Introduction

Among chemical reactions which are promoted by catalysts are the acid-catalyzed and base-catalyzed reactions which are initiated by acid-base interactions between reactants and catalysts followed by catalytic cycles. In acid-catalyzed reactions, the catalysts act as an acid toward the reactants, whereas in base-catalyzed reactions, the catalysts act as a base toward the reactants.

Although acid and base are paired concepts, acid catalysis has been extensively studied in heterogeneous catalysis but fewer studies have examined heterogeneous basic catalysis because the catalysts employed for the cracking process in petroleum refining are acidic catalysts such as activated clays, silica-alumina, and acidic zeolites. The cracking process is the largest process in chemical industries. In addition to the cracking process, there are several refining processes that involve acid catalyzed reactions.

In 1955, Pines et al. reported that sodium metal dispersed on alumina acted as an efficient catalyst for double bond migration of alkenes. Sodium metal dispersed on alumina will act as a solid base catalyst because of the strong tendency of sodium to donate electrons. In the 1970s, studies of solid base catalysts became more popular. A number of single component metal oxides were found to act as solid base catalysts in the absence of alkali metals. In addition to the single component metal oxides, alkali ion-exchanged X and Y type zeolites were found to be catalysts for base-catalyzed reactions. Following these findings, a wide variety of solid base catalysts have been identified. The types of solid base catalysts are listed in Table 1. The materials listed in Table 1 function as a base toward most reactants, and are generally called solid base catalysts.

The breakthrough in catalysis was the recognition that many materials act as solid base catalysts if properly pretreated. Before the 1970s, catalysts were pretreated normally at low temperatures of around 723 K, at which the surfaces of basic materials are covered with carbon dioxide, water, oxygen, etc., and showed no activities for base-catalyzed reactions. Removal of the carbon dioxide, water, and oxygen etc. on the surfaces by pretreatment at high temperature allowed the...
since the 1970s, a number of industrial processes. Since the 1970s, a number of catalytic cycles.

(1) Characterizations of the surfaces by various methods such as color change of acid-base indicators, adsorption of acidic molecules, and several spectroscopic methods indicate that basic sites exist on the surface.

(2) Catalytic activities correlated with the amount of basic sites or strength of basic sites. In addition, the active sites are poisoned by acidic molecules such as HCl, CO₂, and H₂O.

(3) Reactions proceeding over the materials are similar to the “base-catalyzed reactions” well-known in homogeneous systems.

(4) Mechanistic studies of the reactions and spectroscopic observations of the surface species indicate that anionic intermediates are involved in the reactions.

The materials listed in Table 1 do not necessarily function as a base in all cases. Some materials in Table 1 may act as an acid if the reactants are strongly basic. The terms, acid and base, should be used according to the function. The materials may be called solid base catalysts only if acting as a base toward the reactants by abstraction of a proton (Broensted base) or by donation of an electron pair (Lewis base) to form anionic intermediates that undergo catalytic cycles.

Some of the solid base catalysts have been used in industrial processes. Since the 1970s, a number of reactions have been found to proceed on a variety of solid base catalysts. Replacement of homogeneous basic catalysts by solid base catalysts in industrial processes is desirable for the simplification of the process and protection of the environment.

Tanabe and Hoelderich reviewed industrial applications of solid base catalysts as well as solid acid catalysts. Among 127 processes, 10 processes use solid base catalysts and 14 processes use acid-base bifunctional catalysts according to their classification. Table 2 lists the industrial processes in which solid base catalysts are used in the present classification. Most processes were developed within the last 20 years. The studies of solid base catalyst starting in the 1970s have been crystallized into industrial processes in the last 20 years.

Table 1: Types of Heterogeneous Basic Catalysts

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single component metal oxides</td>
</tr>
<tr>
<td>Alkali metal oxides</td>
<td></td>
</tr>
<tr>
<td>Alkaline earth oxides</td>
<td></td>
</tr>
<tr>
<td>Rare earth oxides</td>
<td></td>
</tr>
<tr>
<td>TiO₂, ZrO₂, ZnO, TlO₂</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Zeolites</td>
</tr>
<tr>
<td>Alkali ion-exchanged zeolites</td>
<td></td>
</tr>
<tr>
<td>Alkali ion-added zeolites</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Supported alkali metal ions</td>
</tr>
<tr>
<td>Alkali metal ions on alumina</td>
<td></td>
</tr>
<tr>
<td>Alkali metal ions on silica</td>
<td></td>
</tr>
<tr>
<td>Alkali metal on alkaline earth oxide</td>
<td></td>
</tr>
<tr>
<td>Alkali metals and alkali metal hydroxides on alumina</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Clay minerals</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td></td>
</tr>
<tr>
<td>Chrysotile</td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Non-oxides</td>
</tr>
<tr>
<td>KF supported on alumina</td>
<td></td>
</tr>
<tr>
<td>Lanthane imide and nitride on zeolite</td>
<td></td>
</tr>
</tbody>
</table>

Underlined catalysts were studied in our laboratories.

Tables 1 and 2 list the types of solid base catalysts and the industrial processes in which they are used. The materials listed in Table 1 have been recognized as solid base catalysts for the reasons listed below.

1. Characterizations of the surfaces by various methods such as color change of acid-base indicators, adsorption of acidic molecules, and several spectroscopic methods indicate that basic sites exist on the surface.

2. Catalytic activities correlated with the amount of basic sites or strength of basic sites. In addition, the active sites are poisoned by acidic molecules such as HCl, CO₂, and H₂O.

3. Reactions proceeding over the materials are similar to the “base-catalyzed reactions” well-known in homogeneous systems.

4. Mechanistic studies of the reactions and spectroscopic observations of the surface species indicate that anionic intermediates are involved in the reactions.

The materials listed in Table 1 do not necessarily function as a base in all cases. Some materials in Table 1 may act as an acid if the reactants are strongly basic. The terms, acid and base, should be used according to the function. The materials may be called solid base catalysts only if acting as a base toward the reactants by abstraction of a proton (Broensted base) or by donation of an electron pair (Lewis base) to form anionic intermediates that undergo catalytic cycles.

