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Solid base catalysts for the synthesis of fine chemicals

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Abstract

Although catalysis by solid acids has received much attention due to its importance in petroleum refining and petrochemical processes, relatively few studies have focused on catalysis by bases. Base catalysts, however, play a decisive role in a number of reactions essential for fine-chemical synthesis. Solid-base catalysts have many advantages over liquid bases in many respects. Here, recent developments in catalysis by solid bases is described, especially regarding catalytic materials and catalytic reactions. The reactions include isomerization, aldol condensation, Knoevenagel condensation, Michael condensation, oxidation, and Si–C bond formation.

1. Introduction

Carbanions are important intermediates in many organic reactions for fine-chemical synthesis. They are formed by abstraction of a proton from a C–H bond of an organic molecule by a base. Many organic reactions often require a stoichiometric amount of liquid base to generate carbanions and produce a stoichiometric amount of metal salts as by products. For example, the methylation of phenylacetonitrile with methyl iodide proceeds in the presence of a base under a phase-transfer condition.

$$\mathrm{PhCH_2CN + CH_3l + NaOH \rightarrow PhCH(CH_3)CN + Nal + H_2O} \qquad (1)$$

In this case, more than a stoichiometric amount of sodium hydroxide is required to neutralize the hydrogen iodide produced and to keep the system basic. Furthermore, a stoichiometric amount of sodium iodide is inevitably formed and has to be disposed of in an appropriate manner. We have shown that phenylacetonitrile can be methylated in vapor phase with basic zeolites by using methanol as a methylating agent [1]:

$$\mathrm{PhCH_2CN + CH_3OH \rightarrow PhCH(CH_3)CN + H_2O.} \qquad (1')$$

Organometallic compounds such as Grignard reagents and alkyl lithium are frequently used as donors of carbanionlike species. Here again, a stoichiometric use of these reagents is required.

$$\mathrm{(CH_3)_3SiCl + PhC{\equiv}CLi \rightarrow PhC{\equiv}CSi(CH_3)_3 + LiCl} \qquad (2)$$

Various silicon compounds can be synthesized by reactions using solid-base catalysts, as described later.

Solid-base catalysts have many advantages over liquid bases or organometallics. They present fewer disposal problems, while allowing easier separation and recovery of the products, catalysts, and solvent. They are noncorrosive. Thus, solid-base catalysts offer environmentally benign and more economical pathways for the synthesis of fine chemicals. Because of these advantages, research on the synthesis of fine chemicals using solid bases as catalyst has increased over the past decade.

This short review surveys the recent development of solid-base materials and the reactions catalyzed by solid bases. Review articles published recently describe more detail of some aspects of catalysis by solid bases [2–9]. In Refs. [6,8], the industrial processes using solid-base catalysts are listed.

2. Catalytic materials

2.1. Strong bases

Various types of strongly basic catalysts are reported. They are characterized by high catalytic activities for alkene

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Table 1
The Catalytic activities of solid-base catalysts for the isomerization of 2,3-dimethylbut-1-ene at 201 K [9]

Catalyst	Pretreatment temperature (K)	Reaction time (min)	Conversion (%)
$RbNH_2/Al_2O_3(2.6)^a$	573	10	90.2
$KNH_2/Al_2O_3(2.6)^a$	573	10	87.3
$NaNH_2/Al_2O_3(2.6)$	523	10	0.1
$KNO_3/Al_2O_3(2.6)$	873	30	49.4
$K_2CO_3/Al_2O_3(2.6)$	873	30	4.2
$K/Al_2O_3(12.0)$	573	10	7.0
$CsOH/Al_2O_3$	873	30	67.8
$RbOH/Al_2O_3$	873	30	36.4
KOH/Al_2O_3	873	30	34.1
$NaOH/Al_2O_3$	873	30	0
CaO	998	10	63.0
$4MgO \cdot Al_2O_3^b$	773	1200	1.3
KY^b	773	1200	< 0.1

Conditions: catalyst, 0.25 g; 2,3-dimethylbut-1-ene, 24 mmol; pretreatment time, 1 h; number in parentheses, supported amount in millimoles per gram.
[a] Catalyst, 0.063 g.
[b] Reaction temperature at 313 K.

isomerization at relatively low temperatures [10]. Alkene isomerization is a good test reaction for strongly basic catalysts, since alkenes have high pK_a values (pK_a value of propene = 38 [11]). In Table 1, the catalytic activities of highly basic catalysts for the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene at 201 K are listed [10].

Alkaline earth metal oxides such as MgO and CaO are active for various types of reactions. The catalytic properties of alkaline earth oxides are described in detail elsewhere [2,6,12]. Various alkali metal compounds were found to be very strong bases when supported on alumina and to catalyze a variety of reactions.

2.1.1. KF/Al_2O_3

Potassium fluoride supported on alumina (KF/Al_2O_3) has been used by organic chemists and considered a convenient catalyst to handle because of its easy workup after reactions. Though KF/Al_2O_3 has wide application in organic chemistry, the idea of its catalytically active species is still controversial [11].

Conventionally, preparation and drying (usually below 473 K) are done in an ambient atmosphere. Therefore, adsorption of water and carbon dioxide is unavoidable and the effects of these adsorbed molecules have never been studied in detail.

Tsuji et al. revealed that KF/Al_2O_3 showed much higher activity when treated at higher temperature under vacuum [14]. The activity of KF/Al_2O_3 for 1-pentene isomerization showed a sharp maximum at 623 K. The sharp dependence of the catalytic activity on evacuation temperature was also found for the Tishchenko reaction of benzaldehyde [15] and the disproportionation of trimethylsilylacetylene [16]. In the case of the Tishchenko reaction of benzaldehyde, no activity was observed at an evacuation temperature of 473 K, while it was about 50% on evacuation at 623 K, as shown in Fig. 1. These phenomena indicate that the active species developed on evacuation at high temperatures may be entirely different from those of the KF/Al_2O_3 used in usual practice.

