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NOTE

Heterogeneous Catalysis by Metal Chelates—Isomerization of Butenes

Little is known about the catalytic properties of metal chelates (*1*), especially with respect to the effect of the central metal ion in heterogeneous reactions (*1*b). We have found that bis(acetylacetonato)-palladium mounted on silica gel is an efficient catalyst for butene isomerization and that the catalytic activity changes remarkably with the central metal ion.

Bis(acetylacetonato)palladium [Pd-$(acac)_2$] was prepared by following the reported procedure (*2*). (*Anal.* Calcd: C, 39.43; H, 4.60. Found: C, 39.17; H, 4.54.) The chloroform solution of this chelate was impregnated on silica gel (surface area, 830 m^2/g) [$Pd(acac)_2$-SiO_2]. After the evacuation of $Pd(acac)_2$-SiO_2 (200–400 mg) at 61.5°C for 0.5 hr, the substrate was introduced and gas-chromatographic analysis was made intermittently to pursue the reaction occurring in a circulating system which was the same as previously described (*3*). The catalytic activity of $Pd(acac)_2$-SiO_2 for *cis*-2-butene isomerization increased with the amount of the supported $Pd(acac)_2$ (given in parentheses) in the ratio of 1 (0.02 wt%):6 (0.2):20 (1.0), indicating that the activity is not due to the carrier but to the metal chelate.

Typical results of 1-butene isomerization over $Pd(acac)_2$-SiO_2 (1.0 wt%, 200 mg) are shown in Fig. 1. Since a change in the starting butene isomer had no essential effect on the results, the more reactive 1-butene was used in the experiments shown in Fig. 1. The reactant gas was introduced after evacuation of the catalyst for 1 hr at 61.5°C. The conversion increased linearly with the reaction time (A) Fig. 1. The initial ratios of the isomerized 2-butenes were about unity for all experiments. The second run was made after the subsequent evacuation for 0.5 hr at 61.5°C and slight deactivation occurred (B). Evacuation of the catalyst at 120°C for 1 hr lowered the activity (C). Treatment with hydrogen (circulated) at 100°C for 1 hr caused nearly complete deactivation (D), which was probably due to the poisoning effect of water, as shown below. The catalyst, reduced at 110°C in the stream of dry hydrogen, gave a rather high activity

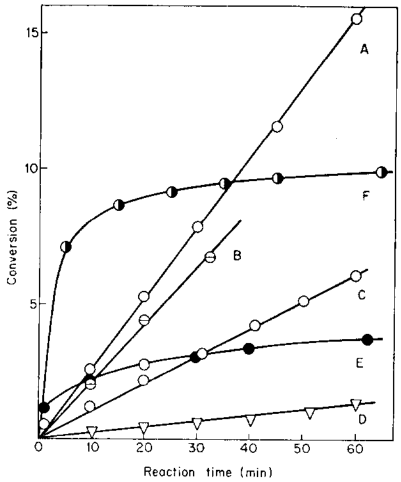

FIG. 1. Isomerization of 1-butene over Pd-$(acac)_2$-SiO_2 at 61.5°C: A, after the evacuation for 1 hr at 61.5°C; B, after the evacuation subsequent to run A for 0.5 hr at 61.5°C; C, after the evacuation for 1 hr at 120°C; D, after the circulation of hydrogen at 100°C for 1 hr; E, after the treatment in the stream of dry hydrogen for 3 hr at 110°C; F, after the same treatment with (E), but the time of the first sampling was delayed intentionally.

but was deactivated immediately after the first sampling (E). This abrupt and efficient deactivation of the reduced catalyst was reproducibly observed after the first sampling, regardless of its time (F). Sensitive poisoning effects of water and oxygen were ascertained for metallic palladium on silica gel by separate experiments. By contrast, the chelate catalyst was not affected by either water or oxygen which was added intentionally. The total pressures of butene plus nitrogen were kept a little lower than atmospheric pressure in the ordinary experiments. It was intended to suppress the catalytic activity of the metal, which might be formed during the reaction, by introducing the small amount of water and oxygen into the reaction system through the gas-sampling syringe. However, this low total pressure did not result in any essential difference for the fresh chelate catalyst from that with more than atmospheric pressure. As for the moderately decomposed products of $Pd(acac)_2$ chelate such as palladium oxide, they were less active than the chelate itself. For example, when evacuation of the chelate catalyst was made for 4 hr at 61.5°C, the reaction rate decreased down to one-half. It is, therefore, certain that the observed activity of fresh catalyst is due to the metal chelate and is indifferent to metal or oxide produced by decomposition of the chelate.