Some of the solid base catalysts have been used in industrial processes. Since the 1970s, a number of reactions have been found to proceed on a variety of solid base catalysts. Replacement of homogeneous basic catalysts by solid base catalysts in industrial processes is desirable for the simplification of the process and protection of the environment.

Tanabe and Hoelderich reviewed industrial applications of solid base catalysts as well as solid acid catalysts. Among 127 processes, 10 processes use solid base catalysts and 14 processes use acid-base bifunctional catalysts according to their classification. Table 2 lists the industrial processes in which solid base catalysts are used in the present classification. Most processes were developed within the last 20 years. The studies of solid base catalysts starting in the 1970s have been crystallized into industrial processes in the last 20 years.

There have been several review articles on solid base catalysis. In the present article, the studies of solid base catalysis undertaken in our laboratories over the last 35 years are reviewed.

2. Generation of Basic Sites by Pretreatment at High Temperature

Although MgO pretreated by outgassing below 723 K has little activity for double bond migration of 1-butene, raising the pretreatment temperature above 723 K greatly increased the activity. The activity was maximum at a pretreatment temperature of 873 K and gradually decreased after pretreatment at higher temperatures. Essentially the same variation of activity with the pretreatment temperature was observed for CaO as shown in Fig. 1. The amounts of evolved water and carbon dioxide during pretreatment are also plotted against the pretreatment temperature. The reaction is characteristic of a base-catalyzed double bond migration of 1-butene in that the ratio of cis-2-butene to trans-2-butene is high. Clearly the surface basic sites appear on removal of water and carbon dioxide from the surface to reveal the oxide surface, and the basic sites act as active sites for the double bond migration of 1-butene.

The finding that pretreatment at high temperatures of MgO and CaO generates basic sites on their surfaces is simple, but important for developing other solid base catalysts. For most basic materials, the surfaces are covered with water and carbon dioxide in air, and do not exhibit their intrinsic catalytic activities. Removal of the adsorbed species from the surface is essential to reveal the oxide surfaces. SrO and BaO easily form peroxides on contact with oxygen, so removal of oxygen is also required to reveal the surface basic sites. The temperature required to remove the adsorbed species depends primarily on the decomposition temperatures of hydroxide, carbonate, and peroxide.
The nature of the basic sites generated by removing the molecules covering the surfaces depends upon the severity of the pretreatment. As the pretreatment temperature increases, the molecules covering the surfaces are successively desorbed according to the strength of the interaction of the molecules with the surface sites. The molecules weakly interacting with the surfaces are desorbed at lower pretreatment temperatures, and those strongly interacting are desorbed at higher temperatures. Therefore, the sites exposed by pretreatment at lower temperatures may be different from those exposed at higher temperatures. If simple desorption of the molecules occurs during pretreatment, the basic sites appearing at higher temperature should be stronger. However, rearrangement of surface and bulk atoms also occurs during pretreatment. This causes complicated changes in the number and nature of the surface basic sites with increasing pretreatment temperature. The changes in the number and nature of basic sites are reflected in the variations of the catalytic activities as a function of the pretreatment temperature. An example is shown in Fig. 2 for the case of MgO. The pretreatment temperatures giving maximum activities are 800 K for 1-butene isomerization, 973 K for methane-D₂ exchange, and 1300 K for hydrogenation of 1,3-butadiene. This figure shows that the nature of the basic sites changes with pretreatment temperature, and that the nature of basic sites relevant to the reaction varies with the type of reaction.

The change in the nature of basic sites on metal oxide surfaces may be understood based on the model proposed by Coluccia and Tench for MgO. As shown in Fig. 3, several Mg-O ion pairs of different coordination numbers are present on the surface of MgO after outgassing at a high temperature to remove all adsorbed molecules. Ion pairs of low coordination numbers exist at the corners, edges, and high Miller index surfaces. Different basic sites generated by increasing the pretreatment temperature appear to correspond to the ion pairs of different coordination numbers. Among the ion pairs of different coordination numbers, the ion pair of three-fold Mg²⁺-three-fold O²⁻ is most...
reactive and adsorbs carbon dioxide and water most strongly. To reveal this ion pair, the highest pretreatment temperature is required. This ion pair, however, is most unstable, and tends to rearrange and disappear at high temperature. The exposure of such highly unsaturated sites by the removal of adsorbed molecules and the elimination by the rearrangement of the surface atoms compete, which results in activity maxima with increasing pretreatment temperature. This competition occurs for ion pairs of different coordination numbers.

Rare earth oxides which are stable at the oxidation number of 3 act as solid base catalysts, and those which are stable at oxidation numbers higher than 3 are not efficient solid base catalysts\(^{22}\). The variations of the activity with pretreatment temperature for rare earth oxides are different from those observed for MgO, CaO, etc. The activity maxima are observed for all reactions examined if pretreated at 923 K\(^{17,23,24}\). The surface sites generated by removal of water and carbon dioxide seem to be rather homogeneous in the sense that the same surface sites are relevant to all the reactions. The variations of the activities of La\(_2\)O\(_3\), a representative basic rare earth oxide, are shown in Fig. 4.

Essentially the same variations of the activities as a function of pretreatment temperature were obtained for KF/alumina as shown in Fig. 5\(^{21}\). The activity maxima were observed at a pretreatment temperature of 623 K for all reactions examined, though the degree of the change in the activity depended on the type of reaction. The increase in activity with pretreatment temperature up to 623 K may be caused by the exposure of basic sites by removal of water and carbon dioxide from the
surface, and the decrease in the activity above 623 K may be caused by change in the surface structure at high temperature resulting in the elimination of basic sites.

In some cases, particularly oxides of transition elements, basic sites are generated by reduction, which is typically observed for TiO$_2$\cite{26, 27}. Reduction of TiO$_2$ by treatment with hydrogen or outgassing at a high temperature causes an increase in basic character, and increases the catalytic activities for base-catalyzed reactions.

