Evaluation of the base strength of solid base catalysts by temperature-programmed desorption using propylene as a probe molecule

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ABSTRACT

Temperature-programmed desorption using hydrocarbons (propane, propylene, isobutane, and isobutene) was applied to investigate the base strength of solid bases. Among the used probe molecules, propylene showed acid–base interaction with base sites on solid bases. The activation energies of propylene desorption for CaO, MgO, and Al_2O_3–MgO prepared by thermal decomposition of hydrotalcite were 53, 41, and 34 kJ mol^{-1}, respectively. Our results show that propylene is superior as the probe molecule for base site analysis.

KEYWORDS: solid base, base strength, temperature-programmed desorption, propylene.

INTRODUCTION

Base strength and the number of base sites are fundamental properties of solid base catalysts. Temperature-programmed desorption (TPD) is a well-known method to determine the strength of interaction between an active site and an adsorbed probe molecule. In general, CO_2 is used as a probe molecule for the measurement of base strength on a solid catalyst surface [1]. However, the interaction between CO_2 and base sites is very strong. The CO_2 desorption temperature is sometimes higher than that of solid base preparation [2-12]. In this case, the desorption of CO_2 is accompanied by the thermal decomposition of base sites. An exchange of O atoms in CO_2 molecules with those of the

oxide surface has been observed [13]. To avoid base site decomposition at the elevated temperatures, the temperature increase should be stopped at the catalyst preparation temperature [14-16]. However, this temperature is not high enough for complete desorption of CO_2. In many studies, the sample temperature in TPD analysis was increased to a temperature higher than that of sample preparation. In this case, CO_2 evolution by thermal decomposition of active sites was strongly suspected. Additionally, CO_2 desorbed at these higher temperatures was not eliminated by the sample pretreatment in TPD analysis. In this line of reasoning, it was logically expected that these sites did not act as the catalytic active sites in base-catalyzed reactions. The base strength of active sites is not evaluated precisely for this reason. For a better understanding of base strength on a solid base surface, an appropriate probe molecule, which has weaker interaction with the base sites than CO_2, must be used.

For the detection of acid sites, carbon monoxide, nitrogen, and rare gas molecules, which had not been previously considered as base, can be used in the analysis of acid properties, in place of typical base molecules, such as ammonia or pyridine. Argon has a strong interaction with both Brønsted- and Lewis-type acid sites on solid acids [17-19]. A single electron pair is donated to a vacant orbital on the Lewis acid site, and a hydrogen bond is formed on the Brønsted acid site with argon.

Wakabayashi and coworkers have reported that inert gases, such as Ar, exhibit a strong interaction with silanol groups on the H-ZSM-5 zeolite,

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which leads to a red shift in the IR-stretching bands of the zeolite acidic –OH groups [17]. The interaction strength was related to the proton affinity. The data indicate that Ar is useful for the characterization of solid acids [20].

On the other hand, a small hydrocarbon was expected to be suitable as a probe for base sites, because protons in hydrocarbons have positive charge, resulting from the electronegativity difference between hydrogen and carbon. We attempted to use propane, propylene, isobutane, and isobutene as probe molecules in TPD to analyze the base strength of solid base catalysts. Propylene gave a desorption peak related to the base catalytic activity of CaO.

MATERIALS AND METHODS

TPD procedures

The TPD apparatus was composed of an injector, U-tube, and a flame ionization detector. In the experiment, 10 mg of solid base, which was activated in air as described below, was placed in the U-tube. Solid bases placed in the sample tube were heated in a He stream at 573 K for 1 h before hydrocarbon adsorption.

Hydrocarbons were purified by passing through molecular sieves 4A, and taken up in an airtight-type syringe. The adsorption of probe molecules on the solid base sample was carried out at 143–203 K. The sample was exposed to 0.02 mL of hydrocarbons injected in He flow (30 mL min^{-1}). After exposure, the sample was kept in a He flow at the same temperature to remove excess hydrocarbon. Afterward, the temperature of the sample bed was dropped to 133 K. TPD experiments were performed in the temperature range 133–273 K at the programmed rate of 1–8 K min^{-1} [21]. The desorbed hydrocarbon was detected by the flame ionization detector. The desorption of probe molecules used in this study was complete at 273 K. Consequently, destruction of the base site was completely prevented.