The effect of the central metal ion species on the catalytic activity for *cis*-2-butene isomerization is summarized in Table 1. Metal chelates prepared according to the reported procedures were $Ni(acac)_2$ (*4*), $Pt(acac)_2$ (*5*), $Ni(dmg)_2$ (*6*), $Cu(dmg)_2$ (*6*), $Pd(dmg)_2$ (*7*), and $Pt(dmg)_2$ (*7*), where acac and dmg mean acetylacetonato and dimethyloximato, respectively. They were confirmed by carbon, hydrogen, and nitrogen analysis. Metal chelates were impregnated on silica gel from chloroform solutions. The supported metal chelates exhibited the same color as their chloroform solutions. The color of $Pt(dmg)_2$, for instance, was grayish violet in the crystalline state but yellowish orange in the chloroform solution or on silica gel. The color of all catalysts except for $Pd(acac)_2$-SiO_2 was unchanged during the reactions. In the case of $Pd(acac)_2$-SiO_2, the color changed slowly from yellowish orange to dark green, which was thought to be due to some complex formation with butene. The rate constants were calculated by assuming first order reactions. The initial ratios of *trans*-2-butene to 1-butene produced were about 4.5 for $Pd(acac)_2$-SiO_2 and between 1 and 3 for other catalysts. It may be worthwhile to mention that the acidity of silica gel cooperates with the metal chelates for the catalytic action, because $Pd(acac)_2$ mounted on Na-exchanged silica gel showed much less activity, as given in Table 1.

Table 1 shows that the Pd^{2+} chelates are the most active catalysts and the Pt^{2+} chelates are also active, whereas the Ni^{2+}

TABLE 1

THE CATALYTIC ACTIVITIES OF METAL CHELATES OF *cis*-2-BUTENE ISOMERIZATION AT 61.5°C

Catalyst	Color of catalyst	Rate constant ($g^{-1}min^{-1}$)
$Pd(acac)_2$-SiO_2	Yellowish orange	4.3×10^{-3}
$Pd(acac)_2$-SiO_2-Na[a]	Yellowish orange	2.1×10^{-4}
$Pt(acac)_2$-SiO_2	Pale yellow	2.3×10^{-4}
$Ni(acac)_2$-SiO_2	Greenish yellow	$\sim 8 \times 10^{-6}$
$Pd(dmg)_2$-SiO_2	Yellowish orange	4.9×10^{-4}
$Pt(dmg)_2$-SiO_2	Yellowish orange[b]	1.0×10^{-4}
$Ni(dmg)_2$-SiO_2	Yellowish orange[b]	$\sim 8 \times 10^{-6}$
$Cu(dmg)_2$-SiO_2	Brown	$\sim 3 \times 10^{-6}$
SiO_2	White	8×10^{-5}
SiO_2-Na[a]	White	$\sim 2 \times 10^{-5}$

[a] Silica gel was exchanged with sodium hydroxide aqueous solution.

[b] The color turned to red by the water adsorption.

and Cu^{2+} chelates are scarcely active. 1-Butene isomerization was also examined for some of these catalysts and almost the same relative rates were obtained. This trend in activity among metal ion species must be associated with the intrinsic properties of the metal ion, because the amount of metal chelates on the surface is the same for all the catalysts and the trend is the same for both ligands.

The acidity can be quantitatively represented by a dual scale of hardness and softness of metal ions (*8*). For the isomerization of 2-butenes over a series of metal sulfates, the activity and selectivity were well correlated with the hardness or the electronegativity of metal ion, x_i (*3*). This fact was reasonably explained in terms of the strength of the protonic acid which increases with the electronegativity of the metal ion. However, the high activities of the Pd^{2+} and Pt^{2+} chelates and the diminished activities of the Ni^{2+} and Cu^{2+} chelates for butene isomerization cannot be similarly explained, because x_i is only slightly different: Pt^{2+} ($x_i = 7.3$); Pd^{2+} (7.5); Cu^{2+} (7.2); and Ni^{2+} (6.9). On the other hand, the softness scale, Y, of these ions is closely correlated with the catalytic activity: Pd^{2+} ($Y = 4.3$) and Pt^{2+} (4.8) as compared to Ni^{2+} (2.8) and Cu^{2+} (2.9) (*8*).

Soft acids should show a stronger interaction with soft unsaturated compounds. It is well known that Pd^{2+} and Pt^{2+} form complexes with olefins and catalyze olefin reaction in homogeneous systems (*9*). Therefore, isomerization of butenes over soft metal chelates does not proceed through the protonic mechanism but through some coordination complex as a result of the soft–soft interaction between the reactant and the catalyst.

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