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CATALYTIC ACTIVITIES OF ALKALINE EARTH METAL OXIDES FOR ISOMERIZATIONS OF 2-PINENE AND 2(10)-PINENE

Ryuichiro OHNISHI* and Kozo TANABE**

* Research Institute for Catalysis, Hokkaido University, Sapporo 060

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

The isomerization of 2-pinene or 2(10)-pinene over evacuated MgO, CaO, SrO and BaO catalysts was carried out at room temperature or 150°C. All catalysts were found to exhibit extremely high selectivities for the formation of 2(10)-pinene or 2-pinene. The highest activity was observed over SrO, where the isomerization took place at room temperature and attained its equilibrium in only 15 min.

The isomerization of 2- or 2(10)-pinene is known to be catalyzed by various solid acids such as mineral clays,1) titanium oxide,2) alumina,3) silica-alumina,2) and metal sulfates.4) However, over the solid acid catalysts are formed the diversified products such as camphene, 1,7,7-trimethyl-tricyclo[$2.2.1.0^{2,6}$] heptane, p-mentha-1,8-diene (limonene), and p-cymene. In the present work, we examined whether the isomerization be catalyzed by solid bases and what kinds of products are formed over basic catalysts. Alkaline earth metal oxides were used as basic catalysts, since they were found recently to show strongly basic character and high catalytic activity for the isomerization of 1-butene when calcined in vacuo.5)6)

2- and 2(10)-pinene were purified from turpentine oil (reagent of Wako Pure Chemical Co.) and crude 2(10)-pinene (Takasago Perfumery Co.) by preparative gas chromatography (Perkin-Elmer F-21) with a column containing 20% polyethylene glycol 1500 on chromosorb W and distillation over sodium under a stream of nitrogen. The purified materials were stored in sealed ampoules until use. Magnesium and calcium oxide catalysts were prepared by calcining the guaranteed reagents of MgO and CaO in vacuo at various temperatures in quartz tubes. Strontium and barium oxide catalysts were prepared similarly from their carbonates. The surface areas were determined by BET method using nitrogen. The catalysts prepared in vacuo were introduced into a reaction vessel containing pinenes through a breakable joint to prevent the contact with air. The reaction was started by putting the reaction vessel into an oil bath maintained at desired temperatures and operating by a magnetic stirrer. The reaction products were analyzed by a gas chromatograph with FID (Hitach-Perkin-Elmer F-6D), using a 45 m capillary column of Ucon LB-550-X. The amount (mole %) of each product was obtained by measuring each peak area with an integrator (DISC Co.).

The results on the isomerization of 2(10)-pinene over calcium oxide catalysts evacuated at various temperatures are shown in Fig. 1. The products distribution for the isomerization of 2-pinene including 98.2 mole % of 2-pinene, 0.5 of 2(10)-pinene, 0.8 of camphene, and 0.2 of limonene was found to be 95.9 mole %, 2.4, 0.9, and 0.4 respectively, under the same experimental conditions as in Fig. 1 except reaction time (46 hr). These results indicate that 2-pinene isomerizes to 2(10)-pinene, and vice versa. The equilibrium constant of 2-pinene to 2(10)-pinene obtained is ca. 0.03. The catalytic activity of CaO begins to appear when the catalyst is evacuated at 500°C, attains a maximum value at about 600°C and decreases on evacuation at higher temperatures. Since the surface areas of CaO evacuated at 400, 600, and 900°C are calculated to be 5, 3, and 0.6 m^2/g respectively, it is apparent that the pronounced increase in activity from 400 to 600°C is not caused by the change in surface area, though the activity decrease from 600 to 800°C seems to be due to the decrease in surface area. Very small amounts of camphene and limonene which were included originally in 2(10)-pinene did not react over CaO and remained almost constant independent of evacuation temperatures of the catalyst as shown in Fig. 1.

