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# Selective reactions over solid base catalysts

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## Abstract

A variety of organic reactions are catalyzed in a very selective manner by base catalysts. Especially, solid bases offer convenient and environmentally-benign routes for organic synthesis. This review overviews the recent development on the catalysis by solid bases. The catalytic materials described are zeolites, modified zeolites, alkaline earth oxides, alkali metals on supports, $KNH_2$ on alumina, KF on alumina, hydrotalcites and oxynitrides. Stress are also placed on novel reactions catalyzed by the solid bases. The reactions include isomerization of alkenes, reactions of alkynes, methylations, addition reactions, Knoevenagel condensations, reactions of silanes.

*Keywords:* Base catalyst; Solid base; Organic synthesis

## 1. Introduction

The studies on the catalysis by solid acids are enormous. Though a little attention is devoted to solid base catalysts in comparison with solid acid catalysts, high activities and selectivities are often attained only by solid bases for many kinds of reactions. Actually, numerous reactions such as isomerizations, additions, alkylations and cyclizations are carried out industrially by using liquid bases as catalysts. Furthermore, many organic reactions require a stoichiometric amount of liquid bases. The replacement of liquid bases by solid base catalysts would have the advantages of decreasing corrosion and environmental problems, while allowing easier separation and recovery of the catalysts. Excellent reviews by Hattori on the catalysis by solid bases have been published [1,2]. Here, the recent developments on solid bases will be reviewed. The main topics will be zeolites as solid bases and solid superbases, namely, $KNH_2/Al_2O_3$. Catalytic reactions over KF/alumina, hydrotalcites and several novel base catalysts will also be touched.

## 2. Zeolites as bases

It has long been known that alkali ion-exchanged zeolites, especially faujasites, are weak bases and show unique selectivities [3–6]. For example, alkylation of toluene, RbX or CsX affords styrene and ethylbenzene, while acidic zeolites give xylenes [7]. The origin of the basicity is considered to be the oxygen ions in the zeolite framework. The basic strength of alkali ion-exchanged zeolites has been rationalized by the negative charge of the oxygen atoms calculated by using the Sanderson's electronegativity equalization principle [8]. The base strength of X-zeolites is higher than that of the corresponding Y-zeolites. The base strength depends on the exchangeable cations and increases in the order,

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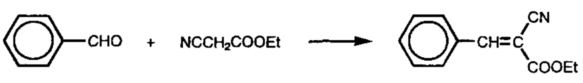
Li < Na < K < Rb < Cs [8]. This tendency was also confirmed experimentally by the XPS study of the zeolites [9–12] and infrared spectroscopy of adsorbed pyrole [13,14].

The acid strength of alkali ion-exchanged zeolites can be estimated by using catalytic reactions. Corma et al. studied the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate ($pK_a = 8.6$) [Reaction (1)], ethyl acetoacetate ($pK_a = 10.7$), and ethyl malonate ($pK_a = 13.3$) over alkali ion-exchanged X and Y zeolites [15].



(1)

The activity of the zeolites is Li < Na < K < Cs and Y < X zeolites. The order of activity increases with increase in the average negative charge on the oxygen atom calculated by electronegativity equalization principle. They concluded that most of the basic sites on alkaline X and Y zeolites have $pK_a \leq 10.3$ and sites with $pK_a \leq 13$ were present only in CsX. This catalyst is more active than pyridine ($pK_b = 8.8$), and less active than piperidine ($pK_b = 11.12$). Corma et al. studied the Knoevenagel condensations over Na form of germanium-substituted faujasite (Ge/Al = 1.03) and found that it was more active than NaX [16]. They concluded that the most of the basic sites have a $pK_b \approx 11.2$ and that sites with the order of $pK_b = 13.3$ also exist.

One of the advantages of weak bases such as zeolites is easy handling. They can be handled in ambient atmosphere, since the adsorption of carbon dioxide or water is not too strong and can be removed by high temperature treatment. They can be used even in the systems, where these molecules are involved as reactants or products. One of such examples is the ring transformation of $\gamma$-butyrolactone into $\gamma$-butyrothiolactone [17]. A 100% conversion was obtained over CsY at 603 K.

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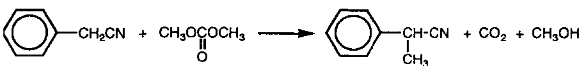
We have recently studied the methylations using dimethyl carbonate (DMC) as a methylating agent. Phenylacetonitrile is very selectively monomethylated into 2-phenylpropionitrile over alkali ion-exchanged zeolites [18].



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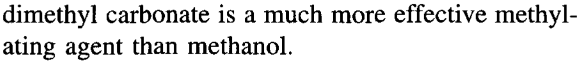
NaY gave the most stable activity. More basic zeolites such as CsX deactivates quickly, probably because of strong adsorption of carbon dioxide, one of the products. Over NaY, the yield of phenylpropionitrile based on phenylacetonitrile was 72% at 533 K. The yield based on dimethyl carbonate was about 80%. The dimethylated product was not observed at all over NaY. This indicates that NaY distinguishes the subtle difference in the acidity of phenylacetonitrile ($pK_a = 21.9$) and 2-phenylpropionitrile ($pK_a = 23.0$) under the reaction conditions.

The methylation of phenylacetonitrile with dimethyl sulfate or methyl iodide requires a stoichiometric amount of a base. Furthermore, the methylation in liquid phase usually gives a mixture of mono- and dimethylated-product.

Phenylacetonitrile is also methylated with methanol over alkali ion-exchanged zeolites [18].



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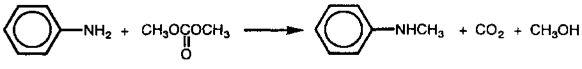
In this case, CsX is the most active catalyst. The methylation with methanol requires higher temperature than that with DMC. Thus, the yield of 2-phenylpropionitrile was 27% at 623 K. This indicates that dimethyl carbonate is a much more effective methylating agent than methanol.

Alkali ion-exchanged zeolites are also effective for N-methylation of aniline with DMC [19].



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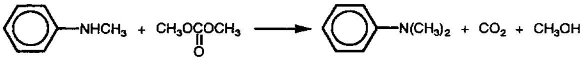

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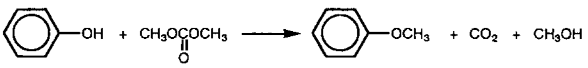
N-methylaniline and N,N-dimethylaniline were obtained exclusively, no ring-methylation products being formed. The ratio of the two products depends on the reaction conditions and the zeolites used. The higher selectivity for *N*-methylaniline was obtained at lower DMC/aniline ratio or lower contact time. Over KY, *N*-methylaniline was selectively formed at 453 K. The selectivity for *N*-methylaniline was 93.5% at aniline conversion of 99.6% at 453 K and DMC/aniline ratio of 1.25. Over NaX, *N*,*N*-dimethylaniline was obtained at 95.6% at 100% conversion of aniline at 513 K and DMC/aniline ratio of 2.5. Rao et al., reported that alkali ion-exchanged EMT zeolites, especially K-EMT, are also very effective for *N*-alkylation of aniline with dimethyl carbonate [20].

The reaction of phenol with DMC selectively yields the *O*-methylation product, anisole. Over NaX, anisole yield of 92% was attained at 533 K [21].



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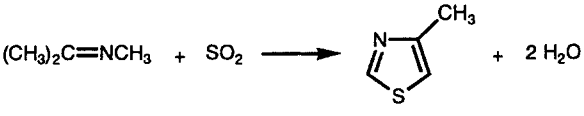
Although alkylation of aniline or phenol can be achieved using methanol as the methylating agent, the reaction needs higher temperatures and appreciable amount of ring-methylation products are formed.