### 3. Characterization of Basic Sites

The surface properties of solid base catalysts have been studied by various methods. Different characterization methods give different information about the surface properties. All the properties of basic sites cannot be measured by any single method. Similar to the case of solid acid catalysts, the existence of basic sites was first realized by the indicator method. Now, temperature-programmed desorption (TPD) of CO$_2$ is more commonly employed. In addition to the indicator method and TPD of CO$_2$ which give information about the strength and amount of basic sites, different information is obtained by tracer study of adsorption of CO$_2$, poisoning by CO$_2$ and NH$_3$, and nuclear magnetic resonance (NMR) studies of Cs and F. In this section, selected results with these methods obtained in our laboratories are described.

Acid-base indicators change color according to the strength of the surface sites and $pK_{BH}$ values of the indicators. The strength of the surface basic sites is expressed by an acidity function ($H^+$) proposed by Paul and Long\cite{28}. The $H^+$ function is defined by the following equation:

$$ H^+ = pK_{BH} + \log[\text{BH}^-]/[\text{BH}] $$

where $[\text{BH}]$ and $[\text{BH}^-]$ are the concentration of the indicator and its conjugated base, respectively, and $pK_{BH}$ is the logarithm of the dissociation constant of BH. The reaction of the indicator BH with the basic site $\text{B}$ is:

$$ \text{BH} + \text{B}^- = \text{B}^+ + \text{BH}^- $$

The amount of basic sites of different strengths can be measured by titration with benzoic acid. The benzoic acid titer is a measure of the amount of basic sites with a basic strength corresponding to the $pK_{BH}$ value of the indicator used. Using this method, the exposure of basic sites on CaO and MgO by pretreatment above 673 K was revealed\cite{29}. The exposure of basic sites correlated well with the appearance of catalytic activity for 1-butene isomerization.

The indicator method, however, has disadvantages. Although the color change is assumed to be the result of an acid-base reaction, an indicator may change color by reactions different from the acid-base reaction. In addition, a long time is required for benzoic acid to reach an adsorption equilibrium during titration carried out in a solution. In some cases, the surface of solid base catalysts may dissolve into the titration solution. If this occurs, the number of basic sites will be overestimated. Therefore, special care should be taken with the indicator method.

TPD of carbon dioxide is frequently used to characterize basic sites. The strength and amount of basic sites are reflected in the desorption temperature and the peak area, respectively, in a TPD plot. The activation energy for desorption of CO$_2$ can be estimated from the change in the peak temperature with the heating rate. The activation energy may be a measure of the strength of basic sites. The estimation of the activation energy for desorption is rarely successful because the surface basic sites are not always homogeneous.

TPD plots of CO$_2$ desorbed from alkaline earth oxides are compared in Fig. 6\cite{30}. In the experiment, a limited amount of CO$_2$ (5 mmol/g) was adsorbed followed by outgassing for 10 min at room temperature. The strength of basic sites is in the order of MgO $<$ CaO $<$ SrO $<$ BaO. The number of basic sites per unit weight that can retain CO$_2$ under the adsorption conditions increases in the order BaO $<$ SrO $<$ MgO $<$ CaO.

**Figure 7** demonstrates enhancement of basic strength by addition of alkali ions to X-zeolite in excess of the ion exchange capacity by TPD of adsorbed CO$_2$\cite{31, 32}. The peak areas are larger for the alkali ion-added zeolites than for the alkali ion-exchanged zeolites.

CO$_2$ is a good probe molecule not only for TPD but also for infrared spectroscopy (IR) and mass spectroscopy. IR of CO$_2$ gives information about the adsorbed state of CO$_2$ on the basic sites, which reflects the structure of basic sites. Mass spectroscopy of $^{18}$O labeled CO$_2$ desorbed from the surface gives information about the dynamic nature of the interaction of adsorbed CO$_2$.
with the surface ion pair\textsuperscript{[33]–[35]}.

TPD plots for C\textsuperscript{18}O\textsubscript{2} adsorbed on MgO are shown in Fig. 8 in which a small amount of C\textsuperscript{18}O\textsubscript{2} (41 × 10\textsuperscript{−6} mol/g) was adsorbed. Most of the CO\textsubscript{2} desorbed from the surface was C\textsuperscript{16}O\textsubscript{2}, indicating that extensive oxygen exchange occurred between CO\textsubscript{2} and the surface. The exchange should involve migration of the CO\textsubscript{2} adsorbed on the surface in the form of bidentate carbonate. Proposed processes for the mechanism of migration of the surface bidentate carbonate are shown in Fig. 9. Repetition of any single one of these processes could not result in C\textsuperscript{16}O\textsubscript{2} evolution. There are at least two ways for the adsorbed carbonate species to migrate over the surface; processes I and II. In process I, the carbonate species (CO\textsubscript{3}) contains two \textsuperscript{18}O atoms, and therefore, repetition of process I can exchange one O atom, but not two O atoms. Repetition of process II also results in the exchange of one O atom. For the evolution of C\textsuperscript{16}O\textsubscript{2}, both processes I and II must be involved. In addition to processes I and II, process III is possible. The carbonate species can migrate on the surface over a long distance by a combination of processes I-III without leaving the surface.

The results of O exchange between the CO\textsubscript{2} and MgO surface suggest an important aspect of the nature of surface basic sites. The basic sites are not fixed on the surface but can move over the surface when CO\textsubscript{2} is adsorbed and desorbed. The position of the basic site, the surface O atom, changes as CO\textsubscript{2} migrates over the surface. In addition, not only surface O atoms but also adjacent Mg atoms participate in CO\textsubscript{2} adsorption. Therefore, the metal cations adjacent to the basic sites are likely to participate in the base catalyzed reactions.

