Supported K-salts as a New Solid Base Catalyst

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A highly basic solid catalyst was obtained by dispersing potassium salts such as KNO_3, K_2CO_3 over alumina at the surface density of 10 -15 × 10^{18} K^+ ions m^{-2} and activating them at 773 -873 K in vacuo; the activity for the double bond isomerization of cis-but-2-ene of thus obtained catalysts was one order of magnitude higher than that of MgO, a typical solid superbase.

Many types of solid acids including solid superacid have been developed and used for industrial applications.[1] Although not so many works on strong solid base catalysts were reported, it is expected that the development of a wide variety of solid bases has an increasing importance for fine chemical industries; one example can be seen in the double bond isomerization of 5-vinyl-2-norbornene to 5-ethylidene-2-norbornene using superbasic $Na/NaOH/Al_2O_3$.[2] Strong solid bases were synthesized by combining low valent lanthanide species and zeolites from liquid ammonia solution.[3] Extremely strong solid bases were also prepared from the combination alumina with ammoniacal solution of potassium ($K(NH_3)/Al_2O_3$) or with potassium amide (KNH_2/Al_2O_3).[4] Application of solid bases to organic reactions has recently been reviewed.[5]

We have prepared catalysts derived from K-salts dispersed on various supports including alumina (JRC-ALO-4, SA = 177 m^2 g^{-1}), silica (Fuji-Davison Type ID, SA = 299 m^2 g^{-1}), titania (JRC-TIO-4, SA = 50 m^2 g^{-1}) and zirconia (Torayceram, SA = 120 m^2 g^{-1}), and assessed their basic properties by the isomerization of butenes at various K contents. Temperature-programmed-decomposition (TPD) technique was used to investigate the generation process of basic properties of thus obtained catalyst.

Potassium salts-derived catalysts were prepared by grinding supports with K-salts (K_2CO_3, KNO_3, KOH and $KHCO_3$) at given weight ratios with a small amount of water. The paste was dried at 383 K overnight. A glass, closed recirculation reactor connected to a gas chromatograph (GC) was employed for the isomerization of *cis*-but-2-ene (*cis*-B). Initial pressure of the reactant was 7.3 kPa (50 Torr) and the reaction was performed at 273 K. A 2.5 - 10 mg portion of the catalysts were used. The catalytic activity was evaluated from the initial rates and expressed as mmol g^{-1} min^{-1}. Prior to reactions, the catalyst was evacuated at desired temperatures (typically at 773K). A TPD procedure can be found elsewhere.[6]

In the *cis*-B isomerization, the initial *trans*-B/1-B ratio was below 0.5 and the reaction was strongly retarded by CO_2 which strongly suggests the reaction is a base-catalyzed reaction. Unsupported K-salts was totally inactive. Loading of K-salts onto an alumina support enhanced the conversion of *cis*-B remarkably. At the same evacuation temperature and reaction conditions, the catalytic activity of MgO which is known to be a typical solid base was about one tenth of that of 20wt% K_2CO_3/Al_2O_3 (12.9×10^{18} K^+ ions m^{-2}; abbr. 12.9-KCA). It was found that the 12.9-KCA sample has an ability of changing the acidic, colorless form of 4-chloroaniline (pKa=26.5) to its basic color (pink).

The nature of support affects strongly the catalytic activity. Figure 1 compares the catalytic activities of alumina and zirconia supported K-salts catalysts with the same surface density of 12.9 ×10^{18} K^+ ions m^{-2}. A combination of K-salts with alumina was more effective than with zirconia to create a high catalytic activity. K_2CO_3 loaded on SiO_2 and TiO_2 did not show any activity for the reaction.

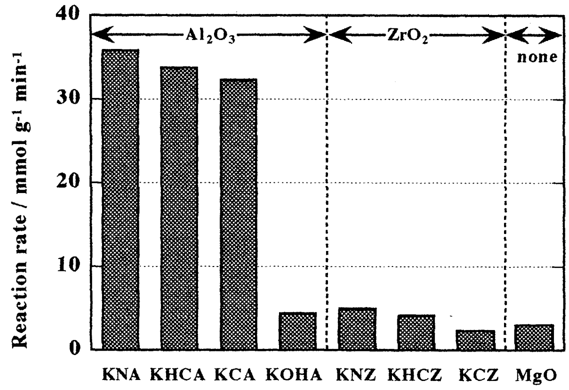

Figure 1. Catalytic activity of alumina- and zirconia-supported potassium salts (12.9 × 10^{18} K^+ ions m^{-2}) for isomerization of *cis*-but-2-ene at 273 K.

Basic properties depend not so strongly on the staring K-salts. Figure 1 also summarized the results. With the same K^+ ion density of 12.9 × 10^{18} K^+ ions m^{-2}, KNO_3/Al_2O_3 (KNA) and $KHCO_3/Al_2O_3$ (KHCA) exhibited similar activity to KCA. This is also true on zirconia support, though the catalytic activities of the zirconia-supported catalysts exhibited lower than those of alumina-supported ones. A KOH/Al_2O_3 (KOHA) sample showed lower conversion for the isomerization of *cis*-B.

Since the dried sample may be a mixture of neutral potassium salt and support, decomposition of K salts is necessary to create basic properties. The degree of decomposition is a function of temperature. The effect of evacuation temperature on the catalytic activity is shown in Figure 2. Evacuation at 773 - 873 K (500 - 600 °C) gave the highest activity.