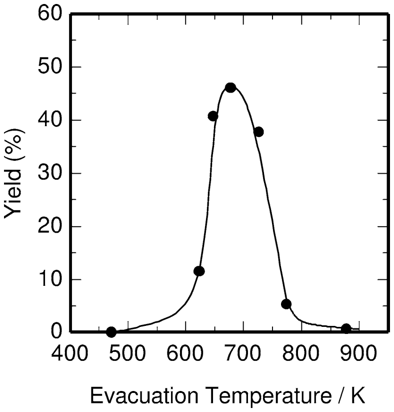


Fig. 1. Effect of evacuation temperature on the yield of benzyl benzoate in the reaction of benzaldehyde over KF/Al_2O_3 [13]. Reaction conditions: temperature, 273 K; reaction time, 3 h; catalyst, 0.25 g; benzaldehyde, 29.5 mmol.

2.1.2. Alkali metal compounds supported on Al_2O_3

Potassium compounds such as KNO_3, $KHCO_3$, and K_2CO_3 supported on alumina when heated at high temperature are highly active catalysts for the isomerization of 1-butene at 273 K [17]. Table 1 also shows that these materials are very active for the isomerization of 2,3-dimethylbut-1-ene. The supported compounds are decomposed at least partly during heat treatment, but the origin of the basic sites is not clear [18].

Hydroxides of alkali metals supported on alumina such as KOH/Al_2O_3, $RbOH/Al_2O_3$, and $CsOH/Al_2O_3$ show very high catalytic activity for the isomerization of 2,3-dimethylbut-1-ene even at 201 K when pretreated at high temperatures, as shown in Table 1, indicating that these materials are very strong solid bases [11].

These classes of catalysts have the advantage of ease of preparation and strong basicity.

2.1.3. KNH_2/Al_2O_3

When potassium metal is supported on alumina from the ammoniacal solution, the resulting solid shows high basicity when heated under vacuum [3,19]. A detailed study of this catalyst has revealed that the active species in this catalyst is potassium amide. The activity of this catalyst (KNH_2/Al_2O_3) for the isomerization of 2,3-dimethylbut-1-ene is far greater than that of K/Al_2O_3, which is prepared by the vapor deposition of K on alumina. The activity of $RbNH_2/Al_2O_3$ is still higher (Table 1) [9]. The NH_2 groups in KNH_2/Al_2O_3 react even with methane (pK_a = 50) [20]. Thus, the H–D exchange reaction proceeds between KND_2/Al_2O_3 and CH_4 at room temperature. The H–D exchange reaction was also observed between KND_2/Al_2O_3 and C_2H_6.

2.2. *Modest or weakly basic materials*

These materials may be characterized by negligible activity for alkene isomerization. One of the advantages of weak bases such as zeolites is their easy handling. They can be handled in an ambient atmosphere, since adsorption of carbon dioxide or water is not too strong, and they can be removed by high-temperature treatment in the reactor. They can be used even in the systems where these molecules are involved as a reactant(s) or product(s). Here, among weak bases, zeolites, hydrotalcites, AlPONs, and mesoporous silica functionalized with amines are described.

2.2.1. *Zeolites*

Zeolites are usually used as solid-acid catalysts. Alkali ion-exchanged zeolites, especially faujasites, however, behave as weak bases. The origin of the basicity is believed to be the oxygen ions in the zeolite framework. The base strength of alkali ion-exchanged zeolites has been rationalized by the negative charge of the oxygen atoms [3,5,21].

Strongly basic catalysts can be prepared by impregnating CsNaX and CsNaY with cesium acetate followed by thermal decomposition of the acetate into the oxide, which act as basic sites [22–24]. The catalytic activity for the dehydrogenation of isopropyl alcohol to acetone increased an order of magnitude by loading Cs onto CsY. The isomerization of 1-butene proceeds over these catalysts at 273 K. Various evidence including ^{133}Cs NMR indicates that the active species is nanophase cesium oxide occluded in the supercage of the zeolites.

Another method for obtaining strongly basic catalysts is the loading of ytterbium or europium metal on Y–zeolites from the ammoniacal solution [25,26]. Temperature-programmed desorption and infrared spectroscopic study revealed that the catalytically active species are imide or amide of these metals.

Microporous titanosilicate ETS-10 is more basic than alkali ion exchanged faujasite [27,28]. In the 2-propanol conversion, Cs-exchanged X-type zeolite gave a 49.4% selectivity for acetone, while Cs-exchanged ETS-10 gave a 85.8% selectivity at 623 K.

2.2.2. *Hydrotalcite*

Hydrotalcite has the unit cell formula $Mg_6Al_2(OH)_{16}(CO_3{}^{2-}) \cdot 4H_2O$; the ratio of Mg/Al ratio can vary in the range of 1.7–4 in synthetic samples [9,29]. Their structure consists of positively charged brucite layers, altering with negatively charged interlayers containing anions and water molecules. Materials with Mg replaced by Zn, Fe, Co, Ni, and Al replaced by Cr, Ga, and Fe have been synthesized. The materials with different kind of anions can also be prepared. Anions can also be introduced by ion exchange of an as-synthesized material. Application of hydrotalcite as catalysts were recently reviewed by Sels et al. [9]. Hydrotalcite and the analogues are used in different forms as catalysts.

2.2.2.1. Hydrotalcite as synthesized As-synthesized hydrotalcite showed a high catalytic activity for decomposition of 2-methyl-3-butyn-2-ol into acetone and acetylene [30]. Halide exchange reactions between alkyl chloride and bromide/iodide are catalyzed by the material having Cl^-, Br^-, or I^- in the interlayers [31]. Hydrotalcite introduced t-$C_4H_9{}^-$ ions by ion exchange has a high catalytic activity for transestrification of normal and β-ketoesters with a variety of alcohols and amines [32].