## 3. Modified zeolites

Various efforts have been made to increase the base strength of alkali metal-ion exchanged zeolites. Martens et al., formed metallic sodium particles in zeolites by the decomposition of occluded sodium azide [22–24]. These sodium particles are capable of performing base-catalyzed reactions. These catalysts catalyze the isomerization of butenes at 300 K and the reaction intermediate is a carbanion type. In fact, substrates without allylic proton like 3,3-dimethy-l-butene cannot be isomerized at all. The catalyst is also active for the side-chain alkylation of toluene with ethylene at 523 K [24].

Hathaway and Davis prepared catalysts by impregnation of CsNaX and CsNaY with cesium acetate followed by thermal decomposition of the acetate into oxide and showed that they act as base catalysts [25–28]. The catalytic activity for the dehydrogenation of isopropyl alcohol to acetone increased an order of magnitude by loading Cs onto CsY [25]. Tsuji et al. followed the synthesis procedure of Hathaway and Davis and carried out the isomerization of 1-butene over a series of MX and $M^+$ loaded-MX (M = alkali metal) [29]. At 273 K, all the ion-exchanged zeolites (MX) showed practically no activity, while $M^+$ loaded MX showed a considerable activity, which has never been reported before for any basic zeolites, alkali oxides, and alkali hydroxides. A Cs-loaded CsX showed the highest activity ($1.4\times 10^{-4}$ mol $g^{-1}$ $min^{-1}$). The authors claim that these materials are solid superbases. The various evidence including $^{133}$Cs-NMR and temperature-programmed desorption (TPD) of carbon dioxide indicates that the active species is nanophase cesium oxide occluded in the supercage of the zeolites [25–31]. Rodriguez and coworkers carried out the Knoevengagel reaction of benzaldehyde and ethyl cyanoacetate (Reaction (1)) and found that the rate of the reaction increased with a loading amount of Cs on CsX [32].

A very important application of base catalysis using zeolites is the synthesis of 4-methylthiazole, which is used as a systematic fungicide [33]. Thus, cesium-loaded ZSM-5 zeolite gave excellent performance characteristics, e.g., activity, selectivity, and life time. The reaction was run in the vapor phase (700 K) with the presence of water vapor, and zeolites with high hydrothermal stability were chosen.



(8)

Ytterbium or europium species were introduced into Y-zeolites from the ammoniacal solution of the corresponding metals [34–39]. The zeolites thus loaded with Yb or Eu have a high catalytic activity for the isomerization of 1-butene at 273 K, when they were heated under vacuum at 500 K. The isomerization proceeds via allylic-carbanion type intermediates, indicating that these materials act as base catalysts. Their catalytic activity is greatly influenced by the alkali-metal cations present in the Y-zeolite as shown in Fig. 1 [35]. The rate of 1-butene isomerization over Eu-loaded KY reached $2.7\times 10^{-3}$ mol $g^{-1}$ $min^{-1}$, which is much larger than Cs-loaded CsX. TPD and infrared spectroscopic study revealed that the catalytically active species for 1-butene isomerization are imide or amide of these metals. The material also catalyses the Michael reactions. Thus, reaction of cyclopent-2-enone with dimethyl malonate over

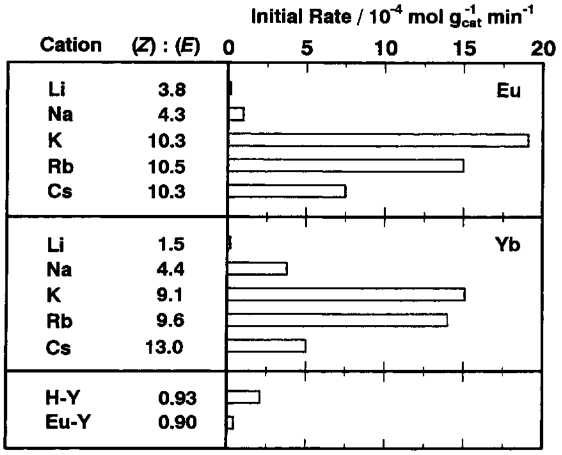
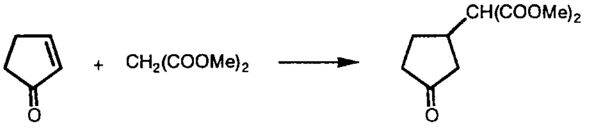


Fig. 1. Catalytic activity of Eu or Yb supported on alkali ion-exchanged Y-zeolite at 273 K. Degree of ion-exchange: Li 67%, Na 100%, K 99%, Rb 47%, and Cs 39% [35].

Eu-loaded KY at 303 K for 20 h gave a coupling product in a 81% yield [38].



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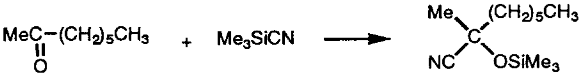
## 4. Alkaline earth oxides

The catalysis of CaO and MgO have been demonstrated on a variety of organic reactions; the isomerization of alkenes, the hydrogenation of alkenes, the addition of amines to dienes, and the aldol condensation of acetone [1,2,40]. The catalytic activities of MgO and CaO prepared from $Ca(OH)_2$ and $Mg(OH)_2$ depends very much on the pretreatment temperature under vacuum. High temperature is required to remove adsorbed water and carbon dioxide [1,41]. MgO and CaO free from impurities are superbases, which is defined as materials having basic sites stronger than $H_- = -26$ [40]. Here, reactions which reported recently to be catalyzed by MgO or CaO are described below.

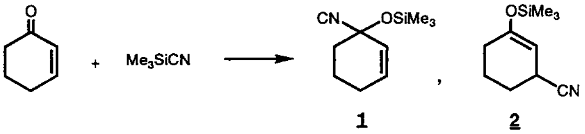
The reaction of 2-octanone with cyanotrimethylsilane proceeds on MgO or CaO to afford 2-methyl-2-(trimethylsiloxy)octanenitrile in a high yield (96–97%) at 273 K [42,43].



$$\mathrm{MeC(=O){-}(CH_2)_5CH_3 + Me_3SiCN \longrightarrow Me(NC)C(OSiMe_3)(CH_2)_5CH_3} \quad (10)$$

Benzaldehyde, acetophenone, and benzophenone also undergo cyanosilylation with cyanotrimethylsilane over alkaline earth oxides. The amount of basic sites on CaO was estimated as 0.27 mmol $g^{-1}$ by poisoning effect of trichloroacetic acid on the cyanosilylation of benzophenone.

In the case of 2-cyclohexen-1-one with cyanotrimethylsilane, the product was almost exclusively 1,2-adduct, 1, at 233 K [43].



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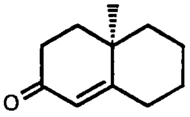
On the other hand, acidic catalysts such as Al-montmorillonite gave the 1,4-addduct, 2, selectively. Other conjugated dienes such as 3, 4, and 5, also react with cyanotrimethylsilane to give 1,2-adducts over MgO and CaO [43].



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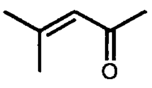

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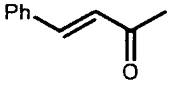

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For these types of reactions, $CaF_2$, $CaSiO_3$, and hydroxyapatites are also effective as catalysts [43].

