Comparison of base-catalytic activity of MgO prepared by thermal decomposition of hydroxide, basic carbonate, and oxalate

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Abstract: To obtain more active MgO under atmospheric conditions, hydroxide ($Mg(OH)_2$), basic carbonate ($Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O$) and oxalate ($MgC_2O_4{\bullet}2H_2O$) were examined as starting material of MgO. Magnesium oxide samples were prepared from these materials by heating in air at various temperatures. Diacetone alcohol decomposition, a retro-aldol reaction, was performed to compare the activity of prepared MgO. The order of activity of MgO for the reaction was oxalate > basic carbonate > hydroxide, as starting material. The highest activity was given by heating at 773 K, and that was decreased gradually in higher temperatures in all samples. A clear relation was not observed between surface area or crystal size and catalytic activity.

Keywords: MgO, thermal decomposition, retro-aldol reaction.

1. Introduction

Alkaline earth metal oxides are well known as representative solid base. Particularly, MgO has much attention. Many research papers have been published concerning preparation, active site structure, and applications to many base-catalyzed organic reactions. Solid base catalysts have been applied to several C-C bond formation reactions, such as aldol reaction; these being important for synthesis of fine chemicals.

An active MgO has been prepared by decomposition of hydroxide of carbonate at higher temperatures under high vacuum or in an inert gas conditions. Magnesium oxide, which was the most active for 1-butene isomerization, was prepared by heating in vacuum at 973 K. Active sites on prepared MgO surface are strongly poisoned by H_2O and CO_2 in the atmosphere. The strong base sites, prepared in a vacuum or inert gas conditions, are not necessary for general organic reactions. Magnesium oxide activated in the air showed sufficient activity for retro-aldol reaction[1]. Catalyst usable in atmospheric conditions is more desirable than that prepared and used in vacuum conditions. From the view point of activation and handling MgO in air, it is important to study a preparation method to obtain more active MgO under atmospheric conditions. In this study, we used hydroxide, carbonate and oxalate[2] for the starting material of MgO, and compare the activity of MgO catalysts obtained by heating in air at various temperatures.

2. Experimental

As the starting materials for MgO preparation, $MgC_2O_4{\bullet}2H_2O$ (Wako Pure Chemical Industries), two kind of $Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O$ (Wako Pure Chemical Industries and Sigma–Aldrich), and $Mg(OH)_2$ were used. Magnesium hydroxide was prepared as follows. Pure MgO (Merck, analytical grade) was placed in a beaker, heated for 1 h in distilled water, and dried at 373 K. The starting materials were pressed into a pellet, and powdered through a 32–50 mesh.

Thermal decomposition of starting materials into MgO was carried out in a muffle furnace. The starting materials were placed in the furnace, and the temperature of furnace was raised to a desired temperature from room temperature for 30 min, and maintained the temperature for 180 min. The sample was kept in a sealed ampoule until use.

A retro-aldol reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) into acetone was performed in a batch-reaction system. The reaction was carried out at 299 K for 3 h using 25 mg of catalyst and 100 mmol of diacetone alcohol in a round-bottom flask. Samples were taken every 30 min and analyzed using gas chromatography. An equilibrium conversion of this reaction is 88 %. The product was acetone, and formation of mesityl was not observed.

3. Results and discussion

Effects of starting material and activation temperature are illustrated in Figure 1. Activities of prepared catalysts were compared using those rate constants calculated by applying first order reaction equation. Catalysts showed activity in all activation temperature in the range from 723 K to 1173 K. The most active MgO was obtained from oxalate by applying the activation temperature of 773 K. This temperature was very close to that of oxalate decomposition. The conventional starting material of $Mg(OH)_2$ provided the catalyst of lowest activity among tested MgO in this study. The activity was decreased in monotonous trend in higher activation temperature range in all samples.

Thermogravimetry–differential thermal analysis was performed to clarify a decomposition profiles of starting materials. The oxalate was decomposed at 756 K into MgO, CO_2, and CO. The evolved CO was converted into CO_2 when the decomposition was carried out in air; the endothermal reaction being changed to exothermal one. The basic carbonate was decomposed in two steps. First one was conversion of hydroxide into oxide at 695 K, and second one was that of carbonate at 786 K. The decomposition of $Mg(OH)_2$ was observed at 648 K. This was lower than that of hydroxide part in $Mg_5(CO_3)_4(OH)_2$. These results showed a tendency that the starting material, which had higher decomposition temperature, and which gave larger amount of evolving gas molecules accompanying decomposition, gave the MgO of higher activity.

A relation between activation temperature and crystal size calculated from XRD peak width applying a Scherrer equation. The crystal sizes of four kinds of MgO were increased with increasing activation temperature monotonous in very similar way. There was no relation in the changes of the crystal size of prepared MgO and base catalytic activity.

Magnesium oxide prepared by oxalate decomposition showed the largest surface area among the tested MgO, ca. 300 $m^2\ g^{-1}$. Magnesium oxide samples prepared from basic carbonate and hydroxide also had a larger surface areas, more than 200 $m^2\ g^{-1}$. The difference of surface areas of prepared samples did not agree with that of base catalytic activities.

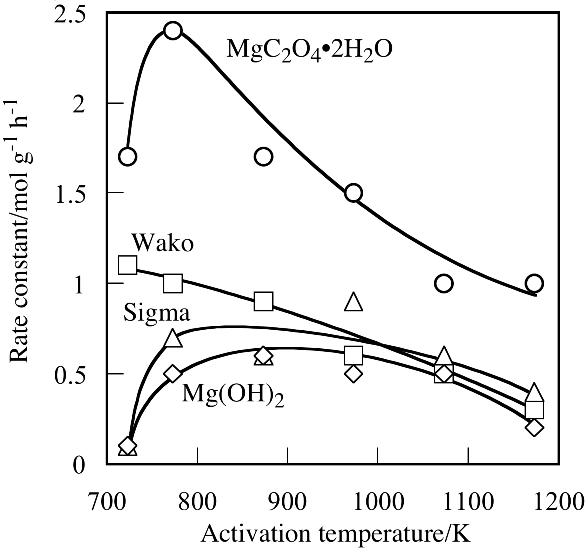

Figure 1. Change of activity for retro-aldol reaction of MgO prepared from various starting materials against activation temperature. ○: $MgC_2O_4{\bullet}2H_2O$, □: $Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O$ (Wako Pure Chemical Industries), □: $Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O$ (Sigma–Aldrich), ◇ $Mg(OH)_2$.

4. Conclusions

To obtain more active MgO under atmospheric conditions, hydroxide, basic carbonate and oxalate were applied as starting material. The order of activity of prepared MgO for the retro-aldol reaction was oxalate > basic carbonate > hydroxide, as starting material. The highest activity was obtained by heating at 773 K, and decreased gradually in higher temperature range in all samples. A tendency that the starting material, which had higher decomposition temperature, and which gave larger amount of evolving gas molecules accompanying decomposition, provided the MgO with higher activity. A clear relation was not observed between surface area or crystal size and catalytic activity.

References

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