J. CHEM. SOC. FARADAY TRANS., 1994, 90(1), 187-191

Superbase Character of Alumina loaded with Potassium by Impregnation from Ammoniacal Solution

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Al_2O_3 has been loaded with potassium by impregnation from an ammoniacal solution and heated under vacuum at 573 K. The resulting catalyst [$K(NH_3)/Al_2O_3$] showed extremely high catalytic activity for the isomerization of alkenes. These catalysts had much greater activity than that of Al_2O_3 loaded with alkali metals by vapour deposition. The isomerization, over $K(NH_3)/Al_2O_3$, of pent-1-ene to pent-2-ene gave a 98% yield in 6 min at 201 K. The temperature-programmed desorption and IR spectra of Al_2O_3 after impregnation indicated that the metal amide-like species formed on the alumina is a catalytically active species.

Al_2O_3 loaded with KNH_2 was found to be more active than $K(NH_3)/Al_2O_3$ for the isomerization of 2,3-dimethylbut-1-ene. The basic strength of these catalysts was estimated to be at least $H_- = 37$.

Alkali metals loaded on supports by deposition from the metal vapour have been reported as highly active catalysts for the isomerization of alkenes and the related compounds.[1,2] For example, Haag and Pines[3] described that sodium metal deposited on Al_2O_3 (Na/Al_2O_3) isomerized alkenes such as but-1-ene and pent-1-ene at room temperature. Malinowski *et al.*[4,5] 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 $H_- = 35$.

Suzukamo and co-workers[6–8] reported that a solid base prepared by successive treatment of Al_2O_3 with sodium hydroxide and sodium metal at 553–623 K under nitrogen ($Na/NaOH/Al_2O_3$) was highly effective for the isomerization of alkenes such as 2,3-dimethylbut-1-ene (DB-1) to 2,3-dimethylbut-2-ene (DB-2) at room temperature. The basic strength of $Na/NaOH/Al_2O_3$ is higher than $H_- = 37$,[7] the highest value among solid-base catalysts known to date.

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 in the isomerization of alkenes. Blouri *et al.* reported that $Na(NH_3)/Al_2O_3$ isomerized but-1-ene to but-2-ene between 273 and 753 K.[9] The catalytic activity, however, was rather low. Moreover, the chemical nature of active metal species on the surface has not been discussed and the conditions of loading alkali metal from ammoniacal solution have not been explored in detail.

Recently, we studied Yb and Eu species introduced into Y-zeolite from their ammoniacal solution and found that the catalytically active species for alkene isomerization is not metallic, but probably amide- or imide-like species of the rare-earth metals.[10] These findings prompted us to study the catalytic properties of alkali metals loaded on Al_2O_3 from the ammoniacal solutions.

We have found that alumina loaded with potassium from the ammoniacal solution [$K(NH_3)/Al_2O_3$], when properly prepared, has far higher activity for isomeriztion of alkenes, such as pent-1-ene (PT-1) and DB-1, than alkali metals loaded on a support by vapour deposition.

In this paper, the procedures for obtaining the highly active solid-base catalyst are explored and the chemical nature of the catalytically active species on the alumina is examined. The isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene (VBH) to 5-ethylidenebicyclo[2.2.1]hept-2-ene (EBH) is also described.

Experimental

Catalyst Preparation

Al_2O_3 support had a surface area of 243 m^2 g^{-1} and an average pore diameter of 15 nm. The catalysts, such as $K(NH_3)/Al_2O_3$, were prepared as follows: Al_2O_3, placed in a quartz reactor of 76 cm^3, was heated under vacuum (10^{-3} Pa) at 773 K for 3 h. A piece of a metal (M) was then put into the reactor under nitrogen. After evacuating the system to 10^{-3} Pa at room temperature, ammonia was liquefied into the reactor, kept at dry-ice–ethanol temperature, to dissolve the metal. After 1 h, the reactor was returned to room temperature for removal of most of the ammonia and then heated under vacuum at programmed temperatures for 1 h.

Catalytic Reactions

Reactants, DB-1 and PT-1, obtained from Wako Pure Chemicals, and VBH, obtained from Nippon Oil Company Ltd., were dried over molecular sieve 4A after distillation. The purities of DB-1, PT-1 and VBH were 98.4, 99.3 and 99.8%, respectively as determined by gas chromatography.