Itoh and coworkers found that interesting reactions, dehydrogenative coupling reactions between silanes and monosubstituted alkynes are catalyzed by solid bases [44]. For example, phenylsilane reacted with alkynes to produce monoalkynylphenylsilane, dialkynylphenylsilane, and trialkynylphenylsilane with evolution of hydrogen in the presence of magnesium oxide. Typical results are shown in Table 1.

$$\mathrm{PhSiH_3 + HC{\equiv}CR \longrightarrow Ph(RC{\equiv}C)SiH_2 + Ph(RC{\equiv}C)_2SiH + Ph(RC{\equiv}C)_3Si}$$
$$\mathrm{(R = Ph,\ butyl)} \quad (12)$$

Table 1
Reactions of silanes with monosubstituted alkynes over MgO [a] [44]

| Silane (mmol) | Alkyne (mmol) | MgO (g) | Temperature (K) | Conversion (%) [b] | Product (%) [b] | | |
|---|---|---|---|---|---|---|---|
| | | | | | Mono | Di | Tri |
| $PhSiH_3$ (9.7) | 1-hexyne (9.6) | 0.5 | r.t. [c] | 34 | 26 | 5 | 0 |
| $Ph_2SiH_2$ (12.0) | 1-hexyne (11.2) | 0.5 | r.t. | 62 | 52 | 0 | — |
| $PhMeSiH_2$ (11.2) | 1-hexyne (11.2) | 0.5 | r.t. | 49 | 29 | 1 | — |
| $PhSiH_3$ (5.5) | 1-hexyne (13.7) | 0.5 | r.t. | 97 | 29 | 50 | 0 |
| $PhSiH_3$ (5.2) | Pa [d] (12.3) | 1.0 | 353 | 88 | 43 | 24 | 10 |
| $PhSiH_3$ (4.9) | Pa [d] (12.3) | 1.0 | 353 | 31 | 27 | 5 | 0 |

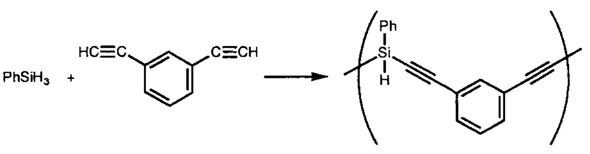
[a] Pentane (10 ml) was used as solvent.

[b] Based on silane Mono = monoethynylsilane, Di = diethynylsilane, Tri = triethynylsilane.

[c] Room temperature.

[d] PA = phenylacetylene.

Based on these results, they carried out the reaction of phenylsilane and *m*-diethynylbenzene to give polymers [45].

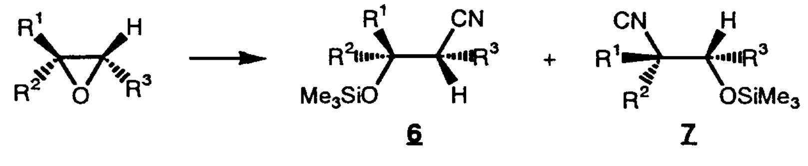


(13)

These polymers are 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.

CaO and MgO are found to be effective for nucleophilic ring opening of epoxides with cyanotrimethylsilane to afford $\beta$-trimethylsiloxy nitriles in a high regioselective manner [46]. Table 2 shows the results of ring openings of unsymmetrical epoxides with $Me_3SiCN$ on CaO. All the epoxides quantitatively afforded $\beta$-trimethylsiloxynitriles by highly regioselective ($>$ 94%) attack of cyanide on the less substituted carbon of epoxides without any formation of isocyanides. Ring opening of 2,3-epoxyhexan-1-ols

Table 2
Ring opening of epoxides with $Me_3SiCN$ on CaO [42]



| $R^1$ | $R^2$ | $R^3$ | Time (h) | Yield (%) | 6 : 7 |
|---|---|---|---|---|---|
| $n$-$C_6H_{13}$ | H | H | 0.5 | 97 | 97 : 3 |
| $CH_3$ | $CH_3$ | H | 0.5 | 98 | >99 : 1 |
| $CH_3$ | $-(CH_2)_4-$ | | 4.5 | 95 | 99 : 1 |
| $CH_3$ | $CH_3$ | $CH_3$ | 24 | 84 | 94 : 6 |

CaO (0.2 g), epoxides (1 mmol), and $Me_3SiCN$ (2 mmol) in hexane, at room temperature.

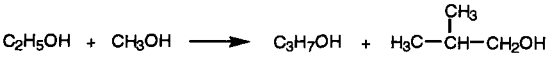
with $Me_3SiCN$ also took place smoothly on CaO in good yields and regioselectivity [46].

The synthesis of $\alpha,\beta$-unsaturated nitriles from saturated nitriles and methanol was achieved with magnesium oxide activated by manganese or chromium ions [47]. The methyl groups of the $\alpha$-position of saturated nitriles are converted into vinyl groups. In the conversion of acetonitrile, the selectivity to acrylonitrile was more than 95%.

$$CH_3CN + CH_3OH \longrightarrow CH_2{=}CHCN + H_2 + H_2O \qquad (14)$$

The propionitrile was converted into methacrylonitrile.

MgO was found to be active for the condensation of primary alcohols with methanol to produce alcohols with one or two more carbon atoms than the starting alcohols in a high selectivity [48]. When ethanol was reacted with methanol at 653 K, main products were propyl alcohol and 2-methylpropyl alcohol. Total selectivity of the two products was about 80%.



$$C_2H_5OH + CH_3OH \longrightarrow C_3H_7OH + H_3C{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_2OH \qquad (15)$$

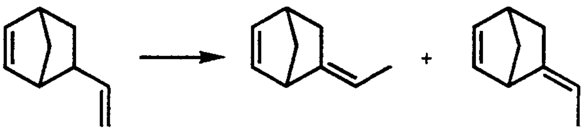
## 5. Alkali metals on supports

Alkali metals loaded on supports by deposition of the metal vapor have been reported as highly active catalysts for the isomerization of alkenes and the related compounds [49,50]. For example, Haag and Pines described that sodium metal deposited on alumina ($Na/Al_2O_3$) isomerized 1-butene and 1-pentene at room temperature [50]. Malinowski et al., also reported that sodium metal deposited on MgO-(Na/MgO) showed a high catalytic activity for the isomerization of alkenes at 293 K and the base sites of Na/MgO are stronger than $H_- = 35$ [51,52].

Suzukamo and coworkers reported a new class of superbase [53,54]. A typical preparation procedure is as follows. To 30.0 g of calcined $\gamma$-alumina was added 4.5 g of sodium hydroxide by portions at 583–593 K with stirring and the water generated was removed by a flow of nitrogen. The stirring was continued for 3 h at the same temperature to give white solid (A). Then, 1.2 g of sodium was added thereto and the reaction mixture was stirred for 1 h at the same temperature to give pale blue solid (B), a superbase.

The intermediate solid (A) is sodium aluminate with much disorder. The solid (B) does not show X-Ray diffraction lines due to sodium metal. The solid-state $^{23}Na$ NMR of the superbase showed only a peak for ionized sodium. In addition, the $O_{1s}$-photoelectron peak shifts to lower binding energy in the order of $\gamma$-alumina, solid (A) and solid (B), indicating that the electron density of the oxygen is much more enriched in solid (B) than those in $\gamma$-alumina or solid (A). They suggests that ionization of metallic sodium on the disordered aluminate plays a key role in giving extremely strong basic sites on the solid (B). Solid (B) will be denoted as alumina/NaOH/Na.

Alumina/NaOH/Na is an effective catalyst for the isomerization of 5-vinylbicyclo[2,2,1]hept-2-ene to 5-ethylidenebicyclo[2,2,1]hept-2-ene which is an important third comonomer of ethylene–propylene synthetic rubber. The reaction proceeds completely even at 243 K.



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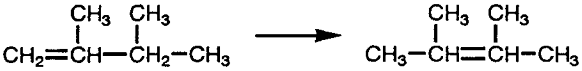
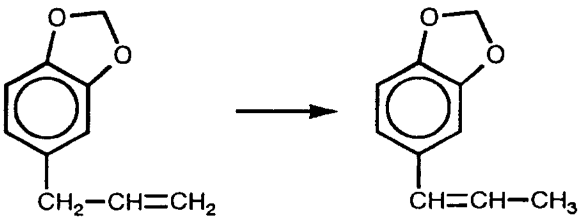
Alumina/NaOH/Na shows also a very high catalytic activity for the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene, which is usable as an intermediate material for synthetic parathyroid. A 94% yield was obtained in 3 h at 293 K.