Catalyst preparation

Calcium hydroxide used in this study was prepared as follows. Commercial Ca(OH)$_2$ (Wako Pure Chemical Industries, Japan) was placed in a beaker and boiled for 1 h in distilled water to obtain Ca(OH)$_2$, which has properties similar to Mg(OH)$_2$ [22]. Excess water was eliminated by evaporation on a hot plate. After that, it was dried at 373 K. The obtained hydroxide was pressed into a pellet, and comminuted to a powder with particle sizes of 32–50 mesh. The granulated calcium hydroxide was placed in a sample tube and heated in air at 773 K or 1173 K for 2 h.

Magnesium oxide was prepared by the same method described above. Pure MgO (Merck) was placed in a beaker and boiled for 1 h in distilled water to obtain Mg(OH)$_2$ [22]. The obtained Mg(OH)$_2$ was dried at 373 K, pressed into a pellet, and powdered to particles of 32–50 mesh size. The sample was heated in air at 773 K for 2 h.

Magnesium oxide covered with Al$_2$O$_3$, denoted as Al$_2$O$_3$/MgO, was prepared as follows. The magnesium hydroxide was prepared as described above. Aluminum isopropoxide (Al(OCH(CH$_3$)$_2$)$_3$) (Wako Pure Chemical Industries) was dissolved in ethyl acetate; Mg(OH)$_2$ was added to the solution and stirred for 1 h. Subsequently, the solvent was removed by evaporation and the sample was dried again at 373 K for 12 h. The sample was activated in air at 773 K for 2 h. The molar ratio of Al^{3+} to Mg^{2+} ions, calculated as Al^{3+}/(Al^{3+} + Mg^{2+}) × 100%, was 10% [23, 24].

Mixed oxide of Al$_2$O$_3$–MgO was obtained by thermal treatment of purchased hydrotalcite (Mg$_6$Al$_2$(OH)$_{16}$CO$_3$•4H$_2$O, Wako Pure Chemical Industries) at 773 K for 3 h in air. All samples prepared by heating in air were heated again in a He stream at 623 K for 2 h before use.

Retro-aldol reaction of diacetone alcohol

A retro-aldol reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) to form acetone was performed in a batch-reaction system to compare the base catalytic activity of used catalysts (Scheme 1). The reaction was carried out at 299 K for 3 h using 100 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. The product was acetone, and mesityl oxide formed by dehydration of diacetone alcohol was not detected in this study. The catalytic activities of the prepared catalysts were compared using the rate constants calculated by applying a first-order reaction equation.
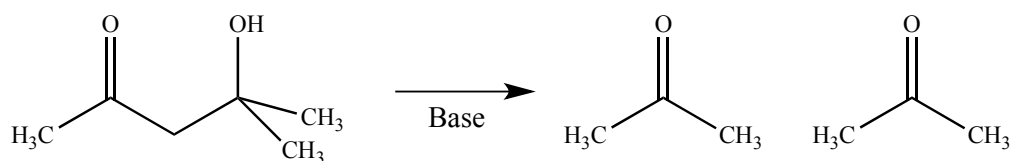
Scheme 1. Retro-aldol reaction of diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) to form acetone.

RESULTS AND DISCUSSION

TPD of hydrocarbons from CaO was performed to identify a suitable probe molecule for selective adsorption on base sites. It has been reported that CaO has base sites with relatively uniform base strength [15]. This solid base property is useful for hydrocarbon TPD.

Figure 1 shows the desorption profiles of the hydrocarbons from CaO activated at 773 K. The adsorption of hydrocarbons was performed at 143 K, and the temperature increase rate was 1 K min^{-1}. We found the desorption peak temperatures increased in the following order: propane, isobutane, propylene, and isobutene. In gas-liquid chromatography, the retention time of hydrocarbons in a polar packing for the analysis of light hydrocarbons in general increases in the following order; propane, propylene, isobutane, and isobutene. This is the order of the strength of interaction between polar packing and probe molecules. This order was different from that of the peak temperatures in TPD analysis, as shown in Figure 1. The position of propylene and isobutane was exchanged in both orders. This observation could be explained by the basicity of CaO in propylene adsorption.

