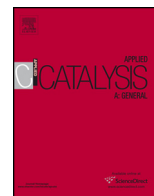




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# Solid base catalysts: fundamentals and their applications in organic reactions

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### ABSTRACT

Solid base catalysis studied over the last half of century is reviewed briefly including mainly those performed in our laboratories. The review begins with advantages of solid base catalysts over homogeneous base catalyst in industrial use followed by definition of Brønsted base and Lewis base. The materials known as solid base catalysts are listed, and four reasons for which these materials are recognized as solid base catalyst are explained. For all solid base catalysts, variations in activity as a function of pretreatment temperature show a volcano shape; an incline with the temperature results from an appearance of basic sites by removal of water and carbon dioxide from the surface and a decline results from an elimination of basic sites by rearrangement of surface atoms. The reactions catalyzed by solid base catalysts can be classified into three types: double bond isomerization, addition of anion and proton to various double bonds, and alcohol decomposition. These are represented by 1-butene isomerization, hydrogenation of conjugated 1,3-butadiene and dehydration of 2-butanol. Their mechanisms are explained. In addition, bifunctional base-catalyzed reactions in which basic sites participate in one step of successive steps are exemplified for methyl isobutyl ketone synthesis, metathesis, Tishchenko reaction and side-chain alkylation of toluene. Some industrial processes and future perspectives are briefly described.

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## 1. Introduction

Study of solid base catalysts started in 1958 with a series of investigations by Pines and Haag [1]. They reported that alkali metal-supported alumina showed catalytic activity for double bond isomerization of alkenes that proceeded via carbanions as intermediates. In 1970's, a number of metal oxides other than those containing alkali metals were found to show catalytic activities for base-catalyzed reactions. In contrast to solid acid catalysts which were already used in industrial processes, we had to wait more than two decades until solid base catalysts were used practically.

Advantages of solid base catalysts over liquid base catalysts in industrial use are as follows:

1. Neutralization of reaction mixture is not required. In liquid base-catalyzed reactions, neutralization of the base is required, while in solid base-catalyzed reactions, neutralization step is not required. Neutralization produces waste which can be minimized by use of solid base catalysts.

2. High temperature reaction is possible. Since solvents are normally used in liquid base-catalyzed reactions, the reaction temperature is limited below boiling temperature under an atmospheric pressure. There is no limitation of the reaction temperature for solid base-catalyzed reactions.
3. Employment of flow reactor system makes the process highly productive.
4. Separation of catalysts from products is easy, and recycled use of spent catalyst is possible.
5. Use of base-tolerant materials is not required for reactor system.
6. Bifunctional (dual functional) catalysis is possible. On the surfaces of solid bases, co-existence of basic sites and acidic sites is possible, while it is impossible in liquid phase.
7. There are some reactions specific to solid base catalysts.

Heterolytic splitting of  $H_2$  into  $H^+$  and  $H^-$  has not been observed for liquid base, while it is observed for solid base and the initial step for base-catalyzed hydrogenation of conjugated dienes.

## 2. Brønsted base and Lewis base

In the definition by Brønsted–Lowry, a base  $B^-$  accepts a proton from a reactant. In the definition by Lewis, a base B donates an electron pair to a reactant.

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**Table 1**  
Types of solid base catalysts.

- (1) Single component metal oxides
  - alkaline earth metal oxides: MgO, CaO, SrO, BaO
  - rare earth oxides: La<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>
  - other oxides: Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, ZnO, TiO<sub>2</sub>, MoO<sub>3</sub>, ThO<sub>2</sub>
- (2) Double components metal oxide
  - ZnO–Al<sub>2</sub>O<sub>3</sub>, MgO–TiO<sub>2</sub>
- (3) Zeolites
  - alkali ion-exchanged zeolites: Na–X, Cs–X
  - alkali ion-added zeolites: Cs<sub>2</sub>O/Cs–X
- (4) Supported alkali metal compounds
  - alkali metal compounds on alumina: Na<sup>0</sup>/Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>
  - alkali metal compound on silica: Na<sup>0</sup>/SiO<sub>2</sub>, Na<sub>2</sub>O/SiO<sub>2</sub>
  - alkali metal ions on alkaline earth oxides: Na<sub>2</sub>O/MgO
- (5) Clay minerals
  - hydrotalcite: Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O
  - chrysotile: Mg<sub>3</sub>(Si<sub>2</sub>O<sub>5</sub>)<sub>2</sub>(OH)<sub>4</sub>
  - sepiolite: Mg<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>2</sub>
- (6) Non-oxide
  - KF supported on alumina: KF/Al<sub>2</sub>O<sub>3</sub>
  - lanthanide imide and nitride on zeolite
  - metal oxynitrides: ALPON, VALPON

Basic sites (B) abstract a proton from the reactant molecules (AH) to form anions (A<sup>−</sup>).



Here, the basic site B<sup>−</sup> on the surface acts as a Brønsted base.

Examples of this type of the formation of anionic intermediates are 1-butene isomerization where an H<sup>+</sup> is abstracted from C<sup>3</sup> position to form allylic anion, and aldol condensation and Knoevenagel condensation where an H<sup>+</sup> is abstracted from ketone with α-H to form anions.