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}\overset{\displaystyle CH_3}{\overset{|}{C}H_2}{-}CH_3 \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{=}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}CH_3 \qquad (17)$$

The isomerization of safrole proceeds smoothly at 393 K to give isosafrol over alumina/NaOH/Na.



(18)

Ethylation of cumene was carried out at 313 K. A very high selectivity (99.6%) was obtained at a cumene conversion of 99.6% over alumina/KOH/K, prepared in a similar manner to alumina/NaOH/Na. The higher basicity of the former is confirmed from the binding energy of $O_{1s}$ by XPS.

## 6. Potassium amide on alumina

### 6.1. *Preparation of $M(NH_3)/Al_2O_3$*

Alkali metals can be loaded onto supports by impregnation from their ammoniacal solution. The catalyst thus prepared [$M(NH_3)$/support] has rarely been examined. Blouri et al., reported that $Na(NH_3)/Al_2O_3$ isomerized 1-butene into 2-butene between 273 and 753 K [55]. The catalytic activity, however, was rather low. Moreover, the chemical nature of active species on the surface has not been discussed and the conditions of loading the alkali metal from the ammoniacal solution have not been explored.

As described earlier, we have reported that Yb and Eu species loaded on alkali ion exchanged faujasite from the ammoniacal solution are highly basic catalysts and that the active species are not metallic, but probably amide- or imide-like species. Later, we also examined the catalytic activities of Yb and Eu species loaded on alumina from the ammoniacal solution for the isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene. Table 3 compares the catalytic activity of these metals on KY and on alumina. In Table 3, the results of Na and K loaded from the ammoniacal solution are also added. It should be emphasized that $M(NH_3)$/support means that the actual state of these metals are not metallic, as described earlier. It is clear that alumina is a far better support than KY. The difference in the catalytic activities of $M(NH_3)/Al_2O_3$ and $M(NH_3)$/KY is tremendous. Table 3 also shows that $Na(NH_3)/Al_2O_3$ and $K(NH_3)/Al_2O_3$ is more active than $Eu(NH_3)/Al_2O_3$ or $Yb(NH_3)/Al_2O_3$. The reaction at shorter reaction time revealed that $K(NH_3)/Al_2O_3$ is more active than $Na(NH_3)/Al_2O_3$. $K(NH_3)/Al_2O_3$ is active for the isomerization of 1-pentene even at 201 K. The conversion reached 98% in 6 min. This activity is far greater than that of $Na/Al_2O_3$, which was prepared by the vapor deposition of Na on alumina [56].

Table 3
Catalytic activities of metals loaded from the ammoniacal solutions for the isomerization of 2,3-dimethylbut-1-ene

| Catalyst | Metal loading (mmol $g^{-1}$) | Conversion (%) |
|---|---|---|
| $Eu(NH_3)/KY$ | 0.50 | 2.3 |
| $Eu(NH_3)/SiO_2$ | 0.50 | 0.2 |
| $Eu(NH_3)/Al_2O_3$ | 0.50 | 83.4 |
| $Yb(NH_3)/KY$ | 0.46 | 1.0 |
| $Yb(NH_3)/Al_2O_3$ | 0.46 | 29.4 |
| $Na(NH_3)/KY$ | 2.0 | 2.3 |
| $Na(NH_3)/Al_2O_3$ | 2.0 | 89.3 (41[a]) |
| $K(NH_3)/Al_2O_3$ | 2.0 | 89.4 (94[b]) |

Catalyst: 0.25 g, Reactant: 24 mmol.
Temperature: 313 K, Reaction time: 20 h.
[a] Temperature: 273 K, Reaction time: 10 min.
[b] Temperature: 273 K, Reaction time: 10 min. Reactant: 48 mmol.

The activities of $Na(NH_3)/Al_2O_3$ and $K(NH_3)/Al_2O_3$ depend very much on the evacuation temperature after the impregnation. We have studied the nature of active species in $K(NH_3)/Al_2O_3$ by infrared spectroscopy and TPD and concluded that the active species in $K(NH_3)/Al_2O_3$ is $KNH_2$ [56].

### 6.2. *Preparation of $KNH_2/Al_2O_3$*

Based on the results described earlier, we attempted to load $KNH_2$ directly on alumina [56]. The catalyst was prepared as follows: alumina and a small amount of $Fe_2O_3$ (a catalyst for converting K into $KNH_2$ in liquid ammonia) were heated in the reactor under vacuum at 773 K for 3 h. A piece of potassium metal was then put into the reactor under nitrogen. After evacuation, ammonia was liquefied into the reactor to dissolve the metal. The blue color due to solvated electrons disappeared in about 10 min, indicating the formation of potassium amide. After 1 h, the reactor was warmed to room temperature for removing the most of ammonia and then heated at 573 K (if not otherwise indicated) for 1 h. The catalyst thus prepared will be denoted as $KNH_2/Al_2O_3$.

Fig. 2 shows that the effect of the loaded amount of potassium on the catalytic activity of $KNH_2/Al_2O_3$ for the isomerization of 2,3-dimethylbut-1-ene [56]. The reaction was carried out at 201 K for 10 min. Alumina

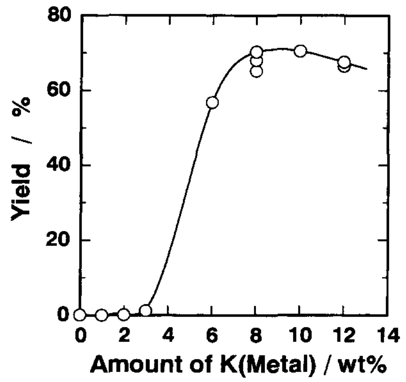


Fig. 2. The dependence of loaded amount of potassium on the catalytic activity of $KNH_2/Al_2O_3$ for the isomerization of 2,3-dimethylbut-1-ene (24 mmol) at 201 K. Reaction time: 10 min. Catalyst: 63 mg.

has no activity at this temperature. The isomerization did not proceed at all when the loaded amount was 3 wt% or below. This potassium content is almost equal to the amount of OH groups on the surface of alumina, which was estimated by thermogravimetric analysis up to 1273 K. This result indicates that the OH groups on the $Al_2O_3$ surface reacts with potassium and potassium loaded in this way is not active for the isomerization. The yield of 2,3-dimethylbut-2-ene increased with increasing potassium content higher than 3 wt%, and the maximum yield of 70% was observed when the potassium content was 8–10 wt%. When the potassium content exceeds 10 wt% the catalytic activity declined. This may be attributed to the pore plugging by excess loading. It is surprising that the catalyst has the isomerization activity at temperatures as low as 201 K. The activity of $K(NH_3)/Al_2O_3$ is slightly lower than $KNH_2/Al_2O_3$.

Fig. 3 shows the dependence of evacuation temperature on the catalytic activity of $KNH_2/Al_2O_3$ for the isomerization of 2,3-dimethylbut-1-ene at 201 K. The catalytic activity strongly depends on the heating temperature and reached maximum around 573 K. At 673 K, the activity sharply declined. Though potassium amide supported on alumina has been proposed as a base catalyst by Hubert et al. [57–59], they dried their material at 338 K. However, the results in Fig. 3 clearly shows that the high temperature treatment (573 K) is essential for obtaining the superactive catalyst.

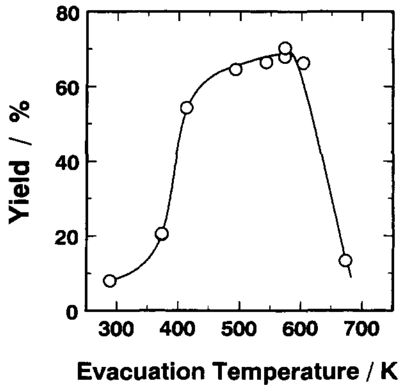


Fig. 3. The influence of the evacuation temperature on the catalytic activity of $KNH_2/Al_2O_3$ for the isomerization of 2,3-dimethylbut-1-ene (24 mmol) at 201 K. Reaction time: 10 min. Catalyst: 63 mg. K-loading: 8 wt.% as K.