The isomerization was started by transferring a reactant from a side-arm of the reactor into the reactor containing a catalyst prepared as described above. The reactant and a suspended catalyst were stirred and the products were analysed by use of a gas chromatograph equipped with an OV 101 glass column.

IR Measurements

IR spectra were recorded on a JASCO FTIR 7000 spectrometer at room temperature by using a home-made IR cell.[11] Al_2O_3 was pressed into thin (10 mg cm^{-2}) self-supporting disk. The disk was placed in a sample holder and then the sample for IR measurements was prepared as follows: a disk of Al_2O_3 was heated under vacuum at 773 K for 3 h and a 0.03 g piece of potassium was put into the bottom of the cell under nitrogen. After evacuating the IR cell to 10^{-3} Pa at room temperature, 4 cm^3 of ammonia were liquefied into the bottom of the cell cooled with a mixture of dry-ice and ethanol. The Al_2O_3 disk was then immersed in the potassium–liquid ammonia solution for 1 h. The pellet was then withdrawn from the solution and most of ammonia was removed by evacuation at room temperature. Here, the amount of K supported on AL_2O_3 was not quantified.

Finally, the pellet was again moved down to be heat-treated under vacuum at a prescribed temperature.

TPD Measurements

The TPD spectrum of $K(NH_3)/Al_2O_3$ was measured as follows: Al_2O_3, which was kept in contact with the ammoniacal solution of potassium, was warmed to room temperature and then heated under vacuum at 303 K for 1 h. The relative amounts of gases desorbed from the Al_2O_3 were determined with a mass spectrometer (ULVAC MSQ-300) with a heating rate of 5 K min^{-1} to 973 K.

Results and Discussion

Isomerization of Alkenes

Isomerization of pent-1-ene with $K(NH_3)/Al_2O_3$

The isomerization of PT-1 to PT-2 was performed at 201 K with $K(NH_3)/Al_2O_3$ heated under vacuum at 573 K for 1 h. PT-1 (9.1 mmol) was reacted over 0.05 g of $K(NH_3)/Al_2O_3$, which contained 12 wt.% potassium as metal base. The proportion of PT-1 to $K(NH_3)/Al_2O_3$ was 180 mmol g^{-1}.

The catalyst was very active for the isomerization at a reaction temperature as low as 201 K. The yield of PT-2 reached 98% in 6 min. The ratio of *cis*:*trans* PT-2 was 73:27.

Haag and Pines reported that the yield of PT-2 was 65.2% in 6 min at about 303 K, when the ratio of PT-1 to Na-Al_2O_3 was 180 mmol g^{-1}.[3] Malinowski *et al.* reported that PT-2 was obtained in 98.5% yield with Na/MgO at 298 K in 120 min. Therefore, $K(NH_3)/Al_2O_3$ showed much higher catalytic activity for the isomerization of PT-1 than Na loaded on Al_2O_3 or MgO by metal vapour deposition.

Isomerization of 2,3-*Dimethylbut*-1-*ene*

Catalytic activity of $M(NH_3)/Al_2O_3$. The catalytic activities of $M(NH_3)/Al_2O_3$ for the isomerization of DB-1 were examined, where M is K, Na, Ca, Eu or Yb metal species supported on Al_2O_3 from the ammoniacal solutions.

As shown in Table 1, $K(NH_3)/Al_2O_3$ showed the greatest catalytic activity for the isomerization of DB-1, the yield of DB-2 reaching 95% in 10 min in 273 K (run 1). The yield of DB-2, 95%, at 273 K in 10 min was independent of the evacuation temperatures of $K(NH_3)/Al_2O_3$ between 423 and 523 K, indicating that the yield of DB-2 is almost equal to the equilibrium value. Al_2O_3 showed no catalytic activity, even when the reaction was carried out for 20 h at 313 K (run 7).

$K(NH_3)/Al_2O_3$ (run 2) has a catalytic activity even at 201 K, the yield of DB-2 being 41% in 10 min. The catalytic activity was much greater than that of potassium metal loaded on Al_2O_3 by vapour deposition of potassium (run 8). This indicates that the potassium species supported on Al_2O_3 from its ammoniacal solution is different from potassium metal supported on Al_2O_3 by vapour deposition.