\textsuperscript{133}Cs and \textsuperscript{19}F NMR provides information about certain aspects of basic sites. The zeolites X containing Cs in excess of the ion-exchange capacity exhibit higher activities for the base-catalyzed double bond migration of 1-butene than ion-exchanged zeolite X if the excess amount of Cs is in the range of 1.1–2.9 Cs atoms per supercage. \textsuperscript{133}Cs NMR can distinguish the Cs located inside the cavity from the Cs located on the outer surface of zeolite and ion-exchanged Cs\textsuperscript{[36]}. The active catalysts contain Cs inside the cavities, indicating that Cs\textsubscript{2}O particles dispersed in the cavities are the
Basic sites catalyzing the double bond migration of 1-butene.

$^{19}$F NMR gives information about the basic sites on KF/Al$_2$O$_3$ which is frequently used for base-catalyzed organic synthesis. Several F containing species were observed at different chemical shifts of $\sim$123, $\sim$132, $\sim$157 and $\sim$166 ppm [37]. These four peaks are ascribed to KF associated with water, KF, K$_3$AlF$_6$, and AlF$_3$, respectively. The main species containing F in KF/Al$_2$O$_3$ was identified to be K$_3$AlF$_6$ formed by the reaction of KF with Al$_2$O$_3$. None of these peaks correlate with the catalytic activity for base-catalyzed reactions such as the double bond migration of 1-pentene and the Tishchenko reaction. In addition to these four peaks, a peak appeared at $\sim$150 ppm which correlates with the catalytic activities. The surface species relevant to the catalytic activities is the F$^-$ containing species which has a peak at $\sim$150 ppm in $^{19}$F MAS NMR, though the state of F is not certain.

4. Catalytic Behaviors in Various Reactions

4.1. Double Bond Migration

Double bond migration of olefins was carried out over the first solid base catalyst, Na dispersed on Al$_2$O$_3$ [1]. In particular, double bond migration of 1-butene is a good test reaction to investigate the active sites and the function of the catalyst. Actually, many catalysts have been recognized as solid base catalysts by their catalytic behaviors in double bond migration of 1-butene.

As shown in Fig. 2, MgO becomes active for double bond migration of 1-butene when pretreated above 673 K at which the oxide surfaces begin to be exposed by removal of H$_2$O and CO$_2$, and the basic sites are generated [7]. The activity of MgO, like the other alkaline earth oxides, is so high that the reaction proceeds even at 223 K if the catalyst is properly pretreated and the reactant is strictly purified to be free of H$_2$O and CO$_2$. The reaction mechanism for double bond migration of 1-butene is shown in Scheme 1. The reaction is initiated by abstraction of an allylic H$^+$ by a basic site to form the cis and trans forms of the allyl anion. The cis form is more stable than the trans form. Therefore, cis-2-butene is predominantly formed at the initial stage of the reaction. A high cis/trans ratio is characteristic of base-catalyzed double bond migration, in contrast to a value close to unity for acid-catalyzed double bond migration. The cis/trans ratio in 2-butenes produced can be used to judge whether the reaction is a base-catalyzed or acid-catalyzed.

The reaction essentially involves intramolecular hydrogen transfer, which was evidenced by the H/D distribution in the products of coisomerization of butene-$d_0$ and -$d_8$ [38]. In the coisomerization, a mixture containing equal amounts of nondeuteriobutene ($d_0$) and perdeuteriobutene ($d_8$) is allowed to react, and the isotopic distributions in the products and reactant are analyzed. If the reaction proceeds by hydrogen addition-abstraction mechanisms, an intermolecular H (or D) transfer is involved, and the products will consist of $d_0$, $d_1$, $d_7$, and $d_8$ isotopic species. On the other hand, if the reaction proceeds by hydrogen abstraction-addition mechanisms, an intramolecular H (or D) transfer is possibly involved, and the products will consist of $d_0$ and $d_8$ isotopic species. In the base-catalyzed double bond migration, an H$^+$ is abstracted first from an allylic C to form allyl anions to which the H$^+$ returns to the terminal C atom, and an intramolecular H (or D) is expected. Intramolecular double bond migration was actually observed for CaO [39], BaO [39], ThO$_2$ [40], and TiO$_2$ [41].

The fundamental studies of double bond migration of butene were extended to double bond migration of olefins with more complex structures such as carene [42], 5-vinylbicyclo[2,2,1]heptene [43], protoilludene [44], illudadiene [44], etc. as shown in Scheme 2. These olefins contain three-membered, four-membered and five-membered rings which are easily opened over acidic catalyst. One of the characteristic features of solid

![Scheme 1 Mechanism Proposed for Double Bond Migration of 1-Butene](image-url)
base catalyst is the lack of C–C bond cleavage ability. The double bond migration occurs without C–C bond cleavages.

Solid base catalysts have another advantage in double bond migration; double bond migration of unsaturated compounds containing heteroatoms such as N and O proceeds smoothly over solid base catalysts. Acidic catalysts, on the other hand, interact strongly with heteroatoms and become poisoned. Allylamine\textsuperscript{45,46} and 2-propenyl ethers\textsuperscript{47,48} undergo double bond migration over solid base catalysts to enamines and to 1-propenyl ethers, respectively. For both types of reactions, the intermediates are mostly cis forms of allyl anions, and the reaction mechanisms are essentially the same as those for double bond migration of 1-butene.

4.2. Hydrogenation

Hydrogenation is catalyzed typically by metallic catalysts and transition metal oxides. In 1969, Dent and Kokes reported that hydrogenation of ethylene over ZnO involves H\textsuperscript{+} and H\textsuperscript{−} formed by heterolytic dissociation of hydrogen molecule\textsuperscript{49}. They, however, did not claim the reaction as a base-catalyzed hydrogenation. Later in 1975, we found that alkaline earth oxide exhibited hydrogenation activity for olefins when the catalysts were pretreated at a high temperature around 1273 K\textsuperscript{18,19,50–53}. We extensively studied the hydrogenation over solid base catalysts, and found that hydrogenation taking place over solid base catalysts has the following characteristic features which distinguish solid base catalysts from conventional metallic hydrogenation catalysts.