2.2.2.2. Mixed oxide In most catalytic applications, hydrotalcite and its analogues are used after calcination at around 773 K to form mixed oxides [11,29,33]. Thus, mixed oxides containing Mg and Al prepared from hydrotalcite are highly basic, with some acidic sites. The materials thus prepared are not hydrotalcite any more. Many "scientific" papers express these materials simply as hydrotalcite, but they should be called "mixed oxides prepared from hydrotalcite." The preparation of mixed oxides from hydrotalcite and its analogs offers oxides with MgO-like structure, where two kinds of metal ions are more homogeneously distributed in comparison with those prepared by other methods, such as coprecipitation.

Corma et al. studied the catalytic activity of Mg–Al mixed oxides prepared from hydrotalcite for the Knoevenagel condensation of benzaldehyde with activated methylenic compounds with different pK_a values and concluded that the mixed oxide has basic strength with $H-$ up to 16.5, with most being in the range of $10.7 < H < 13.3$ [34].

2.2.2.3. Reconstructed hydrotalcite When oxides having MgO-like structure are rehydrated in water or in flowing nitrogen saturated with water, hydrotalcite structure is reconstructed. The reconstructed material contains OH^- ions in the interlayers. It is impossible to introduce OH^- ions by direct ion exchange. Figueras and co-workers found that the reconstructed materials were very useful catalysts for aldol condensation [35,36] and Michael addition [37]. The OH^- ions in the interlayers are believed to be active sites for these reactions. The base strength of the reconstructed hydrotalcite containing OH^- ions is stronger than the original hydrotalcite containing $CO_3{}^{2-}$ ions.

2.2.3. *Oxynitrides*

A gas–solid reaction of amorphous silica with ammonia at 1373 K gives a high-surface-area form of silicon oxynitride, Si_2N_2O, which has a solid-base character [38].

Recently, the synthesis of aluminophosphate oxynitride (AlPON) and its catalytic activities were extensively studied [39,40]. AlPONs are prepared by heating aluminum phosphate under flowing ammonia to 1073 K. The activity depends on the nitrogen content of AlPONs and the active sites are considered to be $–NH_2$ and –NH– groups on the surface [41].

Oxynitrides of galloaluminophosphate (AlGaPON) [42], zirconophosphate (ZrPON) [43], and aluminovanadate

(VAlON) [44] were prepared in a similar manner. Oxynitrides are known to catalyze Knoevenagel condensation reactions. Application of the materials to other types of reactions is highly desirable.

2.2.4. Mesoporous silica functionalized with amino groups

New families of mesoporous silica, such as MCM-41, opened new opportunities for supports due to tunable larger pore sizes. There have been various attempts to link functional groups on the surface of mesoporous silica.

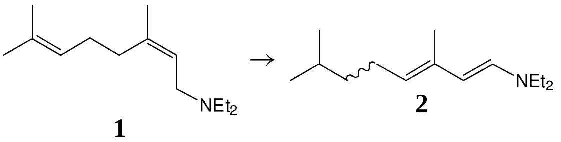
Macquarrie and Jackson [45] reported the direct synthesis of MCM-type silica having 3-aminopropyl-groups. The amino groups can also be introduced postsynthesis by using the reactivity of the OH groups. Mesoporous silica with a variety of amino groups has been tested for the reactions, including the syntheses of monoglycerides from fatty acids and glycidol, Knoevenagel condensation, and aldol condensation [46–50].

3. Reactions catalyzed by solid bases

3.1. Isomerization of alkenes and alkynes

Isomerization of alkenes proceeds through anion intermediates formed by abstraction of an allylic proton from alkene molecules by solid bases. Since pK_a values of alkenes are high, strongly basic catalysts are required for the isomerization. As shown in Table 1, only strong solid bases are active for the isomerization of 2,3-dimethylbut-1-ene. Among them, alkali amides supported on Al_2O_3 and alkaline earth metal oxides show very high activity for isomerization.

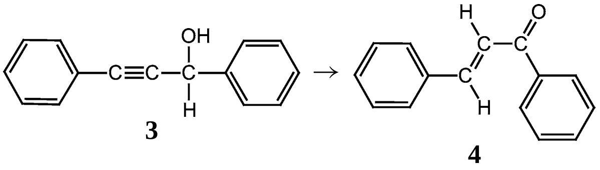
Allylamines are isomerized to enamines. 1-N-pyrrolidino-2-propene isomerizes to 1-N-pyrroridino-1-propene in 100% selectivity over alkaline earth oxides at 313 K [2]. The isomerization of *N*,*N*-diethyl-3,7-dimethylocta-2(*Z*),6-dienylamine **1** proceeds in the presence of KNH_2/Al_2O_3 at 313 K to exclusively afford *N*,*N*-diethyl-3,7-dimethylocta-1,3-dienylamine **2** [51]. The ratio of E/Z of the double bond at position 3 in the product is almost 1/1. The double bond at position 1 is 100% E.



(3)

Passing an ethyl acetate–hexane solution of **2** through a column of silica gel yielded quantitatively 3,7-dimethyloct-2-ene-1-al. The E/Z ratio of the aldehyde was 12 : 1. This shows that the selective isomerization of **1** to **2** offers a convenient route to monoterpene aldehyde, since the reactant is easily prepared by the dimeric addition of isoprene to dialkylamine in the presence of a base catalyst.

The isomerization of alkyn-1-yl alcohol to α,β-unsaturated ketones proceed over solid-base catalysts [52]. Thus, in the reaction of **3** in dioxane with Cs_2CO_3/Al_2O_3 for 20 h at 303 K, **4** was obtained in a 97% yield.