$Na(NH_3)/Al_2O_3$ evacuated at 523 K also showed a high activity and gave a 41% yield of DB-2 in 10 min at 273 K (run 3). Among $Na(NH_3)/Al_2O_3$ heated under vacuum at various temperature, the one evacuated around 523 K showed the highest catalytic activity as mentioned later (Fig. 1).

The catalytic activity of $Ca(NH_3)/Al_2O_3$ was the lowest among $M(NH_3)Al_2O_3$ (run 4): Eu and Yb $(NH_3)/Al_2O_3$ gave 85 and 29% yields of DB-2, respectively at 313 K in 1200 min (runs 5 and 6).

Influence of Evacuation Temperature on the Catalytic Activities of $K(NH_3)$ or $Na(NH_3)/Al_2O_3$

To examine the effect of the heating temperature of $K(NH_3)/Al_2O_3$ under vacuum after impregnation on the catalytic activity, the isomerization of DB-1 to DB-2 was performed at 201 K for 10 min. DB-1 (48 mmol; 6.0 cm^3) was stirred with 0.125 g of $K(NH_3)/Al_2O_3$, which contained 8 wt.% of potassium. The catalytic activity strongly depended on the heating temperature of $K(NH_3)/Al_2O_3$. As shown in Fig. 1, the catalytic activity increased with increasing evacuation temperature and reached maximum around 570 K, the yield of DB-2 being 49%. DB-2 is formed with 100% selectivity. At higher evacuation temperatures, the catalytic activity declined: when $K(NH_3)/Al_2O_3$ was evacuated at 673 K,

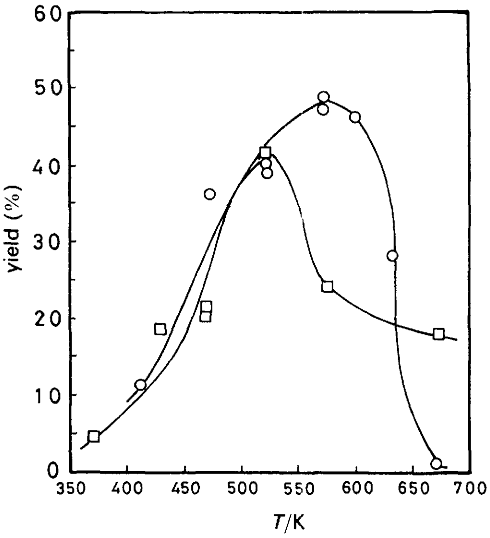


Fig. 1 The dependence on evacuation temperature (*T*) of the catalytic activities of $K(NH_3)/Al_2O_3$ at 201 K (○) and $Na(NH_3)/Al_2O_3$ at 273 K (□) for the isomerization of 2,3-dimethylbut-1-ene

Table 1 The catalytic activities of K, Na, Ca, Eu and Yb metals supported on Al_2O_3 for the isomerization of 2,3-dimethylbut-1-ene (DB-1) to 2,3-dimethylbut-2-ene (DB-2)

run	metal	amount of metal loaded (wt.%) (mmol g^{-1})	catalyst weight /g	evacuation temperature /K	amount of DB-1 /mmol	reaction temperature /K	reaction time /min	yield of DB-2 (%)
1	K	8.0 (2.0)	0.125	573	48	273	10	95
2	K	8.0 (2.0)	0.125	573	48	201	10	49
3	Na	4.4 (2.0)	0.25	523	24	273	10	41
4	Ca	8.0 (2.0)	0.25	423	24	313	1200	1.7
5	Eu	8.0 (0.50)	0.25	523	24	313	1200	53
6	Yb	8.0 (0.46)	0.25	473	24	313	1200	29
7	—		0.25	—	24	313	1200	0
8	K[a]	8.0 (2.0)	0.25	573	24	201	10	7.0

[a] The catalyst was prepared by the deposition of K vapour on Al_2O_3.

the yield of DB-2 was 1%. Thus, the optimum evacuation temperature for this reaction is *ca.* 570 K.

The effect of the heating temperature of $Na(NH_3)/Al_2O_3$ on the catalytic activity in the isomerization was examined at 273 K as shown in Fig. 1. DB-1 (24 mmol, 3.0 cm^3) was stirred with 0.125 g of $Na(NH_3)/Al_2O_3$ which contained 4.4 wt.% of sodium. The catalytic activity also depended strongly on the evacuation temperature as in the case of $K(NH_3)/Al_2O_3$. The optimum evacuation temperature is *ca.* 520 K.