1. There is a large difference in the hydrogenation rate between monoenes and conjugated dienes. Conjugated dienes undergo hydrogenation much faster than monoenes. Butenes undergo hydrogenation above 473 K, whereas 1,3-butadiene undergoes hydrogenation at 273 K. Therefore, the products in hydrogenation of conjugated dienes consist exclusively of monoenes, with no alkanes formed at 273 K.

2. There is a prominent occurrence of 1,4-addition of H atoms in contrast to 1,2-addition which is commonly observed for conventional hydrogenation catalysts. Hydrogenation of 1,3-butadiene mainly yields 2-butenes.

3. There is a retention of the molecular identity of H atoms during reaction. As a hydrogen molecule dissociates on the catalyst surface, two H atoms used for hydrogenation of one reactant molecule originate from the same hydrogen molecule. In hydrogenation of 1,3-butadiene with a mixture containing H\textsubscript{2} and D\textsubscript{2}, the products consist exclusively of d\textsubscript{0} and d\textsubscript{2}-butenes.

The above features are characteristic of hydrogenation in which anionic intermediates are involved. Scheme 3 shows the reaction mechanism for hydrogenation of 1,3-butadiene in which D\textsubscript{2} is used in place of H\textsubscript{2}. Deuterium heterolytically dissociates to form D\textsuperscript{+} and D\textsuperscript{−}. 1,3-Butadiene consists of 93% s-trans conformer and 7% s-cis conformer in the gas phase at 273 K. At first, D\textsuperscript{−} attacks 1,3-butadiene at the terminal C atom to form the allyl anion mostly in the trans form which undergoes either interconversion to form cis allyl anion or addition of D\textsuperscript{+} to form trans-2-butene. Since the electron density of the allyl anion is highest on the terminal C atom, the positively charged D\textsuperscript{+} selectively adds to the terminal C atom to complete 1,4-addition of D atoms to yield 2-butenes. A large difference in reactivity between dienes and monoenes results from the difficulty of alkyl anion formation.

\[
\text{Scheme 2 Double Bond Migration of Olefins with Complex Structure}
\]

\[
\text{Scheme 3 Mechanism Proposed for Hydrogenation of 1,3-Butadiene with D}_2
\]
compared to allyl anion formation. Alkyl anions are less stable than allyl anions. Thus, the reactions of monoenes with H+ to form alkyl anions require high temperatures.

Retention of the molecular identity of H atoms is caused by immobilized adsorption of hydrogen ions (H+ and H2) on one set of active sites (O−-metal cation pair). Each set of active sites is isolated from others, and hydrogen ions cannot migrate on the metal oxide surface.

Carbanionic hydrogenation has a feature common to the other base-catalyzed conjugate additions and C-C bond forming reactions such as amination, aldol addition, Michael addition, cyanohydrination, conjugate addition of alcohols etc. as described later. The basic site abstracts an H+ from a reactant to form an anionic species. The anionic species and the H+ successively add to the double bond.

4.3. Amination

Amines react with conjugated dienes over solid base catalysts to form unsaturated amines at 273 K. The reaction of amine with 1,3-butadiene is shown below as an example.

\[ \text{CH}_2=\text{CH-CH}=\text{CH}_2 + \text{R}_1(\text{R}_2)\text{NH} \rightarrow \text{R}_1(\text{R}_2)\text{N-CH}_2\text{-CH}=\text{CH}_2 \]

Amination with monoenes hardly proceeds over solid base catalyst, for the same reason for slow hydrogenation of monoenes as for conjugated dienes. The mechanisms for the amination of conjugated dienes are essentially the same as those for the hydrogenation in the sense that heterolytic dissociation of amine (RNH2 → RNH− + H+) and hydrogen (H2 → H− + H+) are involved in the reaction(54,55). The sequence of successive addition of the anion and the H+ to the 1,4 positions of conjugated dienes is common to hydrogenation and amination.

4.4. Aldol Addition

Aldol addition of acetone to form diacetone alcohol is well known to be catalyzed by Ba(OH)2. Alkaline earth oxides(50) lanthanum oxide (La2O3) and ZrO2 are also active for this reaction. With MgO, addition of a small amount of water increases the activity, indicating that the basic OH− ions together with O2− ions act as active sites for the reaction. Deuterium tracer study showed the slow step was the attack of the anion formed by abstraction of an H+ from acetone to a second acetoxy molecule(56). If acidic catalyst is present or if the catalyst possesses acidic sites in addition to basic sites, the product diacetone alcohol undergoes dehydration to mesityl oxide, and aldol condensation is completed.

The active sites for aldol addition of n-butyraldehyde are different from those of acetone. The basic OH− ions are not relevant to the aldol addition of n-butyraldehyde, as the surface O2− ions are active for the reaction(57). For n-butyraldehyde, aldol addition product, 2-ethyl-3-hydroxyhexanal, may undergo the Tishchenko reaction with n-butyraldehyde to form trimeric ester(58). The Tishchenko reaction does not proceed with alkali/alumina, but does proceed with alkaline earth oxides. This may be due to the difference in the structure of basic sites between alkaline earth oxides and alkali modified alumina. Participation of metal cations is possible for alkaline earth oxides, but not for alkali modified alumina. Participation of metal cations is crucial for the Tishchenko reaction, but not for aldol addition.

4.5. Nitroaldol Reaction

Nitroaldol reaction is the reaction of a nitro compound with a carbonyl compound to form a nitroalcohol under basic conditions.

\[ \text{R}_1\text{C}=\text{NO}_2 + \text{R}_2\text{C}=\text{O} \rightarrow \text{R}_1\text{C}=\text{C}=\text{O}_2\text{R}_2 \]

MgO, CaO, Ba(OH)2, KOH/Al2O3, KF/Al2O3, Sr(OH)2, hydrotalcite, and MgCO3 all exhibit high activity, in this order, for the nitroaldol reaction of nitromethane with propionaldehyde at 313 K. Moderate activities were observed with Mg(OH)2, Sr-Al2O3, SrO, Ca(OH)2, BaCO3, SrCO3, BaO, and La2O3(59). The oxide form is more active than the hydroxide form for Mg and Ca, whereas the hydroxide form is more active than the oxide form for Sr and Ba. The activity is not so strongly dependent on the pretreatment temperature of the catalyst as for hydrocarbon reactions. For MgO, CaO and KF/Al2O3, considerable activities were observed even after pretreatment at a low temperature of 473 K. Apparently strongly basic sites are not required for the reaction, probably because abstraction of an H+ from a nitro compound is easy.