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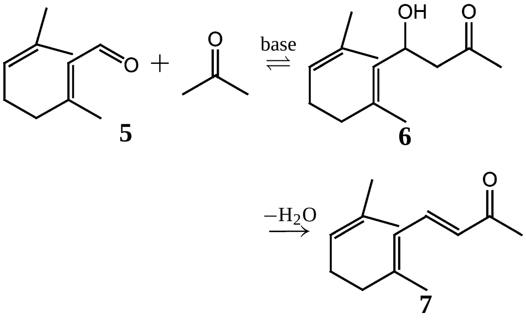
3.2. C–C bond formation

3.2.1. Aldol condensation

Aldol addition of acetone to diacetonealcohol is catalyzed by a variety of solid bases, such as alkaline earth oxides, La_2O_3 and ZrO_2, and $Ba(OH)_2$ [2,6]. Cross aldol condensation of acetone with substituted benzaldehyde gives selectively the corresponding dehydration products of the corresponding aldols at 333 K in the presence of hydrotalcite bearing OH^- ions [33]. When diamino-functionalized mesoporous silica was used as a catalyst, the products were a mixture of the aldols and their dehydration products [50].

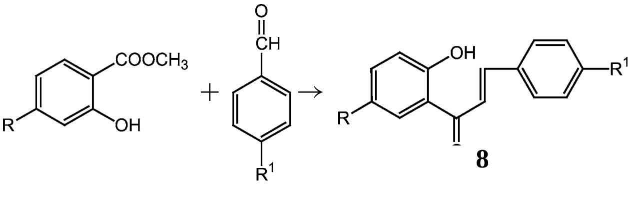
Hydrotalcite bearing OH^- ions exhibits high activity and selectivity in the condensation of citral (a mixture of neral, **5**, and geranial) and acetone into pseudoionone **7**, which is an intermediate in the commercial production of vitamin A [53]. The hydrotalcite has higher activity when the water in the interlayers is replaced by ethanol. At 273 K, a conversion of 92% was obtained with a 79% selectivity for ($\mathbf{7}+\beta$-hydroxyketone, **6**).



(5)

Similarly, the condensation between citral and methylethylketone gave a 76% conversion at 273 K.

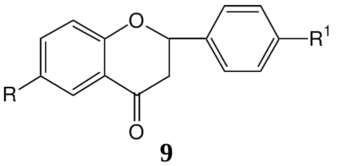
The Claisen–Schmit condensation of 2-hydroxyacetophenones and benzaldehyde derivatives proceeds at 423 K in air using mixed oxides derived from hydrotalcites as the catalysts [54].



$+\ H_2O$ (6)

The primary product **8** further isomerized to flavone **9** under the reaction conditions.

8 →



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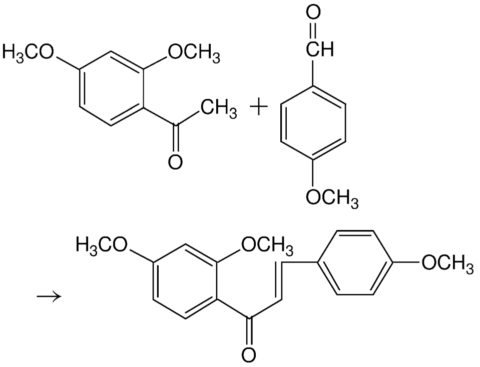
(7)

The following reaction proceeds to yield Vesidryl (2′,4′,4-trimethoxychalcone) **10** in a 85% yield at 443 K [54].



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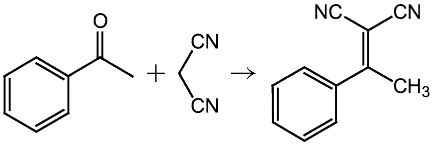
(8)

3.2.2. Knoevenagel condensation

Knoevenagel condensation is the reactions between a ketone and active methylene compounds and proceeds over a variety of weakly basic catalysts, such as alkali-ion-exchanged zeolites, alkali-ion-exchanged sepiolite, oxynitrides, and t-BuOK supported on xonotlite [3,5].

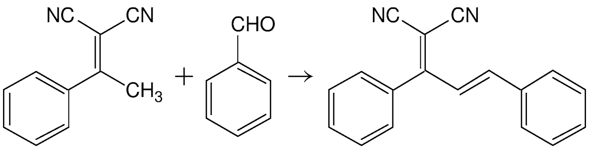
Reconstructed hydrotalcite is reported to give quantitative yields for a variety of Knoevenagel condensations [36]. Mesoporous silica modified with amino groups were also effective [45–47]. AlPON is effective for the synthesis of α-phenylsulfonylcinnamonitrile by the condensation of phenylsulfonylacetonitrile with benzaldehyde [55].

The two-step synthesis of dicyanomethylene derivative dyes was performed using different solid bases [56]. The first step is the Knoevenagel condensation of acetophenone and malononitrile to give the corresponding α-methylbenzylidenemalononitrile **11**. Subsequent condensation of **11** with benzaldehyde gives the 1,1-dicyano-1,3-butadiene dye **12**.



+ H_2O (9)

11



11 **12**

+ H_2O (10)

The first step, the Knoevenagel condensation, was catalyzed by a variety of solid bases such as MgO, calcined hydrotalcites, and AlPONs. Only AlPONs are able to catalyze efficiently the second step. The two-step reaction could also be performed in a "one-pot" system.

The reaction of salicylaldehyde with diethylmalonate in the presence of montmorillonite gave ethyl coumarine-3-carboxylate [57].

3.2.3. Nitroaldol reactions

The nitroaldol condensation of aldehydes with nitroalkanes proceeds in the presence of bases. The reactions often proceed further to afford nitroalkenes.

$$\begin{aligned} R^1CHO + R^2CH_2NO_2 &\rightarrow R^1CH(OH)CH(NO_2)R^2 \\ &\rightarrow R^1HC{=}C(NO_2)R^2 \end{aligned} \tag{11}$$

Mg–Al mixed oxides prepared by calcination of hydrotalcite catalyze the nitroaldol condensation to nitroalcohols. The reaction is diastereoselective. For example, when 3-nitrobenzaldehyde and nitroethane was refluxed in THF, 1-(3-nitrophenyl)-2-nitropropan-1-ol was obtained in a 95% yield with a threo/erythro ratio of 12.5 [58].