Dependence of the Isomerization Activity on the Amount of Potassium loaded

The influence of the amount of potassium loaded on Al_2O_3 on the catalytic activity for the isomerization of DB-1 was examined at 201 K (Fig. 2). Al_2O_3 did not have any catalytic activity at all. The catalytic activity of $K(NH_3)/Al_2O_3$ depended strongly on the amount of potassium. The isomerization did not proceed at all when the loaded amount was 3 wt.% or below. This potassium content is almost equal to that of OH groups on the surface of Al_2O_3, which were estimated by thermogravimetric analysis up to 1273 K. This result indicates that the OH groups on the surface of Al_2O_3 react with potassium and potassium loaded in this way is not active for the isomerization. This phenomenon will be discussed further later.

The yield of DB-2 sharply increased with increasing potassium content higher than 3 wt.%, and the maximum yield of DB-2, 59%, was observed, when the potassium content was 12 wt.%. When the amount of potassium content exceeded 12 wt.%, the catalytic activity declined. This may be attributed to the pore plugging by excess loading.

Characterization of Potassium loaded on Al_2O_3

TPD Spectrum of $K(NH_3)/Al_2O_3$

In order to investigate potassium species on $K(NH_3)/Al_2O_3$, the gases desorbed from $K(NH_3)/Al_2O_3$ were analysed with a TPD technique. The sample was prepared by immersing Al_2O_3 in potassium–ammonia solution for 1 h followed by evacuation at 303 K for 1 h. The sample contained 8 wt.% of potassium.

The gases desorbed from $K(NH_3)/Al_2O_3$ were ammonia, hydrogen and nitrogen. Fig. 3 shows the desorption profiles of NH_3, H_2 and N_2 from $K(NH_3)/Al_2O_3$. The NH_3 desorption peaks were observed around 360 and 650 K. The former desorption is caused by the desorption of physisorbed ammonia on Al_2O_3.

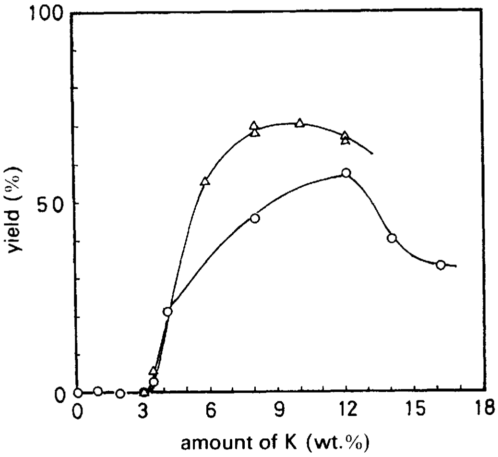


Fig. 2 Influence of loaded amount of potassium on Al_2O_3 on the catalytic activity of $K(NH_3)/Al_2O_3$ (○) and KNH_2/Al_2O_3 (△) for the isomerization of DB-1. The isomerization was carried out at 201 K for 10 min.

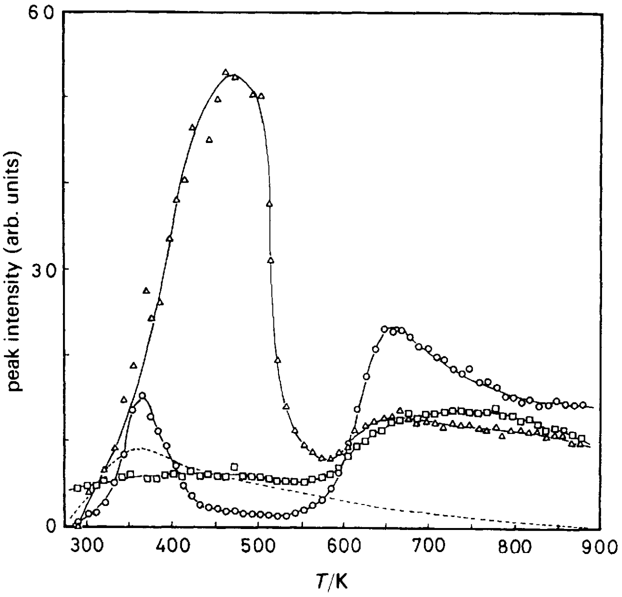


Fig. 3 TPD spectra of gases desorbed from $K(NH_3)/Al_2O_3$ and Al_2O_3. (○), NH_3; (△), H_2; (□), N_2; (---), NH_3 desorbed from Al_2O_3.