TPD profiles of 11.8-KCA, -KHCA, and -KNA are also shown in Figure 2. K_2CO_3, $KHCO_3$, and KNO_3 on alumina seem to decompose in two steps. The generation of the catalytic activity coincides with the decomposition of the first step and not with the second step. It should be pointed out that the TPD profiles of KCA and KHCA are the same and this indicates the precursor of decomposing compounds is the same regardless the starting carbonates.

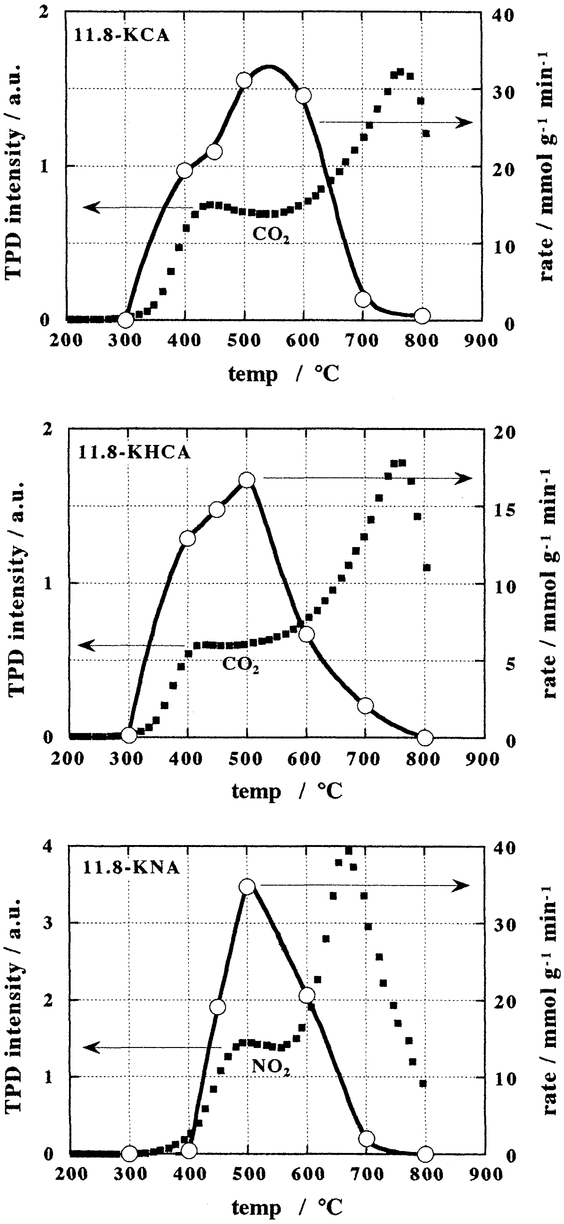

Figure 2. Change of catalytic activity (-○-) by evacuation temperature and TPD profiles (■) of alumina-supported potassium salts. Alumina used in KHCA is different from that used in KCA and KNA.

A two step decomposition process suggests the existence of two types of carbonates or nitrates. The decomposition temperature of neat K_2CO_3 and $KHCO_3$ exhibits over 1073 K (800 °C) and that of KNO_3 is over 973 K (700 °C). A high temperature branch in the two step decomposition found in the TPD profiles of 11.8-KCA, -KHCA, and -KNA may correspond to the decomposition of the bulk potassium salts. Loading of these salts on support may enhance the decomposition and hence lower the decomposition temperature slightly. A low temperature branch found around 673 - 873 K (400 - 600 °C) may be attributed to the decomposition of carbonate or nitrate species adsorbed on an alumina surface. Lower decomposition temperature suggests the interaction of these species and counterparts (potassium cation and alumina surface) is weak. During preparation processes, a part of potassium salts is dispersed dissociatively to yield adsorbed or ion exchanged K^+ and adsorbed carbonate or nitrate species. Thus the decomposition starts from the species bound weakly with K^+ cations. After this decomposition, K^+ cations are left on the alumina surface and contribute to create the basic sites, though a picture of active species can not be drawn yet.

It is speculated that K^+ cations involved in active sites are lost by the reaction with alumina at elevated temperature (over 873 K) and the catalytic activity decreased. Around this temperature, the decomposition of bulk potassium salts may start, however, liberated K^+ cations can not participate to create active sites because of the reaction with alumina surface. Efforts have been paid to evidence the surface reaction of K^+ cations by using XRD and FT-Raman spectroscopy but not successful yet.

When the K^+ ion density of 10 - 15 $\times$ 10^{18} K^+ ions m^{-2} has been dispersed on the surface of the alumina support, optimum activity was obtained. This value corresponds to the amount of potassium oxide that covers the support surface two-dimensionally. Higher amount of loading may result in agglomeration of active oxide phase and hence lower the surface area of active components and lower catalytic activity.

It is noteworthy to point out that a high catalytic activity can be obtained by the heat treatment at relatively mild temperature under inert atmosphere, though typical strong solid base such as MgO and CaO is necessary to elevate temperature to 900 - 1100 K to create its strong basic properties.

The catalyst is very active not only to the isomerization of *cis*-but-2-ene, but to the double bond isomerization of 3-methyl-but-1-ene, propa-1,2-diene to methylacetylene, and α-pinene to β-pinene. Details will be described elsewhere.

References and Notes

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