Table 4
Influence of supports on the catalytic activity of $KNH_2$

| Support | Reaction time (min) | Conversion (%) |
|---|---|---|
| $Al_2O_3$ | 10 | 70 |
| $Al_2O_3$-MgO (Mg/Al = 2) | 30 | 19 |
| CaO | 30 | 19 |
| $SiO_2$ | 30 | 0 |
| $TiO_2$ | 30 | 0 |
| CaO [a] (pure) | 10 | 63 |

Reaction conditions: 201 K, Catalyst: 63 g.
Reactant: 24 mmol.
[a] Without $KNH_2$.

Alumina is a unique support for KNH2. Table 4 shows the effect of supports on the catalytic activity of $KNH_2$. Though $KNH_2/Al_2O_3$ has a very high activity for the isomerization of 2,3-dimethylbut-1-ene, $KNH_2/SiO_2$ and $KNH_2/TiO_2$ are totally inactive. $Al_2O_3$–MgO(Al/Mg = 1/2) obtained by the decomposition of hydrotalcite has some activity. This material is known to be a solid-base, as described later. $KNH_2$/CaO also have some activity, but the activity is much lower than CaO or $KNH_2/Al_2O_3$. The basic property of the support seems to be important in development of the high catalytic activity in $KNH_2$/support system. The nature of the strong interaction of $KNH_2$ and alumina is still an important problem to be solved in future.

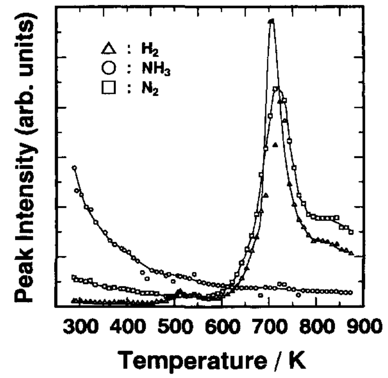


Fig. 4. The TPD desorption spectrum of $KNH_2/Al_2O_3$ evacuated at 303 K.

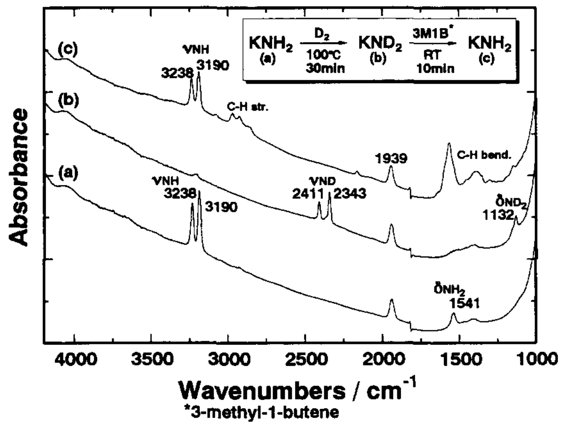


Fig. 5. The infrared spectrum of $KNH_2/Al_2O_3$ and its reaction with $D_2$ and 3-methylbut-1-ene. (a) $KNH_2/Al_2O_3$ as prepared. (b) the sample was exposed to $D_2$ at 373 K for 30 min and then (c) 3-methylbut-1-ene at room temperature for 10 min.

## 6.3. *The properties of* $KNH_2/Al_2O_3$

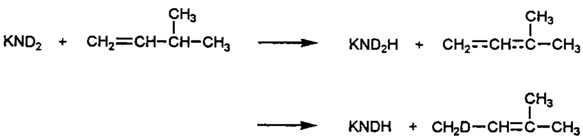
TPD from the catalyst was examined, which was evacuated at 303 K for 1 h. The TPD spectrum is shown in Fig. 4. Below 570 K, the main desorbing gas is ammonia. The amount of desorbed ammonia decrease with temperature, indicating that ammonia is mildly held on the alumina surface even after evacuation at 303 K. The desorption of ammonia may be related to the increase in the catalytic activity in this temperature range. Between 600 and 800 K, a large amount of hydrogen and nitrogen is evolved, indicating the decomposition of potassium amide in this region. This is in conformity with a sharp decline of the catalytic activity in this temperature region.

The TPD spectrum of $KNH_2/Al_2O_3$ is quite different from that of $K(NH_3)/Al_2O_3$, where a large amount of hydrogen was evolved around 500 K. This indicates that the formation of $KNH_2$ occurs when the catalyst was heated to 500 K in the case of $K(NH_3)/Al_2O_3$ [56], while $KNH_2$ was formed during impregnation by the action of $Fe_2O_3$ in the case of $KNH_2/Al_2O_3$.

The infrared spectrum of $KNH_2/Al_2O_3$ is shown in Fig. 5(a) [60]. Two bands at 3238 and 3190 $cm^{-1}$ and a single band at 1541 $cm^{-1}$ are ascribed to N–H stretching and $NH_2$ bending bands, respectively, indicating the presence of $KNH_2$ on the surface. The band at 1939 $cm^{-1}$ may be assigned to a N=N band. When the sample was exposed to deuterium at 373 K for 30 min. The three bands due to $KNH_2$ disappeared, and three new bands appeared at 2411, 2343 and 1132 $cm^{-1}$ (Fig. 5(b)). These three are attributed to $ND_2$ groups, indicating that the exchange reaction between $KNH_2$ and $D_2$ occurred on alumina surface.

$$KHN_2 + D_2 \longrightarrow KND_2 + H_2 \qquad (19)$$

When the sample, which shows the bands due to the $KNH_2$ groups, was exposed to 3-methylbut-1-ene at room temperature for 10 min, the bands due to $ND_2$ groups disappeared and the bands due to $NH_2$ groups reappeared, besides the bands due to CH stretching and bending (Fig. 5(c)). This shows the $NH_2$ groups are involved in the isomerization of alkenes.



$$KND_2 + CH_2{=}CH{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_3 \longrightarrow KND_2H + CH_2{\cdots}CH{\cdots}\overset{CH_3}{\overset{|}{C}}{-}CH_3 \longrightarrow KNDH + CH_2D{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 \qquad (20)$$

It was confirmed that D atoms were contained in the reaction products in the gas phase.

The $NH_2$ groups in $KNH_2/Al_2O_3$ react even with methane as shown in Fig. 6 [60].

Fig. 6(a) is the infrared spectrum of $KNH_2/Al_2O_3$. The sample was then exposed to deuterium to give $KND_2$ as shown in Fig. 6(b). Then the sample was exposed to methane at room temperature. As the exposure time increased, the band due to $ND_2$

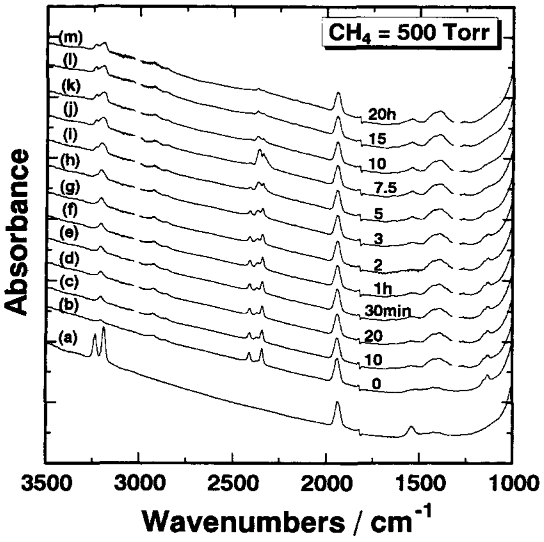


Fig. 6. The infrared spectrum of $KNH_2/Al_2O_3$ and its reaction with $D_2$ and methane. (a) $KNH_2/Al_2O_3$ as prepared (b) the sample exposed to $D_2$ at 373 K for 30 min and then (c–m) to methane at room temperature.