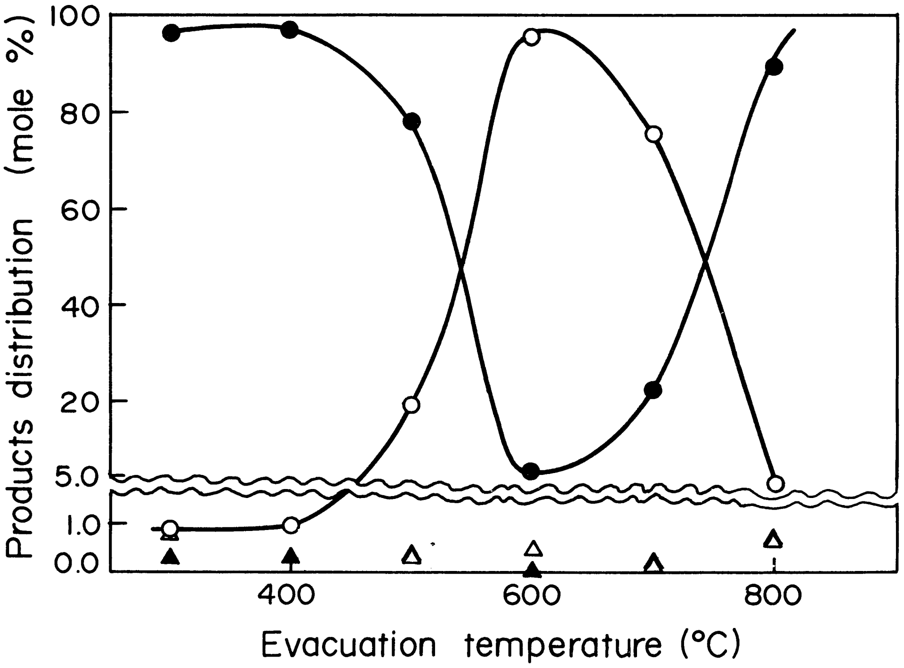

Fig. 1 Isomerization of 2(10)-pinene over CaO
Reaction temp.: 150°C, Reaction time: 1 hr,
Amount of pinene: 4 ml, Weight of catalyst:
ca. 2.5 g, Time of evacuation of catalyst:
5∿7 hr.

○: 2-pinene, ●: 2(10)-pinene, △: camphene,
▲: limonene

Figure 2 shows the catalytic activity and selectivity of SrO. In this case, a maximum activity was observed for the catalyst evacuated at about 1100°C. The relation of the change in activity with that in surface area is similar as in the case of CaO, since the surface areas of SrO evacuated at 500, 900, and 1300°C are 7, 5, and 0.4 m^2/g respectively. It is striking that 2(10)-pinene isomerizes almost completely to the equilibrium value of 2-pinene over SrO evacuated at 900-1100°C at room temperature in only 15 min. High selectivity for the isomerization between 2- and 2(10)-pinene is also seen in Fig. 2. The pronounced activity and selectivity have never been reported for any heterogeneous catalysts. The isomerizations over Pd/Al_2O_3, Raney Ni, etc. were carried out above 200°C.7) Even in the homogeneous catalysis using t-BuOK in DMSO, the half-life period of the reaction was reported to be several hours at 65°C.8)

The activity of MgO or BaO was much or slightly low respectively, compared to that of CaO. In the case of BaO, a maximum activity was observed for the catalysts evacuated at 1100-1300°C. The selectivities of MgO and BaO were almost the same as those of CaO and SrO.

Calcium, strontium, and barium oxides calcined in air are almost inactive, but they become highly active when calcined in vacuo at 600, 900, and 1100°C respectively. At those temperatures, the dissociation pressures of their carbonates are almost the same (several torrs)9) and hence, by evacuation at respective temperatures, almost all carbon dioxides are considered to be removed from strontium or barium carbonate and calcium oxide which contains carbon dioxides as an impurity.

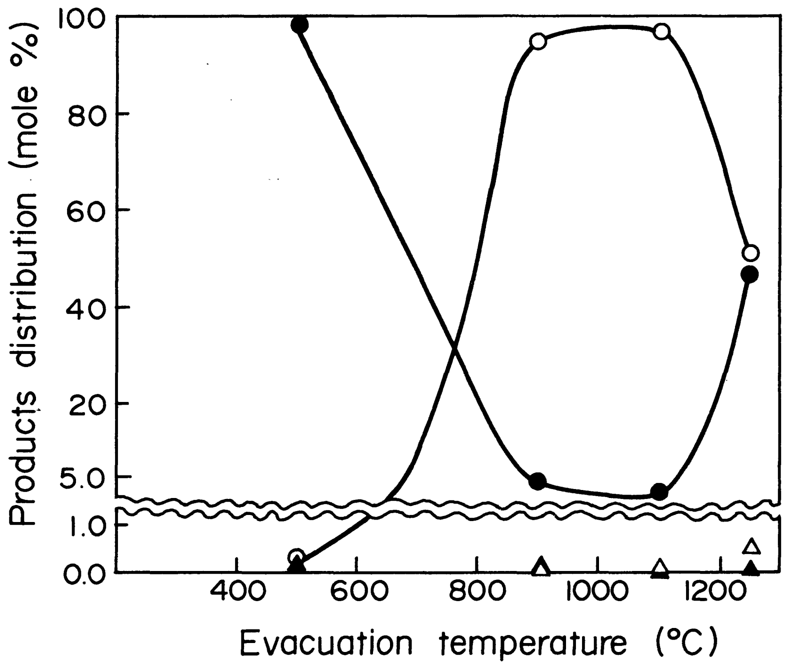

Fig. 2 Isomerization of 2(10)-pinene over SrO
Reaction temp.: room temp., Reaction time: 15 min,
Amount of 2(10)-pinene: 3 ml, Weight of catalyst:
ca. 2.5 g, Time of evacuation of catalyst: 5∿7 hr.
The same symbols are used as in Fig. 1.

The lattice oxygens (basic sites) of the alkaline earth oxides which appear by the removal of carbon dioxides[10)11)] seem to act as active sites for the isomerization.

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