The nitroaldolic reaction of propionaldehyde and nitromethane gives the addition product, 1-nitro-2-hydroxybutane, in the presence of different solid bases at 313 K [6]. Among the solid bases studied, MgO was the most active. The activity was not so strongly dependent on the pretreatment temperature and was scarcely retarded by exposure to air.

The condensation of aromatic aldehydes with nitroalkanes over alkaline ion-exchanged zeolites affords nitroalkenes directly. Thus, in the reaction of benzaldehyde and chlorobenzene with nitromethane, CsNaX gave the corresponding nitroalkenes in 68 and 80% yields, respectively, at 413 K [59].

3.2.4. Michael addition

The Michael addition reaction involves a nucleophilic addition of a carbanion to α,β-unsaturated carbonyl compounds. KF/Al_2O_3 has been known to catalyze Michael additions [13]. Kabashima et al. carried out Michael additions of nitromethane to methyl crotonate, 3-buten-2-one, 2-cyclohexen-1-one, and crotonaldehyde in the presence of KF/Al_2O_3, KOH/Al_2O_3, alkaline earth oxides, or La_2O_3 [60]. In all cases, KF/Al_2O_3 showed high activities, while MgO and CaO exhibited no activity for methyl crotonate and 3-buten-2-one and low activity for 2-cyclohexen-1-one and crotonaldehyde.

Dimerization of methyl crotonate proceeded to yield dimethyl 2-ethylidene-3-methylglutarate [61]. The reaction proceeds through self-Michael addition of methyl crotonate followed by double-bond migration of the addition product. MgO was an only active catalyst among the various solid bases studied.

Mesoporous silica having N,N-dimethyl-3-aminopropyl groups prepared by a templated sol–gel method are shown to be a good catalyst for Michael addition reactions of nitroalkanes to but-3-en-2-one and 2-cyclohaxen-1-one. No leaching of the catalytic component was observed [62]. Reconstructed hydrotalcite having OH^- ions selectively catalyzes Michael additions on methyl vinyl ketone, methyl acrylate, and simple and substituted chalcones by donors such as nitroalkane, malononitrile, diethylmalonate, cyanoacetamide, and thiols [37].

3.2.5. Conjugate addition of alcohols

Cyanoethylation of alcohols such as methanol, ethanol, and 2-propanol with acrylonitrile proceeds at 273 K over alkaline earth oxides and hydroxides, KF/Al_2O_3 and KOH/Al_2O_3. The reaction was not poisoned by adsorption of carbon dioxide at room temperature [63].

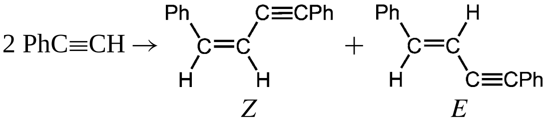
$$ROH + H_2C{=}CHCN \rightarrow ROCH_2CH_2CN \qquad (12)$$

Hydrotalcite reconstituted by rehydration after calcination was found to be also a highly active catalyst for cyanoethylation of alcohols with acrylonitrile. The catalyst was reusable without appreciable loss in activity and was air stable [64].

Conjugate addition of methanol to 3-buten-2-one proceeds to form 4-methoxybutan-2-one over the solid bases such as alkaline earth oxides, strontium hydroxide, barium hydroxide, and KF/Al_2O_3, KOH/Al_2O_3 at a reaction temperature of 273 K [65]. MgO treated at 673 K gave the highest activity. The catalytic activities of MgO, CaO, and KF/Al_2O_3 were not affected by exposure of the catalysts to carbon dioxide or air.

3.2.6. Nucleophilic addition of phenylacetylene

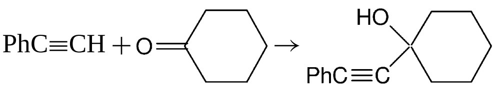
Dimerization of phenylacetylene proceeds in the presence of a KNH_2/Al_2O_3 catalyst to afford (*Z*) and (*E*)-1,4-diphenylbut-1-en-3-yne. The yield was 97% in 20 h at 363 K, with the ratio of *Z* to *E* being 96 : 4 [66].



(13)

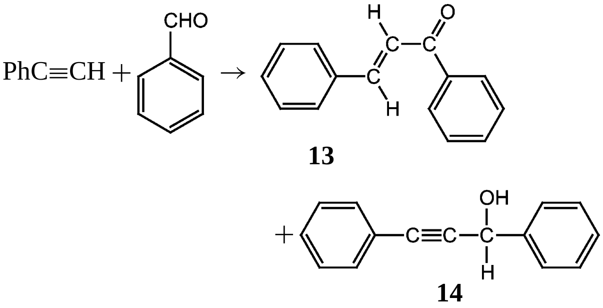
The reaction proceeds by addition of the alkynide ion, $PhC{\equiv}C^-$, to the triple bond of another molecule of phenylacetylene.

The reaction of phenylacetylene with cyclohexanone in dioxane in the presence of KNH_2/Al_2O_3 affords 1-phenylethynylcyclohexanol in a 67% yield in 20 h at 363 K [52].



(14)

The reaction of phenylacetylene with benzaldehyde in the presence of $CsOH/Al_2O_3$ in DMF gives chalcone **13** in a 75% yield in 20 h at 343 K, together with 3% of **14** [52].

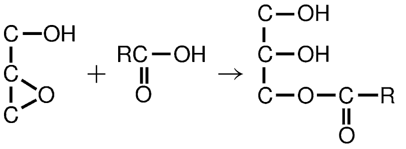


(15)

Chalcones are usually prepared by the cross aldol condensation of benzaldehyde and acetophenone in the presence of base such as KOH. The reaction (15) offers a new synthetic route for chalcones.