(2411, 2343, 1132 $cm^{-1}$) decreased monotonously. Instead new bands appeared at 3210 and 2364 $cm^{-1}$. These two bands are assigned to a NH stretching band and a ND stretching band in the KNHD group, respectively. Finally, these two bands disappeared and the bands due to $NH_2$ groups appeared at 3238, 3190, and 1541 $cm^{-1}$.

$$KND_2 + CH_4 \longrightarrow KNHD + CH_3D$$

$$KNHD + CH_4 \longrightarrow KNH_2 + CH_3D \qquad (21)$$

A similar exchange reaction was also observed between $KND_2/Al_2O_3$ and $C_2H_6$. The rate of the exchange of $KND_2$ with $CH_4$ was faster than that with $C_2H_6$ in conformity with the difference in their acidities.

### 6.4. *Catalytic reactions over $KNH_2/Al_2O_3$*

#### 6.4.1. *Isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene*

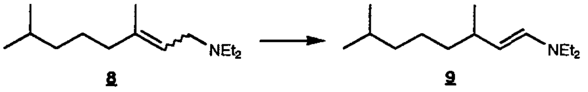
As described earlier, the isomerization (Reaction (17)) proceeds very fast even at 201 K. The conversion reached 70% in 10 min and 95% in 30 min. The activity is higher than CaO (Table 3) [56].

#### 6.4.2. *Isomerization of 5-vinylbicyclo[2,2,1]hept-2-ene to 5-ethylidenebicyclo[2,2,1]hept-2-ene*

The isomerization (Reaction (16)) was carried out at 273 K. The conversion of the reactant (21 mmol) reached 98% in 10 min in the presence of 63 mg of the catalyst [56].

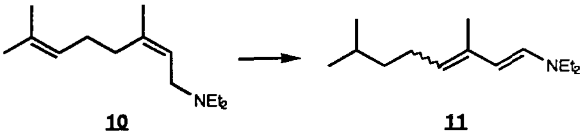
#### 6.4.3. *Isomerization of olefinic amines*

The isomerization of two olefinic amines were carried out in a quartz reactor using $KNH_2/Al_2O_3$ as the catalyst [61]. The reactant were introduced to the rector from the side arm, after the catalyst was prepared. The isomerization of *N,N*-diethyl-3,7-dimethyloct-2-enylamine, 8, was carried out with 0.2 ml (0.8 mmol) of the reactant in 2 ml hexane with 125 mg of $KNH_2/Al_2O_3$ at 353 K for 1 h. The product was corresponding enamine, 9, which was obtained in a 91% yield with a 95% selectivity. The isomerized product, 9, has 100% *E* configuration. This proves that the catalyst $KNH_2/Al_2O_3$ is very effective for the isomerization of olefinic amines as well as simple alkenes.



(22)

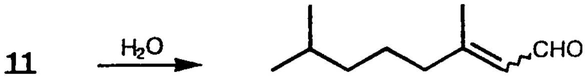
The isomerization of *N,N*-diethyl-3,7-dimethylocta-2(Z),6-dienylamine, 10, was carried out at 313 K with or without a solvent(hexane). The reaction proceeds almost quantitatively. The product under this reaction condition was exclusively *N,N*-diethyl-3,7-dimethylocta-1,3-dienylamine, 11. The ratio of *E*/*Z* of the double bond at 3 position in the product was almost 1/1. The double bond at 1 position was 100% *E*.



(23)

Though 11 was a sole product at 313 K, the selectivity was not always high. When the reaction was carried out at 273 K, the conversion of **10** was 57%, and the yield of **11** was 37%. The rest of products includes intermediate isomers such as *N,N*-diethyl-3,7-dimethylocta-4,6-dienylamine and *N,N*-diethyl-3,7-dimethyl-octa-3,5-dienylamine. The very high yield of **11** at 313 K indicates that this product is obtained as the thermodynamically most stable isomer. For this reaction, CaO also showed a reasonably high activity. Thus, a 97% yield was obtained at 313 K in 20 h.

The hydrolysis of **11** proceeded quantitatively to yield 3,7-dimethyloct-2-en-1-al, **12**, upon passing its ethyl acetate-hexane solution of **11** through a column of silica gel at room temperature. The *E*/*Z* ratio of **12** was 12 : 1.



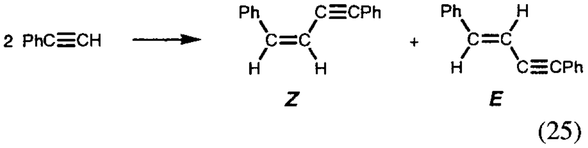
(24)

These results show that the selective isomerization of **10** to **11** offers a convenient route to monoterpene aldehydes, since **11** can be easily prepared by the dimeric addition of isoprene to dialkylamine with base catalysts [62].

### 6.4.4. *Dimerization of phenylacetylene*

$KNH_2/Al_2O_3$ is effective for the isomerization of alkynes as other bases. For example, 1-hexyne is easily isomerized to inner alkynes.

The reaction of phenylacetylene over base catalysts has been reported. A homogeneous catalyst, $NaNH_2$-crown ether, yields the polymerization product [63], while the reaction in a KOH–DMSO suspension gives the dimerization [64]. The products are (*Z*) and (*E*)-1,4-diphenylbut-1-en-3-yne. The ratio of *Z* to *E* was 6 : 1.



(25)

The reaction of phenylacetylene was carried out with a $KNH_2/Al_2O_3$ catalyst at 363 K [65]. The products are (*Z*) and (*E*)-1,4-diphenylbut-1-en-3-yne, the ratio of (*Z*) to (*E*) being 96 : 4. Thus, the selectivity is quite opposite to the dimerization with KOH suspension in DMSO. The change in the yield of the dimers with reaction time is shown in Fig. 7. The yield increased with reaction time and reached 97% at 20 h. The isomer ratio of the dimers did not change with reaction time within 20 h. However, prolonged reaction resulted in the increase in the fraction of the (*E*)-isomer.

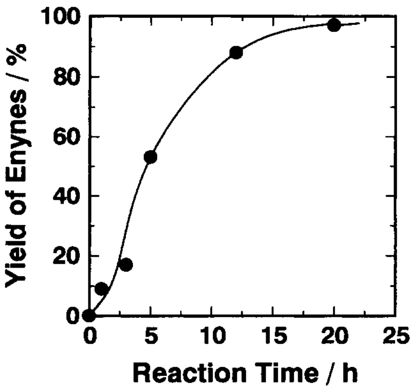


Fig. 7. Change in the dimer yield with reaction time in the reaction of phenylacetylene with $KNH_2/Al_2O_3$. Reaction conditions: Phenylacetylene = 27 mmol, Catalyst: 0.25 g, Reaction temperature: 363 K.

The catalytic activities of various solid bases for the dimerization of phenylacetylene were examined and the results are given in Table 5. It is clear that $KNH_2/Al_2O_3$ is far more active than other solid bases. The ratio of the two isomers in the dimers is different from one catalyst to the other. In general, catalysts giving higher conversions give higher *Z*/*E* ratio.

Table 5
The catalytic activities of various solid bases for the dimerization of phenylacetylene

| Catalyst | Yield (%) | *Z* : *E* |
|---|---|---|
| $KNH_2/Al_2O_3$ | 53 | 96 : 4 |
| CaO | 21 | 57 : 43 |
| $Eu(NH_3)/Al_2O_3$ | 16 | 70 : 30 |
| $Yb(NH_3)/Al_2O_3$ | 7 | 62 : 38 |
| MgO | 4 | 62 : 38 |
| $Al_2O_3$ | 2 | 55 : 45 |

Phenylacetylene = 27 mmol, Catalyst = 0.5 g, Reaction time = 5 h, Reaction temperature = 363 K.

