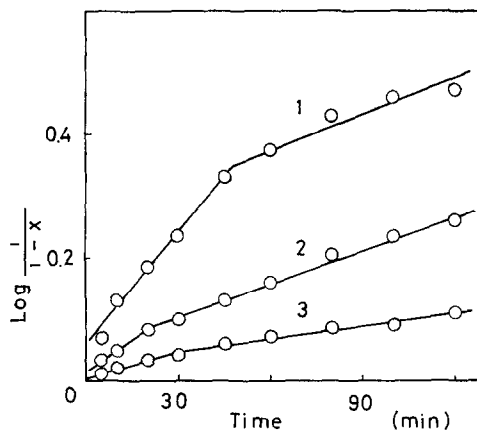


FIG. 4. Plots of the first-order rate equation (circulation system). x : Total conversion of the reactant *cis*-2-butene. Temperature: 100°C. Initial pressure of *cis*-2-butene: 100 Torr. Catalyst: 300 mg, (1) ZnO-Ga-02; (2) ZnO-pure; (3) ZnO-Li-02. ZnO(II) series.

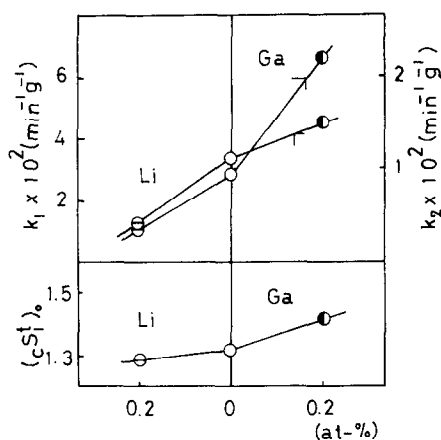


FIG. 5. Effect of doping on the catalytic activity and the selectivity over ZnO(II) series (circulation system). Reaction: 100°C.

by the first order rate equation, though the plots seem to consist of two straight lines. Thus, the catalytic activity of ZnO(II) series can be represented by the rate constants, k_1 and k_2 , corresponding to each slope of a run. The initial selectivity was indicated by the initial ratio ($trans-1-$)₀, which was obtained by extrapolating to time zero.

The effects of doping of ZnO(II) with foreign cations are shown in Fig. 5. This result shows that the *n*-type property enhances the catalytic activity and favors the *cis-trans* isomerization rather than the double-bond migration. These observations

are consistent with the above results with ZnO(I) series in the flow system. Similar tendencies in the doping effect on the isomerization reaction were also found for ZnS (3a, 22) and for ZnO at higher temperatures (2a).

(3) TPD of Butenes from ZnO(II) Series

Table 2 and Fig. 6 show the result with a temperature-programmed desorption (TPD) of butenes from the pure and the modified surfaces of ZnO(II) series. The following facts suggest that two types of adsorption sites may be present over these catalysts: (1) a large peak of desorption at about 80°C was observed; (2) after the desorption was completed below 100°C and the desorbed butenes were removed with a liquid nitrogen trap, the second peak of desorption from stronger sites appeared at about 160°C, as shown in Fig. 6. Other minor peaks of desorption were detected up to 400°C but they were negligibly small except that of ZnO(II)-Li-10. The amounts of butenes desorbed from the weaker site of adsorption were more than 87% of those of the initially adsorbed *cis*-2-butene at room temperature. The ratios of the isomers ($trans-1-$) in the first desorption from the pure-ZnO and the Ga-doped ones were nearly equal to those of the equilibrium, while the ratios of those from the Li-doped ones were considerably low. These

TABLE 2
TPD of Butenes from ZnO(II) Series

Catal.	Adsorption ^a × 10 ⁶ (mol/g)	Desorption (1) ^b × 10 ⁶		Desorption (2) ^b × 10 ⁶	
		(mol/g)	(t/1)	(mol/g)(%)	(t/1)
ZnO-pure	35.6	32.6	10.0	3.0 (8.5)	12.6
ZnO-Ga-02	37.6	32.7	9.9	4.7 (12.9)	11.0
ZnO-Li-02	21.6	20.4	6.3	1.2 (5.4)	6.7
ZnO-Li-10	7.04	6.19	—	0.85 (12.1)	—

^a *cis*-2-Butene was adsorbed to the equilibrium at room temperature and preevacuated for over 30 min before desorption started.