The reactivities of nitro compounds are nitroethane > nitromethane > 2-nitropropane, and those of carbonyl compounds are propionaldehyde > isobutyraldehyde > pivalaldehyde > acetone > benzaldehyde > methyl propionate. Based on infrared spectroscopy (IR) study of adsorbed reactants together with relative reactivities of the reactants, the reaction probably proceeds by the nucleophilic addition of the carbanion formed by the abstraction of an H+ from nitro compounds to the cationic species formed by the adsorption of carbonyl compounds on the metal cations. The mechanism proposed for the nitroaldol reaction of 1-nitro-2-butanol with nitromethane over MgO is shown in Scheme 4.

The nitroaldol reaction of nitromethane with propionaldehyde over MgO and CaO is little retarded by exposure to the catalyst to air. Nitromethane is adsorbed on the basic surface much stronger than CO2, and pre-adsorbed CO2 can be replaced by nitromethane as evidenced by an IR study(59).
4.6. Michael Addition

Michael addition is the addition of active methylene compounds to \( \alpha,\beta \)-unsaturated carbonyl compounds. The Michael addition of nitromethane to \( \alpha,\beta \)-unsaturated carbonyl compounds is shown below.

The mechanism of the reaction involves the formation of an anion from the active methylene compound by abstraction of an H\(^{+}\), and conjugate addition of the anion to the \( \alpha,\beta \)-unsaturated carbonyl compound, followed by acceptance of an H\(^{+}\).

The efficiency of the catalyst varies with the type of the reactant\(^{60,61}\). For self-Michael addition of methyl crotonate, for example, MgO exhibits higher activity than other solid base catalysts such as CaO, SrO, BaO, KF/Al\(_2\)O\(_3\), K-X zeolite, etc. For Michael addition of nitromethane to \( \alpha,\beta \)-unsaturated carbonyl compounds, KF/Al\(_2\)O\(_3\) and KOH/Al\(_2\)O\(_3\) exhibit high activities, whereas MgO and CaO exhibit low activities.

The factors affecting the efficiency of the catalyst are basic strength of the site, acidity of the reactant, and charge on the C atom in the \( \beta \)-position to the carbonyl group. For a strongly acidic reactant, relatively weak basic sites are sufficient to abstract an H\(^{+}\) from the reactant.

4.7. Conjugate Addition of Alcohols to Unsaturated Ketones

Conjugate addition of alcohols to unsaturated ketones to form ether is catalyzed by solid base catalysts such as alkaline earth oxides and KF/Al\(_2\)O\(_3\) and KOH/Al\(_2\)O\(_3\).\(^{62}\)

In particular, MgO and CaO exhibit high activities for the conjugate addition of methanol to different types of unsaturated ketones. The reactions proceed at 273 K. Alkaline earth hydroxides also exhibit considerable activities although not as high as those of alkaline earth oxides. Weakly basic as well as strongly basic sites act as active sites for the reactions, supported by the fact that the maximum activity of MgO is observed when MgO is pretreated at 673 K.

Similar to the nitroaldol reaction, the active sites of MgO, CaO and KF/Al\(_2\)O\(_3\) for the conjugate addition of methanol to 3-butene-2-one are not retarded by exposure of the catalyst to air, because of the strong adsorption of methanol on the basic sites compared to CO\(_2\) and H\(_2\)O. Methanol can be adsorbed to form methoxy groups on the surfaces on which CO\(_2\) is preadsorbed. Although adsorption of CO\(_2\) does not cause deactivation of alkaline earth oxides, none of the alkaline earth carbonates exhibit any activity.

4.8. Cyanoethylation

Acrylonitrile undergoes cyanoethylation with a variety of compounds containing active hydrogen to form nitriles of different types.

\[
R-OH + CH_2=C=CH-CN \rightarrow RO-CH=CH-CN
\]

Cyanoethylation of methanol, ethanol, and 2-propanol proceed at 273 K over alkaline earth oxides and hydroxides, KF/Al\(_2\)O\(_3\) and KOH/Al\(_2\)O\(_3\).\(^{63,64}\). The activities vary with the type of alcohols and type of catalysts. For strongly basic catalysts such as alkaline earth oxides and KF/Al\(_2\)O\(_3\), the activities with different
alcohols are in the order 2-propanol > ethanol > methanol. For weakly basic catalysts such as alkaline earth hydroxides, the activities are in the opposite order, with methanol most reactive. The difference in the activity order with the type of catalyst is caused by differences in the slow step. The slow step is the addition of alkoxy anion to acrylonitrile for the strongly basic catalysts, whereas the slow step is the abstraction of an H⁺ from alcohols for the weakly basic catalysts.

Similar to the cases of nitroaldol reaction and conjugate addition of alcohols to unsaturated ketones, cyanohydrination with alcohols is not poisoned by adsorption of CO₂ at room temperature. In this case too, alcohols are adsorbed strongly on the basic sites compared to CO₂.

4.9. Transesterification of Ethyl Acetate and Alcoholysis of Propylene Oxide with Alcohols

Alcohols undergo transesterification with ethyl acetate, and alcoholysis with propylene oxide over solid base catalysts at room temperature. Transesterification

\[
\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{ROH} \rightleftharpoons \text{CH}_3\text{COOR} + \text{CH}_3\text{CH}_2\text{OH}
\]

Alcoholysis of propylene oxide

\[
\text{CH}_3-\text{CH}=\text{CH}_2 + \text{ROH} \rightarrow \text{CH}_3\text{COOR} \quad \text{CH}_3\text{CH}_2\text{OH}
\]

For both reactions, the rates vary with the type of alcohol and the type of solid base catalyst. The strength of basic sites is the decisive factor to control the activity of the catalyst.