TPD profiles of hydrocarbons from CaO prepared at 773 K and 1173 K are illustrated in Figure 2. As previously reported, CaO prepared by thermal decomposition of hydroxide at 773 K was most active, and that treated at 1173 K was almost inactive [25, 26]. All the tested hydrocarbons, except propylene, gave a small difference in desorption profile for both active and inactive CaO catalysts. In the case of propylene, the desorption amount of the probe molecule from inactive CaO was much smaller than that from an active CaO. This result indicates that the propylene adsorption sites were the active sites for base-catalyzed reactions. From these results, it can be concluded that propylene is a suitable probe molecule for the basicity analysis of solid catalysts by TPD.
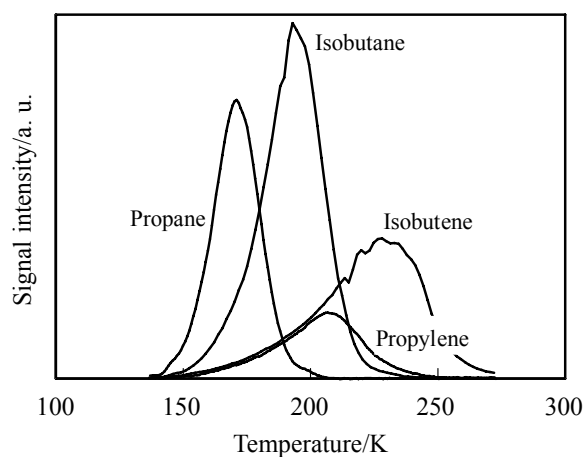

Figure 1. Desorption profiles of hydrocarbons from CaO activated at 773 K.

The effect of temperature on propylene adsorption was also examined. In general, base sites on a metal oxide vary in base strength. The TPD profiles are given as a combination of desorption peaks from a few kinds of base sites. To eliminate desorption peaks from lower-strength sites, adsorption of the probe molecules was performed at a higher temperature. The peak top was moved to a higher temperature with increasing adsorption temperature as shown in Figure 3. This is caused by the disappearance of adsorbed molecules on base sites of lower strength. Subsequently, the peak area decreased with increasing adsorption temperature. For the adsorption at 213 K and 223 K, moving of the peak top temperature was not observed; only a decrease in desorption peak area was observed. This was caused by the decrease in adsorption amount on the base sites of the highest strength.

Additionally, the fact that the peak temperature was independent of the amount of adsorbed probe molecule indicates that the experimental conditions used in this study were in the kinetically controlled region. If the TPD signal was controlled by the
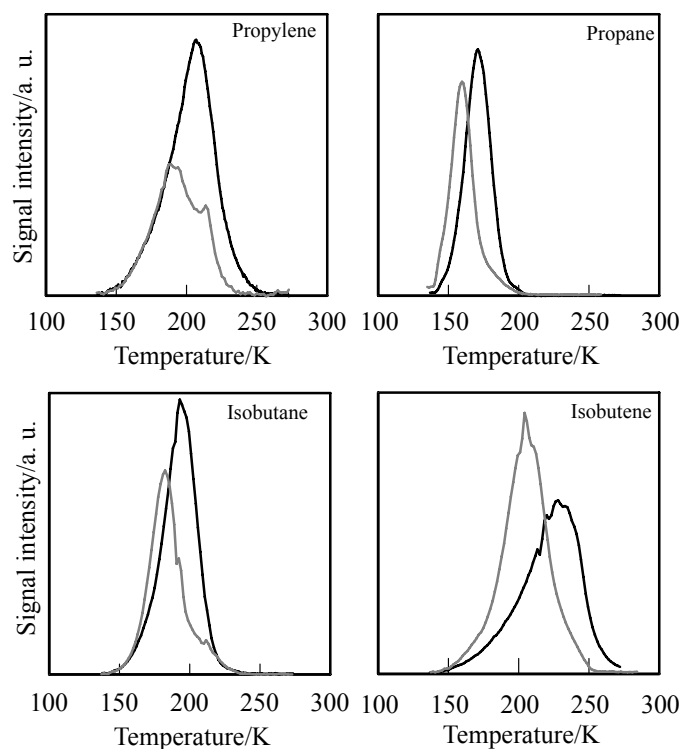
Figure 2. TPD profiles of hydrocarbons from CaO prepared at 773 K (black line) and 1173 K (gray line).
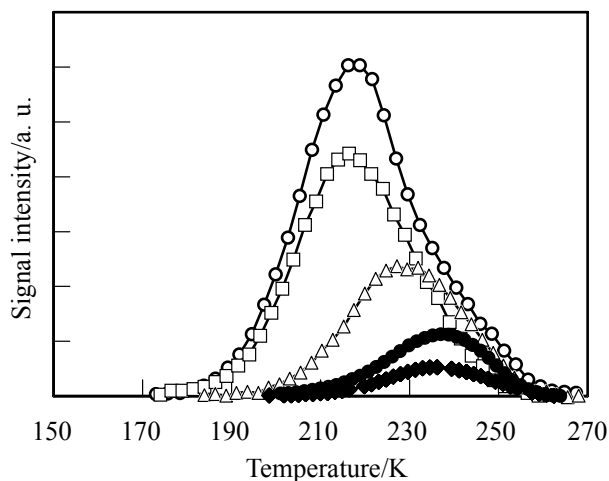

Figure 3. Effect of propylene adsorption temperature on TPD profile. ○: 183 k, □: 193 K, Δ: 203 K, ●: 213 K, ♦: 203 K.

adsorption equilibrium or diffusion rate, the peak temperature is affected by the desorption amount of hydrocarbon. From these results, a suitable temperature of propylene adsorption on CaO was determined to be 213 K.