^b The amount of butenes desorbed in the temperature range: desorption (1), up to 100°C; desorption (2), 100 ~ 400°C.

values of the desorbed butenes in TPD process did not correspond to the observed selectivity (${}_cS_1'$)₀ in the catalysis. However, the general tendency that the doping with the trivalent cation increases the ratio and the doping with the monovalent one acts reversely was consistent with those for the kinetic selectivity.

(4) Adsorption of NH_3 and CO_2

It was found that over these doped zinc oxides, both acid and base, e.g., CO_2 and NH_3 , were adsorbed at the reaction temperatures. These sites for the adsorption seem to be ascribed to basic and acidic sites over the surface, respectively. Table 3 shows that the both sites of acidic and of basic nature coexist over the pure and the modified zinc oxide catalysts and that the number of them is comparable with each other. Furthermore, it should be noted that they are in the same order of magnitude with those of the butene adsorption. The number of the acidic sites seemed to increase slightly by doping with trivalent cations but evidently seemed to decrease by doping with the monovalent one. On the other hand, the number of

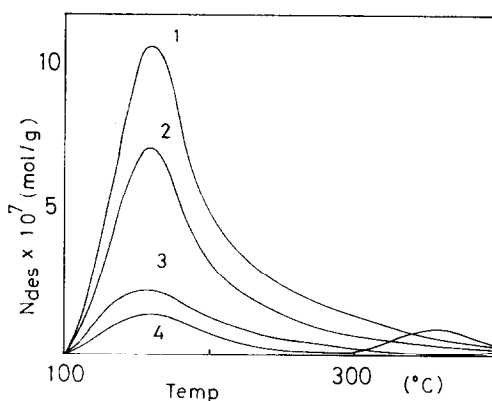


FIG. 6. TPD spectra of butenes from the stronger sites over ZnO(II) series. (1) ZnO-Ga-02; (2) ZnO-pure; (3) ZnO-Li-02; (4) ZnO-Li-10. The samples were predesorbed at 100°C to remove the species on the weaker sites. See text.

the basic sites seemed to decrease by either doping.

The effect of the preadsorption of NH_3 on the successive adsorption of CO_2 was in the following order: ZnO(II)-Ga-02 > ZnO(II)-pure > ZnO(II)-Li-02, while the effects of the preadsorption of CO_2 on the adsorption of NH_3 were hardly varied by the different dopings. This indicates that the acidic nature of the surface sites can be

TABLE 3
Adsorption of NH_3 and CO_2 over ZnO(II) Series

Pretreatment		Adsorption		Amount adsorbed $\times 10^5$ (mol/g)		
		Pressure (Torr)	Temperature (°C)	ZnO-Li-02	ZnO-pure	ZnO-Ga-02
Evacuation 400°C	NH_3	15	100	2.89	4.43	4.92
	CO_2	15	100	2.86	3.64	3.21
	CO_2	15	150	2.43	2.90	2.62
	CO_2	15	180	2.23	2.27	2.12
Evacuation 400°C	CO_2	15	150	2.41	2.84	2.62
	Preadsorption (NH_3)* (%-decreased)	CO_2	15	150	1.75 (28%)	1.26 (56%)
Evacuation 400°C	NH_3	15	100	2.90	4.42	4.91
	Preadsorption (CO_2)* (%-decreased)	NH_3	15	100	2.25 (22%)	3.43 (22%)

* Preadsorption was carried out at the adsorption temperature and evacuated.

modified rather easily by cation doping, but the basic nature is more stable against it.

Table 3 also shows that either adsorption, NH_3 on the acidic sites or CO_2 on the basic sites, was partly poisoned by the preadsorption of the other. This suggests that they might consist of a sort of "acid-base pair site." These features of adsorption are consistent with the result that the catalytic activity for the isomerization over ZnO and ZnS was partly poisoned by either of the preadsorptions of NH_3 or CO_2 , but they could not poison completely (3b, 11b, 22).

DISCUSSION

A lot of works has been published concerning the catalysis over various semiconducting oxides. In most cases the catalytic behavior was interpreted in terms of its semiconducting properties (13-16, 23). It is well known that both electronic conductivity (24) and the work function (25) were drastically affected by adsorption of CO, H_2 , and O_2 over the modified surfaces of the semiconductor catalyst. In this view, it should be noted that when butene was introduced over zinc oxide, the conductivity increased instantaneously (26). This fact may suggest that the adsorbed butenes can donate its electron partly to the surface, and in this sense, the catalytic behavior in the isomerization might directly depend on the electronic state of the surface. The results given in Table 1, Figs. 2 and 5 confirmed this.