For transesterification, 2-propanol reacts much faster than methanol over strongly basic catalysts such as CaO, SrO, and BaO, whereas methanol reacts faster than 2-propanol over relatively weak solid base catalysts such as alkaline earth hydroxides. 2-Methyl-2-propanol reacts only over strongly basic catalyst, and the reaction rate is much slower than methanol and 2-propanol.

Alcoholysis with propylene oxide proceeds only over strongly basic catalysts such as alkaline earth oxides and KF/Al₂O₃; alkaline earth hydroxides exhibit little activity. Reactivities of alcohols with propylene oxide are in the order methanol > ethanol > 2-propanol > 2-methyl-2-propanol regardless of the type of catalyst.

One of the features observed for both types of reaction is, like conjugate addition of alcohols and cyanohydrination, that the catalysts are tolerant to air exposure, which is caused by strong adsorptivity of alcohols compared to CO₂ and H₂O.

4.10. Tishchenko Reaction

The classical Tishchenko reaction is dimerization of aldehydes to form corresponding esters catalyzed by aluminum alkoxides. The Tishchenko reaction proceeds over solid base catalysts. Benzaldehyde undergoes the Tishenko reaction over CaO 423 K. More recently, we reported that KF/Al₂O₃ is active for the Tishchenko reaction of benzaldehyde and pivalaldehyde at 323 K. In order to elucidate the activity- and selectivity-determining factors, we studied mixed Tishchenko reactions in which two types of aldehyde were allowed to react at 353 K over a series of solid base catalysts. The aldehydes examined were benzaldehyde, pivalaldehyde, and cyclopropanecarbaldehyde.

The reaction mechanism proposed for the Tishchenko reaction is shown in Scheme 5. The first step is the adsorption of aldehyde onto the basic (O²⁻) and acidic (metal cation) sites, resulting in the formation of the intermediates I and II, respectively. In the next step, hydride ion transfer from I to II occurs to form III and IV, the latter being the active species for ester formation. In the mixed Tishchenko reaction, two types of intermediates IV will be formed, and each intermediate reacts with one of the aldehydes. As a result, four dimers will be produced. The relative reactivities of the aldehydes and the intermediates are reflected on the selectivities of four dimers if the step of the reaction of the intermediate with aldehyde is the slow step.
On the basis of the results of the mixed Tishchenko reactions together with quantum chemical calculations based on the PM3-MO theory, the following conclusions can be obtained. (a) The aldehyde with the more positively charged and sterically less hindered carbonyl carbon atom reacts faster with the intermediate IV. (b) The intermediate IV with the sterically less hindered oxygen atom reacts faster.

Active catalysts for the mixed Tishchenko reactions are alkaline earth oxides except BaO. In particular, SrO and CaO exhibit high activities. The other solid base catalysts such as La2O3, ZrO2, KF/Al2O3, KOK/Al2O3, hydrotalcite, γ-Al2O3, and ZnO are not active at the reaction temperature of 353 K. Strongly basic sites and weakly acidic sites (metal cation) may be indispensable for a highly active catalyst.

High activities of SrO and CaO were demonstrated by the Tishchenko reaction of furfural69).

\[ 2 \overset{\text{O}}{-\text{CHO}} + \text{SrO} (100 \text{ mg}) \rightarrow \overset{\text{O}}{-\text{CHO}} (10 \text{ mmol}) \text{ neat, 353 K, 6 h} \]

The Tishchenko reaction of furfural is regarded as difficult to carry out using traditional aluminum alkoxides, boric acid, or tetracarbonylferrate(II) as catalysts. Only recently some homogeneous catalysts such as (C5Me5)2LaCH(SiMe3)2 and La[N(SiMe3)2]3 were found to be effective. For such a difficult reaction, excellent results were obtained with SrO and CaO at 353 K.

The Tishchenko reaction, when carried out with dialdehydes, can produce lactones via an intramolecular catalytic esterification. Actually alkaline earth oxides except BaO gave good results for the intramolecular Tishchenko reaction of o-phthalaldehyde to phthalide at 313 K70).

\[ \overset{\text{CHO}}{-\text{CHO}} \rightarrow \overset{\text{O}}{-\text{O}} \]

CaO is the most active among the alkaline earth oxides. These results indicate that solid base catalysts are potential catalysts for macro lactonization, which is often required in the synthesis of natural products exhibiting biological activities.

5. Strength of Basic Sites Required for Different Reactions

The most efficient solid base catalyst for a certain reaction varies with the type of reaction. Some reactions need strongly basic sites and some other reactions proceed on weakly basic sites. The variation of the activity as a function of the pretreatment temperature of catalyst also changes with the type of reaction. For some reactions, extensive outgassing of the catalyst at high temperature is required. For some other reactions, the catalyst exhibits sufficient activity after pretreatment at a lower temperature at which hydroxy groups and carbonate groups apparently remain on the surface.

As shown in Fig. 3, MgO has several ion pairs with different coordination number. The appearance and disappearance of these ion pairs depend on the pretreatment temperature as described earlier. Stronger basic sites appear after pretreatment at higher temperatures. The variation of the activity for a certain reaction may reflect the strength of the basic sites relevant to the reaction. The relationship between the appearance and disappearance of basic sites with different strengths may be similar for all the alkaline earth oxides.

As shown in Fig. 6, the strengths of the basic sites among alkaline earth oxides are in the order of BaO > SrO > CaO > MgO. In order to elucidate the relative strength of basic sites relevant to different reactions, it would be helpful to list the activity order among alkaline earth oxides for different reactions, and the pretreatment temperature providing the maximum activity of MgO, which is a representative catalyst. In addition, the surface OH groups of alkaline earth oxides may act as active sites. Many surface OH groups persist on MgO pretreated at 673 K. The activity of MgO pretreated at 673 K relative to that of MgO pretreated at the temperature providing the maximum activity would give information about the possibility that weakly basic sites and OH groups act as active sites for the reaction.