### *6.4.5. Disproportionation of trimethylsilylacetylene*

The reaction of trimethylsilylacetylene over $KNH_2/Al_2O_3$ did not lead to the dimerization, but the disproportionation of the alkyne, the products being bis(trimethylsilyl)acetylene and acetylene [66].

$$2(CH_3)_3SiC{\equiv}CH \longrightarrow (CH_3)_3SiC{\equiv}CSi(CH_3)_3 + HC{\equiv}CH \tag{26}$$

The reaction was carried out at 313 K for 30 min using $KNH_2/Al_2O_3$, $KF/Al_2O_3$ and MgO. The yields of bis(trimethylsilyl)acetylene over $KNH_2/Al_2O_3$, $KF/Al_2O_3$ and MgO were 74, 71 and 25%, respectively. The yields over $KNH_2/Al_2O_3$ and $KF/Al_2O_3$ seem to be limited by the equilibrium. The partial removal of acetylene from the system gave a higher yield (80%) over $KF/Al_2O_3$. Furthermore, the reaction of bis(trimethylsilyl)acetylene and acetylene gave trimethylsilylacetylene over $KNH_2/Al_2O_3$.

### *6.4.6. Reaction of diethylsilane with toluene*

The reaction of diethylsilane with excess toluene over $KNH_2/Al_2O_3$ at 329 K for 20 h gave diethylbenzylsilane in a 74% yield [67].

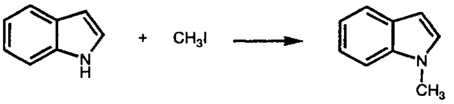
$$Et_2SiH_2 + C_6H_5CH_3 \longrightarrow Et_2SiCH_2C_6H_5 + H_2 \tag{27}$$

Similarly, the reaction of diphenylsilane with excess toluene over $KNH_2/Al_2O_3$ gave benzyldiphenylsilane. In this case, however, the disproportionation of diphenylsilane was accompanied.

## 7. KF/alumina

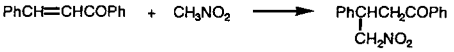
Potassium fluoride supported on alumina is a unique position in base catalysis, since many applications of this material has been developed by organic chemists. $KF/Al_2O_3$ has been thought as a convenient catalyst to handle and offers an easy work-up after the reactions. $KF/Al_2O_3$ is now a commercially available common reagent. The reactions studied include following reactions [68–71].

$$CH_3(CH_2)_7OH + CH_3I \longrightarrow CH_3(CH_2)_7OCH_3 \quad (\text{90\% yield[68]}) \tag{28}$$



( 85% yield[69] )

(29)



$$PhCH{=}CHCOPh + CH_3NO_2 \longrightarrow \underset{CH_2NO_2}{PhCHCH_2COPh} \quad (\text{74\% yield[68]}) \tag{30}$$

$$CH_2{=}CHCOCH_3 + CH_3CH_2NO_2 \longrightarrow CH_3CH(NO_2)CH_2CH_2COCH_3 \quad (\text{100\% yield[96,70]}) \tag{31}$$

$$PhCHO + CH_2(CN)_2 \longrightarrow PhCH{=}C(CN)_2 \quad (\text{82\% yield[68]}) \tag{32}$$

$$2\ PhCHO \longrightarrow PhCOOCH_2Ph \quad (\text{99\% yield[71]}) \tag{33}$$

Though $KF/Al_2O_3$ has a wide application, the catalytically active species is still a controversial problem [68,72,73]. It is well established that the following reaction occurs during the preparation of the catalyst.

$$12\ KF + Al_2O_3 + 3\ H_2O \longrightarrow 2\ K_3AlF_6 + 6\ KOH \tag{34}$$

Weistock et al., concluded that the active species is potassium hydroxide or the aluminate supported on alumina [72]. On the other hand, Ando and coworkers concluded that remaining fluoride ions are the source of the strong basicity [68,73]. There is another complicating factor. Since preparation and drying (usually below 473 K) are done in an ambient atmosphere, adsorption of water and carbon dioxide is unavoidable. The effects of these adsorbed molecules have never been studied in detail. Recently, Hattori and coworkers examined the effect of evacuation temperature on the catalytic activity of $KF/Al_2O_3$ for the isomerization of pent-1-ene and the Michael addition of nitromethane to butene-2-one [74]. The results are shown in Fig. 8. The activity of $KF/Al_2O_3$ for pent-1ene isomerization showed a sharp dependence on the pretreatment temperature. The sharp maximum of the activity was observed around 623 K. The dependence of the activity for the Michael addition is not so sharp, though the maximum was also observed at 623 K. Based on these results, Hattori and coworkers concluded that there are two kinds of active sites in $KF/Al_2O_3$. The present authors also studied the effect of evacuation temperature on the catalytic activities of

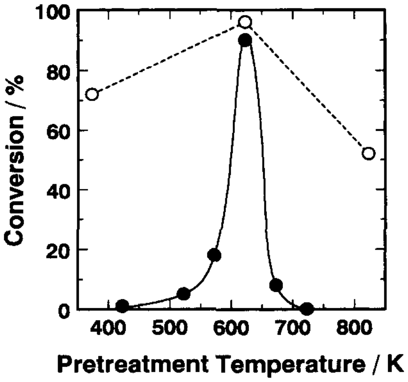


Fig. 8. Change in the activities of $KF/Al_2O_3$ for the isomerization of 1-pentene (○) and Michel addition of nitromethane to butene-2-one (●) at 273 K with reaction temperature [74]. Reaction conditions: 1-pentene isomerization; catalyst = 200 mg, pent-1-ene = 4 mmol, Reaction time = 0.5 h. Michel addition; nitromethane = 12 mmol, butene-2-one = 4 mmol; Reaction time = 0.5 h.

$KF/Al_2O_3$ for the Tishchenko reaction of benzaldehyde (Reaction (33)) [71] and the disproportionation of trimethylsilylacetylene (Reaction (26)) [66]. The catalytic activities for the Tishchenko reaction showed a maximum around 623 K in agreement with the result for the pent-1-ene isomerization [74]. In the case of the reaction of benzaldehyde, no activity was observed when evacuation temperature was 473 K, while it was about 50% upon evacuation at 623 K. This indicates that the active species developed upon evacuation at 623 K may be entirely different from those of $KF/Al_2O_3$ used in usual practice. In any case, further study is definitively required before the catalytically active species in '$KFAl_2O_3$' is finally understood.

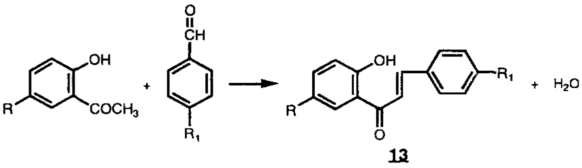
## 8. Hydrotalcite and calcined hydrotalcite

Hydrotalcite has the ideal unit cell formula, $Mg_6Al_2(OH)_{16}(CO_3^{2-})$ $4H_2O$; the ratio of Mg/Al ratio can be variable (1.7–4) in synthetic samples. By synthesis, Mg can be replaced by Zn, Fe, Co, Ni and Co, and Al can be replaced by Cr and Fe. The kinds of anions are widely variable by synthesis or ion exchange. Their structure consists of positively charged brucite layers, altering with negatively charged interlayers containing with anions and water molecules [75,76].

Hydrotalcite-like materials became active as solid base catalysts when heated at about 673 K to give dehydrated and dehydroxylated mixed oxides, especially in the case of Mg–Al combinations [75–77]. The base-catalyzed reactions studied so far includes the polymerization of $\beta$-propiolactone [78] and propylene oxide [79], aldol condensation of acetone [76], cross aldol condensation of acetone and formaldehyde to methyl vinyl ketone [80] and the isomerization of pent-1-ene [77].