The hydrogen desorption peaks were observed around 470 and 650 K. The desorption of H_2 around 470 K may be caused by the formation of KNH_2-like species as follows:

$$K^+ + e^-(NH_3)_n \rightarrow (n-1)NH_3 + KNH_2 + \tfrac{1}{2}H_2 \quad (1)$$

The colour of $K(NH_3)/Al_2O_3$, evacuated at up to 523 K for 1 h was blue, suggesting that electrons (e^-) solvated with ammonia molecules and K^+ cations existed. It is well known that the ammonia solutions of alkali metals such as potassium are relatively stable, existing for many hours without appreciable reaction among the metal cations, electrons and ammonia.[12] When $K(NH_3)/Al_2O_3$ was evacuated at 573 K, its colour changed from blue to grey. The TPD result indicates that reaction (1) is complete up to 573 K.

As shown in Fig. 3, the rates of desorption of NH_3, H_2 and N_2 gradually increased above 573 K and the peaks of H_2 and NH_3 were simultaneously observed around 650 K. These desorptions of H_2 and NH_3 may result from the decomposition of KNH_2-like species to potassium nitride or K metal as follows:

$$2KNH_2 \rightarrow 2K + N2 + 2H_2 \quad (2)$$

$$3KNH_2 \rightarrow K_3N + 2NH_3 \quad (3)$$

Nitrogen desorption was observed at all the measured temperatures. The amount of nitrogen desorption gradually increased at higher temperature above 573 K and reached maximum value around 720 K. The desorption of N_2 at this temperature may be caused by the decomposition of potassium nitride to potassium metal.

$$K_3N \rightarrow 3K + \tfrac{1}{2}N_2 \quad (4)$$

Only ammonia was desorbed from Al_2O_3 which was in contact with liquid NH_3. The desorption maximum was observed around 360 K and the desorption continued up to *ca.* 900 K as shown by the dotted line in Fig. 3. This shows that the decomposition of ammonia into hydrogen and nitrogen occurred only when potassium was loaded on alumina.

IR Spectra of $K(NH_3)/Al_2O_3$

As mentioned above, the catalytic activity of $K(NH_3)/Al_2O_3$ in the isomerization of DB-1 to DB-2 strongly depended on the heating temperature under vacuum (Fig. 1). Moreover, the TPD spectrum from $K(NH_3)/Al_2O_3$ suggests that the chemical species on the surface varied with the evacuation temperature. Therefore, IR spectroscopy was applied to the investigation of the catalytically active species.

When Al_2O_3 was heated under vacuum at 773 K for 3 h, four IR bands were observed at *ca.* 3700 cm^{-1} [Fig. 4(*a*)]. These bands are due to OH groups on Al_2O_3.[13] When Al_2O_3 was immersed in an ammoniacal solution of potassium, the colour of the solution remained blue. The system was then evacuated at 303 K for 1 h. The peaks due to OH groups at *ca.* 3700 cm^{-1} disappeared [Fig. 4(*b*)]. This suggests that OH groups on the surface react with potassium metal as follows:

$$\begin{array}{ccc} \mathrm{OH} + \mathrm{K} & \rightarrow & \mathrm{OK} + \tfrac{1}{2}\mathrm{H_2} \\ | & & | \\ \mathrm{Al} & & \mathrm{Al} \\ \wedge & & \wedge \end{array} \qquad (5)$$

At the same time, a new band appeared at 1553 cm^{-1}, which was assigned to an amide group bound to potassium.