Table 3 lists the order of activities among alkaline earth oxides for 19 types of reaction, the pretreatment temperature to give the maximum activity of MgO, and the activity of MgO pretreated at 673 K relative to that of the MgO pretreated at the temperature to give maximum activity. The order of activities is based on the unit weight of catalyst. However, the specific surface areas of the alkaline earth oxides are quite different. In particular, the specific surface area of BaO is much lower than the others. Therefore, the positions of BaO in the activity order contain some uncertainty. Regardless of such uncertainty, the types of reaction are arranged so that reactions requiring stronger basic sites are listed in the upper rows.

Table 3 indicates that reactions with hydrocarbons need strongly basic sites. Weakly basic sites which are supposed to be present on MgO pretreated at 673 K have little effect on reactions with hydrocarbons. Although not shown, these reactions are very sensitive to the presence of CO2 and H2O in the reaction mixture; the reactions are easily retarded by trace amounts of CO2 and H2O.

Reactions with compounds containing functional groups such as hydroxyl, nitro, and carbonyl groups
Characterization of basic sites

Actually the reactions of entries 12, 13, 16, and 18 are relatively easy. Strong adsorptivity of the compounds with alcohols is possible 59). The adsorption of than that of CO₂, and replacement of adsorbed CO₂. The adsorptivity of alcohol is compatible to or stronger than that of CO₂. However, the compounds may be strongly adsorbed on the basic sites, so the abstraction of an H⁺ from the compound is relatively easy. Strong adsorptivity of the compounds reduces the poisoning effect by CO₂ and H₂O. Actually the reactions of entries 12, 13, 16, and 18 are not poisoned by CO₂ as described earlier. The common feature of these reactions is that one of the reactants is an alcohol except for the nitroaldol reaction. The adsorptivity of alcohol is compatible to or stronger than that of CO₂, and replacement of adsorbed CO₂ with alcohols is possible 59). The adsorption of nitromethane used for nitroaldol reaction is also strong.

6. Prospects for Solid Base Catalysis

The important issues with solid base catalysis requiring further investigation are as follows.

(1) Elucidation of the nature of basic sites; in particular the role of the conjugate acid sites

Most solid base-catalyzed reactions are initiated by abstraction of an H⁺ from the reactant to form an anionic species. The anionic species should be stabilized somewhere, probably on the conjugate acid sites. Where the conjugate acid sites are located, and whether the conjugate acid sites participate in the abstraction of an H⁺ from the reactant should be established.

(2) Characterization of basic sites

Basic sites should be investigated by more methods to obtain better information. Novel methods of characterization should be developed to improve the characterization.

(3) Theoretical calculation

Theoretical calculation of solid base-catalyzed reactions is insufficient compared to that of acid-catalyzed reactions. If theoretical calculations can clarify the factors governing the strength of the basic site and the interaction of the reactant with the surface to initiate the base-catalyzed reaction, such information would contribute much to the development of solid base catalysis.

(4) Application of solid base catalysts to novel reactions

Only selected reactions among the base-catalyzed reactions in homogeneous systems have been examined using solid base catalysts. Application of solid base catalysts to the reactions not yet examined is required as well as exploration of novel reactions catalyzed only by solid base catalysts.

(5) Preparation of shape selective solid base catalysts

Shape selective catalysis is important in solid acid catalysis, but no shape selective solid base catalysis has been developed. Preparation of micro- and meso-porous materials is being developed at present, and it would be possible to prepare the materials with both basic properties and shape selective properties. These materials could open a novel field of solid base catalysis.

(6) Elucidation of the specific properties of alumina supported alkalics

Alumina supported alkalics exhibit high activity in many reactions. Although Pines et al. presented alumina supported Na metal as the first solid base catalysis, 60) it is unknown at what level the Na metal is adsorbed. The basic sites on alumina supported alkalics may be of an intermediate nature, but detailed characteristics of the basic sites have not been elucidated. The characteristics of basic sites on mixed oxide catalysts, for example, alumina supported alkalics, have been partly elucidated. 13) Such characteristics are required for the preparation of shape selective solid base catalysts.
catalyst about half a century ago, the role of alumina in generating the basic sites has not been elucidated yet. It is interesting to elucidate why alumina is so effective when alkalis are supported.

References

要   旨

固体塩基触媒: 塩基点の発現，キャラクタリゼーションおよび触媒作用

服部 英

北海道大学名誉教授，（自宅）063-0035 札幌市西区西野 5 条 10 丁目 2-3

我々の研究室で行ってきた固体塩基触媒の研究をまとめた。多くの固体塩基触媒では、高温の前処理により表面から水と CO₂を除去することによって強い塩基点が発現する。塩基点の性質は前処理の過酷さにより変化する。前処理中に、水と CO₂の除去とともに表面とパルクの原子の再配列が起こる。最適な前処理温度は塩基の種類により変わってくる。

塩基点のキャラクタリゼーションとして、指示薬法、CO₂の昇温脱離法、MgO 表面酸素と CO₂の交換、133Cs および 19F のNMR について述べた。

次の反応に対する固体塩基の触媒作用について述べた。1) 二重結合移行, 2) 水素化, 3) アミノ化, 4) アルドール付加, 5) ニトロアルドール付加, 6) Michael 付加, 7) アルコールの共役付加, 8) シアノエチル化, 9) 酰酸エチルのトランスエステル化とプロピレンオキシドのアルコール分解, 10) Tishchenko 反応。

種々の反応について、アルカリ土類酸化物の活性序列, MgO 触媒の最適前処理温度および表面に多量の水酸基が存在する 673 K 処理の活性に基づいて、有効な塩基点の強度について検討を行った。炭化水素の反応には強い塩基点が必要であるが、官能基を持つ化合物の反応には弱い塩基点でも有効である傾向が見られた。

最後に、固体塩基触媒の重要な課題を提示した。