The free electron concentration in the zinc oxide catalysts was expected to increase by doping with the trivalent cation and to decrease by those with the monovalent one, if the doped cations were substituted for the lattice zinc, though the heat treatment was carried out at the rather low temperature of 500°C. This was confirmed over the modified catalyst of ZnO(I) series by measuring the electron conductivity (26) and by the hydrogen-

evolution method (27, 28). A similar effect of doping on the conductivity of zinc oxide, which was calcined at low temperature, was also reported by Aigueperse and Teichner (29).

The results given in Table 2 and Fig. 6 show evidently that the numbers of adsorption sites for butenes were remarkably influenced by the presence of foreign cations, and further that the catalytic activity and the selectivity also depend on their modified electronic property. Therefore, it may be stated that these results may imply a significant role of the free electrons in the formation of the surface intermediate complexes and their stability on the active sites. However, no strong correlations between the catalytic activity and the free electron concentration determined by the hydrogen evolution method could be proved (28). This may stem from the difference in the properties of the surface and those for the bulk.

If the reaction temperatures applied for ZnO(II) or ZnO(I) series were taken into account, one may assume that the active sites for the isomerization reaction may be ascribed to the stronger adsorption site, although the contribution of the weaker site could not completely be ruled out at present. However, the peak of the desorption from the stronger sites did not appear to shift by the dopings, and thus the relative stability of the surface complexes on this site may be little affected. Consequently, the doping effect observed in the catalytic parameters and the TPD results may suggest that the process of desorption from the stronger sites is not the rate-controlling step of the reaction.

Dent and Kokes have postulated a catalytic mechanism for the isomerization of butenes over pure zinc oxide via the formation of the π -allyl species on a sort of $-\text{Zn}-\text{O}-$ pair site as shown in Fig. 7 (10). They pointed out that since the two forms of the π -allyl species, anti-form (the precursor for *trans*-2-butene) and syn-form

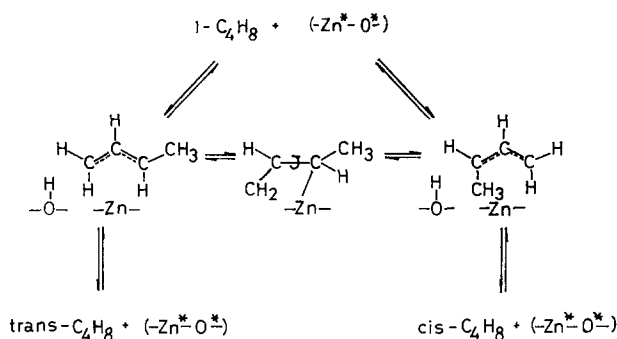


FIG. 7. Proposed mechanism for the isomerization of *n*-butenes over zinc oxide catalyst (Kokes).

(that for *cis*-2-butene), are presumably attached on the electro-positive zinc on the surface, these π -allyl species may have a carbanionic character. The presence of the surface oxygen for the abstraction of hydrogen from butenes was confirmed by ir evidences (18, 19). However, the nature of the pair site was still obscure.

According to the classical acid-base interpretation of the isomerization of butenes, zinc oxide was classified into the nontypical acid-base catalysts. The presence of weak acid sites corresponding to the acid strength, $H_0 = +1.5 \sim +6.8$, was reported over pure zinc oxide (30, 31). Since it has neither strong acid sites nor strong base sites, the classical carbonium ion or the classical carbanion could unlikely be formed.

The coexistence of the adsorption sites for NH_3 and CO_2 and their correlations with the catalytic behavior indicate that the active sites for the isomerization may have the nature of an acid-base pair sites. The functions of the anionic oxygen which can abstract hydrogen from the adsorbed butenes and those of the cationic zinc which can interact with the π -allyl species might be under the influence of the electronic structure of the semiconductor surfaces. The formation of the effective pair sites and their behavior may be controlled by doping with foreign cations.

The selectivity observed in the isomeriza-

tion may depend on the relative stabilities of the two forms of the π -allyl species and on the kinetic barrier between them. If the free electrons in the surface layers could participate to form the σ -alkyl species which was postulated in the interconversion between the two π -allyl species, or could control the barrier of the interconversion, the selectivity change caused by the cation doping could be explained.

Teichner and co-workers reported (29) that, in the case of the hydrogenation of ethylene over cation-doped zinc oxides, no effect of doping could be observed, and they interpreted the result that the surface complex formed in a type of covalent character and the electron transfer to the conduction band might not be required. The difference in the observed doping effects between the two catalytic systems might stem from the differences in the mechanisms, including those of the intermediate surface complexes and the rate-determining steps.

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