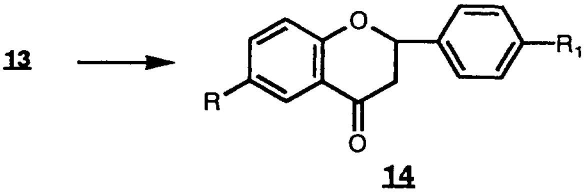
Corma and coworkers studied the catalytic activity and selectivity of a calcined Mg–Al hydrotalcite for the Knoevenagel condensation of benzaldehyde with activated methylenic compounds with different $pK_a$ and concluded that the calcined hydrotalcite has basic sites with $pK_a$ up to 16.5, most of them being in the range of $10.7 < pK_a < 13.3$ [81]. They also studied the condensation of malononitrile with various ketones such as cyclohexanone and benzophenone, *p*-aminoacetophenone and concluded that the calcined hydrotalcite was more active than CsY or cesium sepiolite [82].

Climet et al. studied the Claisen–Schmit condensation using calcined hydrotalcites (mixed Mg–Al oxides) as the catalysts [83].



(35)

The primary product, 13, further isomerized to flavone, 14, under the reaction conditions.



(36)

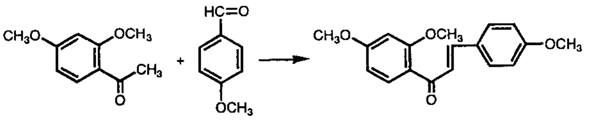
The results of the condensation of 2-hydroxyacetophenone(a–e) and benzaldehyde derivatives in the presence of air at 423 K are shown in Table 6. They also showed that the following reaction proceeded to yield Vesidryl (2′,4′,4-trimethoxychalcone in a 85%

Table 6
The condensation of 2-hydroxyacetophenone and benzaldehyde derivatives [83]

| | R | R′ | Conversion/% | Yield/% | |
|---|---|---|---|---|---|
| | | | | **13** | **14** |
| **a** | H | H | 78 | 50 | 28 |
| **b** | H | $NO_2$ | 61 | 16 | 45 |
| **c** | H | Cl | 35 | 27 | 8 |
| **d** | H | $OCH_3$ | 17 | 7 | 10 |
| **e** | $OCH_3$ | H | 23 | 16 | 7 |

423 K, 1 h in the presence of air, 5 wt% catalyst.

yield at 443 K.



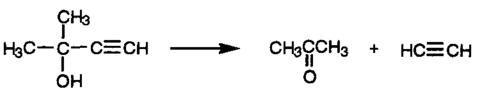
(37)

In the most of the catalytic application of hydrotalcites, they have been used in their calcined form as mixed oxides, there are several reports on the catalysis by hydrotalcites with the as-synthesized structure.

Organic halide exchange reactions producing alkyl bromides and iodides have been catalyzed by hydrotalcites intercalated by $Cl^-$, $Br^-$ or $I^-$ [84–86]. It also catalyzes the disproportionation of $HSi(OCH_3)_3$ to form tetramethoxysilane and silane [87].

$$4\ HSi(OCH_3)_3 \longrightarrow SiH_4 + 3\ Si(OCH_3)_4 \quad (38)$$

Recently, the reaction of 2-methyl-3-butyn-2-ol[MBOH] has been proposed to judge the acid–base properties of the solid acids and bases [88]. 3-Methyl-3-buten-1-yne over solid acids such as $P_2O_5/SiO_2$, while acetone and acetylene are obtained over solid base such as MgO. Furthermore, amphoteric oxides such as $ZrO_2$ give 3-hydroxy-3-methyl-2-butanone.



$$(CH_3)_2C(OH){-}C{\equiv}CH \longrightarrow CH_3C(=O)CH_3 + HC{\equiv}CH \quad (39)$$

Constantino and Pinnavaia carried out the reaction of MBOH over a hydrotalcite [89], $[Mg_{2.34}Al(OH)_{6.68}](CO_3)_{0.5}$ 2.6 $H_2O$, treated at various temperature. Acetone and acetylene were the only products over the temperature range of 353–423 K, demonstrating that all of the hydrotalcites derived catalysts have highly basic selectivities. The surprising result is that the thermal activation below the structural decomposition point (< 523 K) yielded the catalysts with activities approximately with an order of magnitude larger than the amorphous metal oxides formed by thermal activation at 723 K.

Further works are required to elucidate the origin of the base sites in as-synthesized hydrotalcite-like materials.

## 9. Oxynitrides

### 9.1. *Silicon oxynitrides*

Lednor and du Rulter prepared a surface area form of silicon oxynitride, $Si_2N_2O$, by a gas–solid reaction of amorphous silica with ammonia at 1373 K [90,91]. They further found that the material has a solid base character [91,92]. Thus, the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate proceeds at 323 K over the silicon oxynitride suspended in toluene. The origin of the catalytic activity is considered to be surface nitrogen. The Knoevenagel condensations between benzaldehyde and malononitrile and between cyclohexanone and ethyl cyanoacetate also proceeded at 323 K [92]. However, the material was totally inactive for the isomerization of 1-butene even at 673 K [91].

### 9.2. *Aluminophosphate oxynitride*

The synthesis of aluminophosphate oxynitride (ALPON) was also reported [93–95]. ALPONs are prepared by heating aluminium phosphate under flowing ammonia up to 1073 K. The surface area is about 200 $m^2\ g^{-1}$. ALPONs are active for the Knoevenagel condensations of benzaldehyde with malononitrile or ethyl cyanoacetate ($pK_a = 9$), but not for the condensation between benzaldehyde and diethyl malonate ($pK_a = 13$). No by-products were observed, indicating that Michael-type addition or Claisen condensation, which requires stronger base ($pK_a = 11.2$), did not proceed. The basic strength of ALPONs was estimated as $10.7 < pK_a = H_- < 11.2$. The catalytic activity depends on the preparation conditions of ALPONs. Nickel supported on ALPON is active for the selective synthesis of methyl isobutyl ketone from acetone [96]. The catalyst is supposed to be bifunctional, having both basic and metallic sites.

Catalysis by zirconophosphate oxynitride has also been studied [97]. The material was prepared by heating amorphous zirconium phosphate under $N_2$-$NH_3$ for 7 h at 973 K. It catalyzed the Knoevenagel condensation of benzaldehyde with malononitrile at 323 K.

## 10. Future problems

Though the family of solid bases and the reactions catalyzed by them are still increasing, there are many important subjects we have to explore.

(i) The nature of basic sites are not always clear. A good example is $KF/Al_2O_3$. As described earlier, discussion about the active sites remains controversial. Another question in relation to this is why alumina is a very good support of KF. The same question also exists in the case of $KNH_2/Al_2O_3$. In both cases, silica is not a good support. It is important to clarify the nature of the interaction between the support and the catalytically active component. There is even a possibility that the 'support' is a part of the active centers. $KF/Al_2O_3$ or $KNH_2/Al_2O_3$ has been used by organic chemists. Recently, it was found that the catalytic activities of these catalysts enormously increased upon heat treatment under vacuum. It is not clear whether the heat treatment is effective simply because of elimination of adsorbed molecules such as water or carbon dioxide, or it leads to development of different kind of active sites.

(ii) In general, solid base catalysts are easily poisoned by water or carbon dioxide. It is a intriguing problem to prepare water or carbon dioxide resistant solid-bases. For example, creating basic sites in hydrophobic micropores may be of interest.

(iii) When solid bases are applied to organic reactions in liquid phase, diffusion of reactants and products may limit the reaction rate especially in the case of porous catalysts. The use of mesoporous support may offer an opportunity to avoid diffusion problems. One of such attempts ($Cs_2O$ supported on MCM-41) has been published [98].

(iv) The possibility of developing new reactions enlarges with use of acid–base combinations as often stressed by Prof. K. Tanabe [99]. Such examples are seen in the case of syntheses of ethylene imine by dehydration of ethanol amine [100] and methallyl alcohol by transfer hydrogen transfer reaction of methacrolein and ethanol [101].

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