When the evacuation temperature increased to 523 K, the blue colour of the disk became darker. The IR measurement was unsuccessful, since the disk was not transparent to the IR beam. When the sample was evacuated at 573 K, three bands at 3240, 3190 and 1553 cm^{-1} could be observed [Fig. 4(*c*)]. The frequencies of these IR bands agreed with those of KNH_2,[14] indicating that a potassium amide-like species was generated on $K(NH_3)/Al_2O_3$. The intensity of the IR bands at 3240, 3190 and 1553 cm^{-1} due to KNH_2-like species sharply decreased by further increasing the evacuation temperature from 573 K to 603 K. This result indicates that KNH_2-like species decompose around 603 K. These bands disappeared completely at 673 K. At the same time, the band due to OH groups reappeared when $K(NH_3)/Al_2O_3$ was evacuated at 603 K [Fig. 4(*d*)]. Moreover, the band at 2164 cm^{-1} also appeared. The intensity of this band gradually increased by increasing evacuation temperature and reached maximum at 673 K. Kritzenberger *et al.* reported that an IR band was observed at 2115 cm^{-1}, when NH_3 was adsorbed on Al_2O_3 at 623 K and attributed this band to azide species.[15] The IR study shows that amide-like species are formed on the alumina surface when Al_2O_3 is immersed in potassium–ammonia solution, followed by heating at 573 K. This result is in agreement with that of TPD. These facts strongly suggest that the active species for the isomerization is potassium amide, since the activity maximum was observed at the same temperature range.

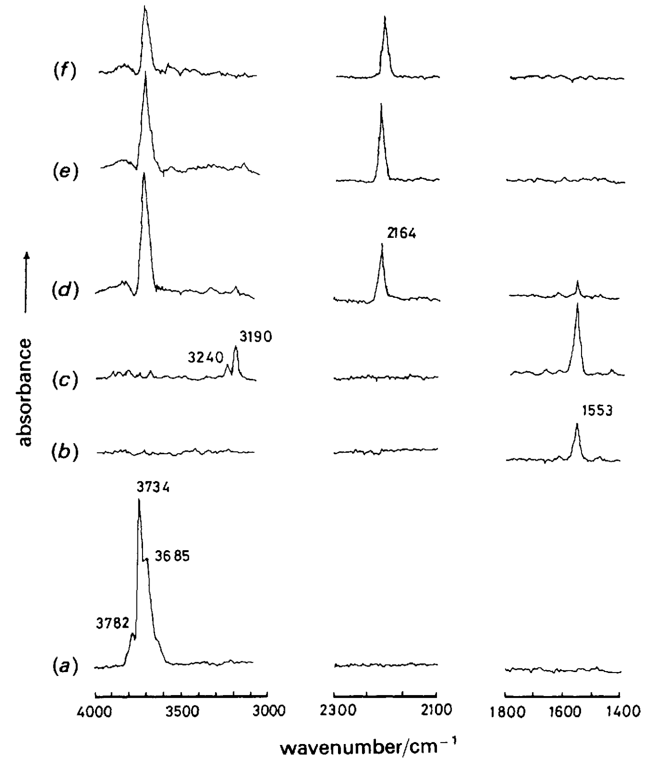


Fig. 4 IR spectra of $K(NH_3)/Al_2O_3$. (*a*) Al_2O_3 evacuated at 773 K for 3 h; $K(NH_3)/Al_2O_3$ evacuated at (*b*) 303, (*c*) 573, (*d*) 603, (*e*) 673 and (*f*) 773 k for 1 h.

Catalytic Activity of KNH_2 *supported on* Al_2O_3

In order to confirm that potassium amide formed on Al_2O_3 is an active species for the isomerization of alkenes, its catalytic activity for the isomerization of DB-1 was examined. KNH_2 is easily prepared from potassium–ammonia solution by using catalytic agents such as Fe_2O_3.[16]

The catalyst was prepared in the same way as $K(NH_3)/Al_2O_3$ except that a small amount of Fe_2O_3 ($K : Fe_2O_3 = 100 : 1$) was added to the system besides potassium and Al_2O_3. Adding liquid ammonia to the Al_2O_3–K–Fe_2O_3 system results in the development of the blue colour, characteristic of solvated electrons.[12] Within 15 min, the blue colour disappeared as a result of the formation of KNH_2. After 1 h, the reactor was warmed up to room temperature to remove most of the ammonia and then heated under vacuum at a prescribed temperature for 1 h. The catalyst prepared in this way will be denoted as KNH_2/Al_2O_3.

Hubert reported that KNH_2 supported on Al_2O_3 showed the catalytic activity in the isomerization of allylamines to prop-1-enylamines at room temperature.[17] However, the conditions of loading KNH_2 and the physicochemical properties of KNH_2 supported on Al_2O_3 have not been explored yet.