Desorption is the reverse process of adsorption. Therefore, the activation energy of desorption indicates the strength of the interaction between the probe molecule and an active site. The apparent activation energy of probe molecule desorption was calculated applying the following equation [27]:

$$2\ln T_m - \ln\beta = E_d/RT_m + \text{constant},$$

where, T_m is the peak temperature, β is the rate of temperature increase, and E_d is the activation energy of desorption.

The solid bases used for E_d measurement were CaO, MgO, MgO covered with Al_2O_3 (Al_2O_3/MgO), and Al_2O_3–MgO mixed oxide. The results are summarized in Figure 4. The activation energies of desorption of each sample were calculated by applying the above equation. The obtained values were 53, 41, 41, and 34 kJ mol^{-1} for CaO, MgO, Al_2O_3/MgO, and Al_2O_3–MgO, respectively.

In TPD studies using CO_2, it has been reported that the CO_2 desorption peak from CaO was observed in a higher temperature range than that from MgO. Comparing MgO and Al_2O_3–MgO, the CO_2
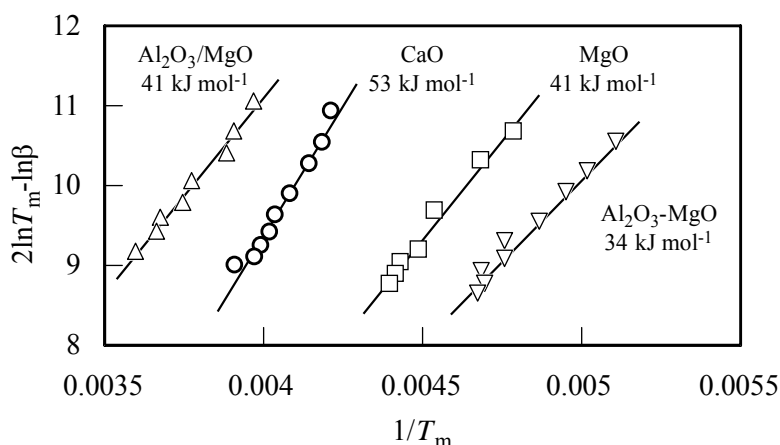
Figure 4. Plot of $2\ln T_m - \ln \beta$ vs. $1/T_m$ of solid bases for the calculation of activation energy of desorption.

Table 1. Activity of solid base catalysts for the retro-aldol reaction of diacetone alcohol.

Catalyst	Rate constant/mmol g^{-1} h^{-1}
CaO	400
MgO	173
Al_2O_3/MgO	19
Al_2O_3–MgO	1

desorption peak of MgO was at a higher temperature. The order of CaO, MgO, and Al_2O_3–MgO in base strength was consistent with that previously reported [2, 15].

The order of obtained activation energy was compared with that of base catalytic activity. Obtained rate constants of used catalysts are presented in Table 1. The order of base catalytic activity was CaO > MgO > Al_2O_3/MgO > Al_2O_3–MgO. The result of activation energy measurement agrees with that of catalytic activity, except for Al_2O_3/MgO, which showed the same value of activation energy as MgO. Alumina-covered MgO was prepared by covering the MgO surface with a thin layer of Al_2O_3. This catalyst might have the same structure of active sites as the simple MgO. The number of active sites was expected to decrease by covering with Al_2O_3. As a result, Al_2O_3/MgO showed the same activation energy of desorption and lower catalytic activity.

As is well known, the desorption peak area corresponds to the quantity of desorbed molecules. The number of active sites is determined from that of desorbed molecules when the probe molecule is adsorbed on all the active sites. In our case, propylene was adsorbed on a part of the active sites because of the higher adsorption temperature for the elimination of adsorption by weak interactions.

CONCLUSION

In this study, we succeeded in evaluating the base strength of solid bases of CaO, MgO, Al_2O_3/MgO, and Al_2O_3–MgO mixed oxide, by means of TPD using propylene as a probe molecule. The obtained activation energies agreed with the order of catalytic activity for the retro-aldol reaction. We showed that propylene is a superior probe for base site analysis compared with the other probes tested.

CONFLICT OF INTEREST STATEMENT

The authors have no conflicts of interest directly relevant to the content of this article.

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