Basic sites (B) donate an electron pair to form anionic intermediates. For example, ketones can be activated without proton transfer.



An example of this type of acid–base interaction is



Here, the basic site acts as a Lewis base.

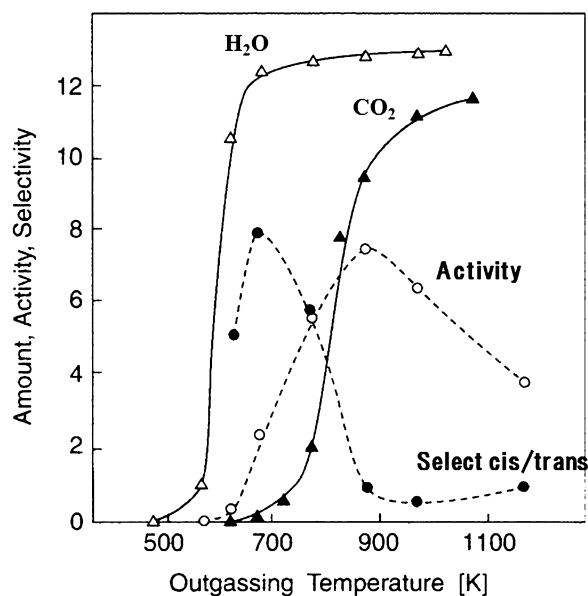
An example of this type for base-catalyzed reaction is Tishchenko reaction where basic site donates an electron pair to the carbonyl C atom to form anionic intermediate.

It should be noted that the same surface site can serve as either Brønsted base (proton acceptor) or Lewis base (electron pair donor) depending on the nature of the reactant. The naming of base should be based on its function (H<sup>+</sup> abstraction or electron pair donation).

### 3. Solid base catalysts

Types of solid base catalysts are listed in Table 1. The reasons for which these catalysts are recognized as solid base catalysts are as follows.

1. Characterization of the surfaces indicates the existence of basic sites. Color change of the acid–base indicators, adsorption of acidic molecules and spectroscopies indicate that basic sites exist on the surfaces.
2. Catalytic activities correlated with the amount or strength of basic sites. In addition, the active sites are poisoned by acidic molecules such as CO<sub>2</sub>, H<sub>2</sub>O, and HCl.
3. The reactions proceeding over the materials are similar to the “base-catalyzed reactions” which are well-known in homogeneous systems. These reactions include alkylation,



**Fig. 1.** Evolution of H<sub>2</sub>O and CO<sub>2</sub> and appearance of catalytic activity for 1-butene isomerization over CaO prepared from Ca(OH)<sub>2</sub>.

isomerization, Michael addition, aldol addition, Tishchenko reaction, etc.

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

### 4. Generation of basic sites

Because of basic properties, the surfaces of basic materials are covered with CO<sub>2</sub> and H<sub>2</sub>O when exposed to atmospheric environment. In some cases, metal oxides are prepared from metal hydroxides and metal carbonates by decomposition. To remove CO<sub>2</sub> and H<sub>2</sub>O from the surfaces or bulk, pretreatment at a high temperature is required to reveal basic sites on the surfaces. The generation of basic sites and catalytic activity vary with the pretreatment temperature.

Fig. 1 shows the variations in the evolution of H<sub>2</sub>O and CO<sub>2</sub> from the starting material Ca(OH)<sub>2</sub> and in the catalytic activity for 1-butene isomerization as a function of the pretreatment temperature in a vacuum [2]. In the temperature range 500–600 K, dehydration of Ca(OH)<sub>2</sub> to CaO takes place, but the surface is still covered with H<sub>2</sub>O and CO<sub>2</sub>. At 600 K, CO<sub>2</sub> and H<sub>2</sub>O begin to remove from the surface to expose the surface of CaO, and the activity also begins to appear.

Appearance of basic sites by removal of CO<sub>2</sub> and H<sub>2</sub>O is commonly observed for solid base catalysts such as MgO, SrO, BaO, La<sub>2</sub>O<sub>3</sub> and Sm<sub>2</sub>O<sub>3</sub>. The basic sites appeared by removal of CO<sub>2</sub> and H<sub>2</sub>O are not uniform as shown in Fig. 2 where the surface model of MgO is shown after complete removal of H<sub>2</sub>O and CO<sub>2</sub> [3]. There are ion pairs (Mg<sup>2+</sup>–O<sup>2−</sup>) with different coordination numbers. The ion pairs with lower coordination numbers are supposed to be stronger and adsorb CO<sub>2</sub> and H<sub>2</sub>O more strongly than the ion pairs with higher coordination numbers. Therefore, as the pretreatment temperature increases, appearance of basic sites is in the order of increasing basic strength. This reflects on the variation in catalytic activity for different reactions. The reaction that needs stronger basic sites shows an activity maximum at a higher pretreatment temperature.

The activity variations of MgO as a function of pretreatment temperature show maximum at 800, 950 and 1300 K for 1-butene isomerization, CH<sub>4</sub>-D<sub>2</sub> exchange and 1,3-butadiene

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