3.3. Nucleophilic ring opening of epoxides

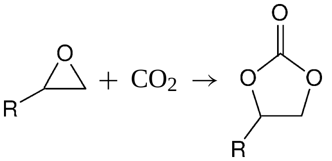
Ring opening of glycidol with fatty acids provides a route to monoglycerides, which are important food additives as emulsifiers and antimicrobial agents. Cauvel et al. found that MCM-41 grafted with 3-aminopropyl and 3-piperidinopropyl groups are active catalysts for the ring opening of glycidol with lauric acid [46]. The selectivity was improved by treating the catalysts with hexamethyldisilazane to block the residual OH groups of the surface. The gas chromatographic and isolated yields of lauric monoglyceride was > 95 and 70%, respectively.



(16)

Lin and co-workers also prepared MCM-41 grafted with various amine functions and carried out the ring opening of glycidol with lauric acid [48,49]. The most active form was MCM-41 on which triazabicyclo[4,4,0]dec-5-ene was immobilized.

MgO is an efficient catalyst for the cycloaddition of carbon dioxide under mild conditions. The reaction of carbon dioxide with (*R*)-styrene oxide gives (*R*)-phenylcarbonate in 97% *ee* with retention of stereochemistry [67]. Cycloaddition of carbon dioxide to epoxides proceeds also in the presence of mixed oxide prepared by calcination of hydrotalcite [68].



(17)

3.4. Oxidation reactions

The recent development in the use of solid bases in oxidation reactions was reviewed by Fraile et al. [7].

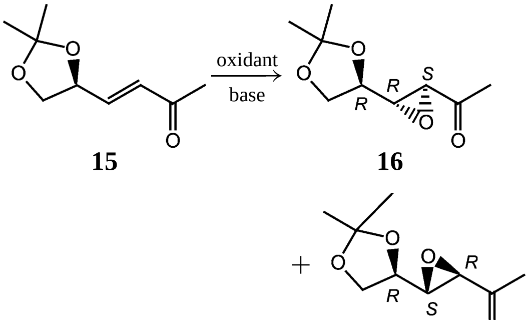
The epoxidation of electron-deficient alkenes is commonly carried out with hydroperoxides in the presence of a base. Here, a proton is abstracted from H_2O_2 or ROOH to form HOO^- and ROO^- ions, respectively. These ions act as nucleophiles and epoxidize electron-deficient alkenes such as α,β-unsaturated carbonyl compounds [69].

Choudary et al. found that hydrotalcite, where t-butoxy ions were introduced by ion exchange, was a much more efficient catalyst than the mixed oxide prepared by calcination of hydrotalcite for the epoxidation of α,β-unsaturated carbonyl compounds such as chalcone [70].

In the case of epoxidation with t-butyl hydroperoxide (TBHP), KF/Al_2O_3 is used as a base. The method was first reported by Yadav and Kapoor [71,72]. For example, cyclopentenones are oxidized in descent to quantitative yields without showing any aldol products [72].

In the epoxidation of α-isophorone, the use of TBHP in combination with KF/Al_2O_3 gave better results over H_2O_2 with hydrotalcite [73]. The epoxide was obtained at a 96% yield after reaction for 24 h at 393 K in toluene.

Fraile et al. carried out the epoxidation of two chiral alkenes derived from D-glyceraldehyde, bearing different electron-withdrawing groups [74]. Here again, TBHP–KF/Al_2O_3 was more efficient and selective than H_2O_2-calcined hydrotalcite, leading to high diastereometric excess (de). Thus, TBHP–KF/Al_2O_3 gave 100% conversion of **15** and **16**, with high diastereoselectivities, 40% de (**16** was the major product) and 50% de (**19** was the major product) and no detectable by-products.



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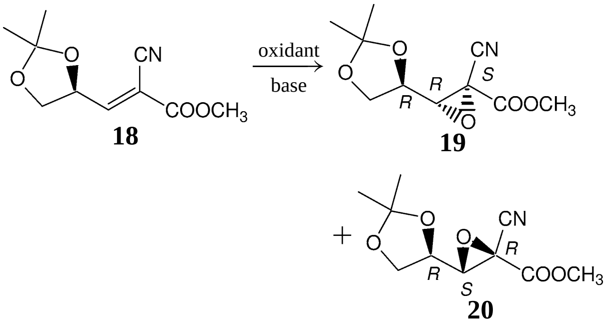
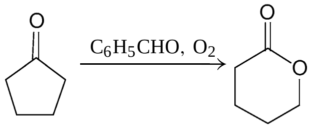


(19)

Various alkenes are epoxidized by hydroperoxide in combination with benzonitrile in the presence of as-synthesized hydrotalcite with ${CO_3}^{2-}$ ions [75,76]. For example, linear and cyclic alkenes such as oct-1-ene and cyclohexene gave the corresponding epoxides in excellent yields. Norbornene and styrene gave *exo*-norbornene oxide and styrene oxide, respectively, in high yields. In this oxidation system, the reaction proceeds in two steps: (i) formation of peroxycarboxyimidic acid by the reaction of nitrile with hydrogen peroxide and (ii) oxygen transfer from peroxycarboxyimidic acid to alkene. This catalytic system was also useful in the epoxidation of limonene [77]. Hydrotalcite with t-butoxide in the interlayers has much higher activity for the epoxidation of unfunctionalized alkenes such as styrene than as-synthesized hydrotalcite with ${CO_3}^{2-}$ ions in the presence of benzonitrile [70].

Kaneda and co-workers reported that Baeyer–Villiger oxidation of ketones by molecular oxygen in combination with benzaldehyde was greatly enhanced by adding as-synthesized hydrotalcite [78,79].



(20)

3.5. Si–C bond formation

Nucleophilic substitution occurs when an anion attacks silicon.

$$Nu^- + R_3SiL \rightarrow NuSiR_3 + L^- \qquad (21)$$

Here, L^- is a leaving group from the Si atom.

The reaction of trimethylsilylacetylene over KNH_2/Al_2O_3 or KF/Al_2O_3 leads to the metathesis of the alkyne, with the products being bis(trimethylsilyl)acetylene and acetylene [80].

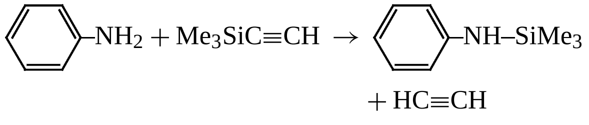
$$Me_3SiC{\equiv}CH \rightarrow Me_3SiC{\equiv}CSiMe_3 + HC{\equiv}CH \qquad (22)$$

The basic sites abstract a proton from $Me_3SiC{\equiv}CH$ to form the alkynide ion, $Me_3SiC{\equiv}C^-$, which attacks at the silicon atom of another reactant molecule. In this case, $HC{\equiv}C^-$ is a leaving group.

The cross-metathesis proceeds when 1-alkynes are reacted with silyl acetylene [80]. For example, the reaction of phenylacetylene and trimethylsilylacetylene in the presence of KF/Al_2O_3 or KNH_2/Al_2O_3 gives phenyltrimethylsilylacetylene in high yield at 318 K.

$$PhC{\equiv}CH + Me_3SiC{\equiv}CH \rightarrow PhC{\equiv}CSiMe_3 + HC{\equiv}CH \qquad (23)$$

When aniline was reacted with trimethylsilylacetylene in the presence of MgO at 318 K for 20 h, N-trimethylsilylaniline was formed in a 90% yield [3].

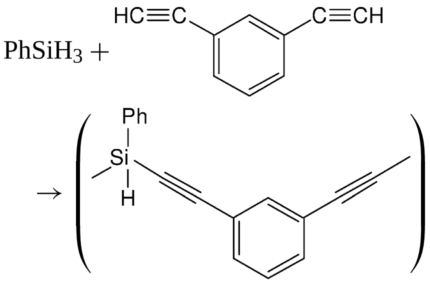


(24)

The reaction of 3,3-dimethylbut-1-yne with diethylsilane in the presence of KF/Al_2O_3 at 303 K affords the silylacetylene [81]. In this case, ^{t}BuC≡C$^-$ attacks silicon, H$^-$ being a leaving group.

$$^{t}\mathrm{BuC{\equiv}CH} + \mathrm{H_2SiEt_2} \rightarrow {}^{t}\,\mathrm{BuC{\equiv}CSiHEt_2} + \mathrm{H_2} \quad (25)$$

Dehydrogenative coupling reactions between hydrosilanes and monosubstituted alkynes are also catalyzed by MgO [82,83]. The reaction of phenylsilane and *m*-diethynylbenzene leads to formation of a polymer [83].



(26)

The polymer is soluble in benzene and THF and showed very little weight loss in thermal cracking under argon. The high heat-resisting property of the polymer was attributed to a crosslinking reaction involving the Si–H bonds and C≡C bonds.

The reaction of diethylsilane with excess toluene over KNH_2/Al_2O_3 at 329 K for 20 h affords diethylbenzylsilane in a 74% yield [84].

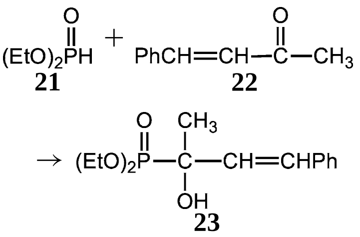
$$\mathrm{Et_2SiH_2 + C_6H_5CH_3 \rightarrow Et_2SiHCH_2C_6H_5 + H_2} \quad (27)$$

Benzene also reacts with diethylsilane in the presence of KNH_2/Al_2O_3 to give diethylphenylsilane in a 7% yield at 329 K in 20 h.

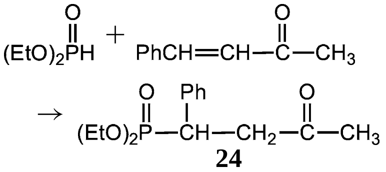
3.6. Pudovik reaction (P–C bond formation)

The Pudovik reaction involves the addition of compounds containing a labile P–H bond to unsaturated systems and is one of the most versatile pathways for the formation of carbon–phosphorus bonds. Semenzin et al. reported that KOH/Al_2O_3 is a very efficient catalyst for some Pudovik reactions [85].

The reaction of diethyl phosphonate **21** with benzalacetone **22** in the presence of KOH/Al_2O_3 instantly gave the 1,2 adduct **23** in a 100% yield at 293 K, while the 1,4 adduct **24** was quantitatively obtained in 5 min at 373 K. The 1,2 adduct **23** is plausibly an intermediate to **24**, since **23** was confirmed to isomerize to **24** by heating.



$$\underset{\mathbf{21}}{\mathrm{(EtO)_2P(=O)H}} + \underset{\mathbf{22}}{\mathrm{PhCH{=}CH{-}C(=O){-}CH_3}} \rightarrow \underset{\mathbf{23}}{\mathrm{(EtO)_2P(=O){-}C(CH_3)(OH){-}CH{=}CHPh}} \quad (28)$$



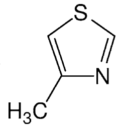
$$\mathrm{(EtO)_2P(=O)H} + \mathrm{PhCH{=}CH{-}C(=O){-}CH_3} \rightarrow \underset{\mathbf{24}}{\mathrm{(EtO)_2P(=O){-}CH(Ph){-}CH_2{-}C(=O){-}CH_3}} \quad (29)$$

The reaction of diethyl phosphonate with acrylonitrile gave the addition product $[(EtO)_2P{=}O]_2CHCH_2CN$ in a yield of 81%. Similarly, diphenylthiophosphine, $Ph_2PH{=}S$, reacted with **22** and acrylonitrile gave the 1,4 adducts in yields 90 and 100%, respectively.

3.7. Synthesis of heterocycles

4-Methylthiazole, a fungicide, can be synthesized by a vapor-phase reaction [7]. Thus, Cs-loaded ZSM-5 zeolite gives excellent performance, e.g., activity, selectivity, and lifetime. The reaction is run at 700 K in the presence of water vapor.

$\mathrm{(H_3C)_2C{=}NCH_3 + SO_2} \rightarrow$

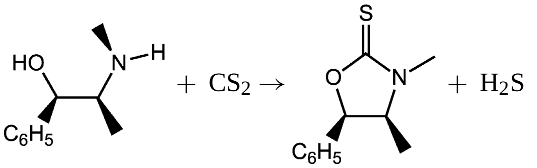


$+ \ 2\,H_2O$ (30)

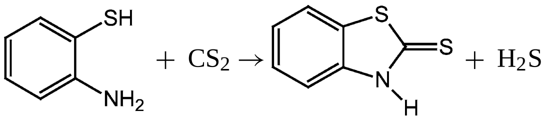
The reactions of primary amines with carbon disulfide at 373 K afford N, N'-disubstituted thioureas in high yields over a Zn–Al mixed oxide prepared from the hydrotalcitelike material [86].

$$\mathrm{RNH_2 + CS_2 \rightarrow (RNH)_2C{=}S} \quad (31)$$

The thiocarbamic acid, RNH–C(=S)SH, which is formed by nucleophilic attack of the amine to CS_2, is suggested to be the intermediate. When the amine has an additional nucleophilic group, the intermediate is quickly converted into heterocyclic thiones.



(32)



(33)

4. Future prospects and problems to be solved

As described above, an increasing number of solid-base materials with a variety of base strengths are available. As a result, more and more base-catalyzed reactions have been tested. Though it is often said that solid-base catalysts can replace the homogeneous base in the reactions which are currently carried out with the latter, this is only a part of the merit of using solid bases. Obviously, solid-base catalysts are free from the problem of solubility of the catalyst. So, we can avoid use of a very polar solvent (to dissolve, i.e., NaOH) or a phase-transfer system. Thus, we can select an appropriate solvent for substrates from a wider range of sources. In addition, we could use higher reaction temperatures, or we could perform reactions even in vapor phase. Under these conditions, we can perform the reactions forming carbon dioxide, which normally poisons the basic catalysts. Thus, aniline can be very selectively N-methylated with dimethyl carbonate over basic zeolites in vapor phase [87].

$$\mathrm{PhNH_2} + \mathrm{(CH_3O)_2CO} \rightarrow \mathrm{PhNHCH_3} + \mathrm{CO_2} + \mathrm{CH_3OH} \qquad (34)$$

Free from the restriction of the reaction medium, many more base-catalyzed reactions will be found, which are not even tried in conventional organic chemistry.

Solid-base reactions can also replace organometallic reagents such as Grignard reagents and alkyl lithium to form C–C and Si–C bonds, and so forth. They can also replace organo-transition metal catalysts. For example, dimerization of phenylacetylene, reaction (13), is usually carried out using organo-transition metals, such as Ru and Rh, as catalysts. Novel reactions should be found and explored not only from the known homogeneous base-catalyzed reactions, but also from a wider range of reactions which might proceed through “anionic or anionlike” intermediates.

Of course, there are problems to be solved. Though a variety of methods have been applied, there is no definitive or unified way of characterizing solid bases, especially base strength [2–6,12]. Many of spectroscopic methods are not easily applicable to characterize solid bases. For example, the XPS binding energy of O_{1s} can be a good measure for determining the electron density of zeolite surfaces [88]. This technique cannot be used for most of base catalysts, since the basic sites are often only a very small fraction of oxygen anions on the surface. The temperature-programmed desorption of carbon dioxide is often utilized for determining base strength, because of technical easiness. It is, however, hard to rationalize the desorption temperature to the strength as Brønsted base, that is, to abstract a proton from a substrate, since the adsorption of carbon dioxide does not involve the proton-transfer step. At present, we have to rely on model reactions such as alkene isomerization and Knoevenagel condensation. The base strength could be conjectured from the $\mathrm{p}K_\mathrm{a}$ values of the reactants. However, it should be noted that the base strength is dependent on reaction conditions. Corma et al. estimated the base strength of alkali-exchanged Y–zeolites from the Knoevenagel reactions [89]. Na-exchanged Y–zeolite has the basic strength of a H value of 10.3 and cannot activate ethyl malonate ($\mathrm{p}K_\mathrm{a} = 13.3$) at 413 K. The same catalyst can activate phenylacetonitrile ($\mathrm{p}K_\mathrm{a} = 21.9$) to react with methanol, reaction (1′), at 533 K. In addition, as in the homogeneous reactions, the reaction rates are often very much dependent on the solvent used. It is clear that base strength determined at a certain condition is not a single factor for determining the catalytic activity.

The reactions of model compounds can also be useful for differentiating acid and base catalysts. Isopropyl alcohol gives acetone and propene over solid bases and solid acids, respectively. The reaction of 2-methyl-3-butyn-2-ol is useful for distinguishing acid, base, and amphotetic catalysts [90]. However, this reaction is not suitable for diagnosing the base strength of the catalysts [11].

Alumina-supported potassium compounds such as KF, $\mathrm{KNO_3}$, $\mathrm{K_2CO_3}$, $\mathrm{KNH_2}$, and KOH are very strong base catalysts and further development in this area is expected. However, the nature of the basic centers is not always clear. For example, these compounds are active only when they are loaded on alumina and calcined at a proper temperature. They are totally inactive when supported on silica gel or titanium dioxide. Strong interaction between the potassium compounds and alumina must exist during calcination. The nature of the interaction is open to further investigation.

As catalytic materials, it is also important to define the reaction environment around the active center to enhance the rate and selectivity of base-catalyzed reactions. This may involve the regulation of pore sizes and hydrophobicity (or hydrophilicity) of the pores. Choudhary et al. attempted the enantioselective base catalysis [91]. Though the *ee* values they attained are still not high, this type of the attempt will be involved in one of the future challenges.

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