The catalytic activity of KNH_2/Al_2O_3 with varying evacuation temperature for the isomerization of DB-1 was examined at 201 K. The results are shown in Fig. 2. When the amount of KNH_2 increased from 0 to 3 wt.%, the isomerization did not proceed at all, as in the case of $K(NH_3)/Al_2O_3$. This result indicates that the reaction of potassium metal with OH groups on Al_2O_3 (eqn. 6) also occurs preferentially in this system.

When the amount of KNH_2 exceeds 3 wt.%, catalytic activity for the isomerization was apparent. Thus, KNH_2/Al_2O_3 is a highly active catalyst for the isomerization and the active species in $K(NH_3)/Al_2O_3$ is the potassium-amide-like species. The greater activity of KNH_2/Al_2O_3 than $K(NH_3)/Al_2O_3$ may be due to a higher concentration of the active species. The highest activity of KNH_2/Al_2O_3 was observed with K-loading of 10 wt.%.

Basic Strength of $K(NH_3)/Al_2O_3$ *and* KNH_2/Al_2O_3

To estimate the basic strength of $K(NH_3)/Al_2O_3$ and KNH_2/Al_2O_3 heated under vacuum at 573 K, the catalysts were put in contact with cumene, as an indicator, at room temperature. The surface of the $K(NH_3)/Al_2O_3$, which was initially light grey, immediately turned to purple, while cumene in the liquid phase remained colourless.

The white colour of KNH_2/Al_2O_3 also turned to purple by putting the sample into contact with cumene. The purple colour can be assigned to 2-phenyl-2-propanide anion $[C_6H_5C^-(CH_3)_2]$, which is thought to be formed by abstraction of proton from cumene by basic sites. This result indicates that the basic strength of KNH_2/Al_2O_3 and $K(NH_3)/Al_2O_3$ is at least $H_- = -37$.[18] Suzukamo and co-

Table 2 Isomerization of 5-vinylbicyclo[2.2.1]hept-2-ene (VBH) to 5-ethylidenebicyclo[2.2.1]hept-2-ene (EBH)[a]

run	catalyst	preparation method	evacuation temperature/K	yield of EBH (%)	ratio of $Z:E$
1	$K(NH_3)/Al_2O_3$	impregnation	573	97	15 : 85
2	KNH_2/Al_2O_3	impregnation	573	98	14 : 86
3	CaO	decomposition of $CaCO_3$	1025	98	12 : 88

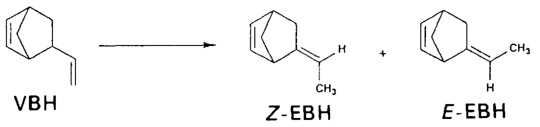
[a] The reaction was carried out at 273 K for 10 min with 21 mmol of VBH and 0.063 g of catalyst.

workers also reported that $NaOH/Na/Al_2O_3$ developed a pink colour upon contact with cumene.[6–8]

Buncel *et al.* have reported that KNH_2 in tetrahydrofuran (THF) metallates to completion 2,4-dixylylmethane and is unreactive towards toluene.[19] When KNH_2/Al_2O_3 and $K(NH_3)/Al_2O_3$ were in contact with toluene, the surface of these catalysts turned orange, which may be caused by benzyl anions. Thus, the basic strengths of the two catalysts may be enhanced by Al_2O_3 and are higher than that of KNH_2 itself in THF. In fact, potassium supported on silica from the ammoniacal solution showed negligible activity for the isomerization of alkenes.

Isomerization of 5-Vinylbicyclo[2.2.1]hept-2-ene to 5-Ethylidenebicyclo[2.2.1]hept-2-ene

As mentioned above, $K(NH_3)/Al_2O_3$ and KNH_2/Al_2O_3 showed the superbasicity. It seems that the solid superbase is able to catalyse the isomerization of alkenes *e.g.* PT-1 and DB-1 under mild reaction conditions to give the products quantitatively. These catalysts were applied to the isomerization of VBH to EBH, which was an important third component of ethene–propene synthetic rubber.[20]



Scheme 1

The isomerization of VBH to EBH was carried out at 273 K. As shown in Table 2, both KNH_2/Al_2O_3 and $K(NH_3)/Al_2O_3$ showed a very high catalytic activity for the isomerization. The reaction was almost complete in 10 min.

This isomerization is easily achieved with CaO prepared by heating $CaCO_3$ under vacuum at around 1000 K.[21] It was found that $K(NH_3)/Al_2O_3$ and KNH_2/Al_2O_3 are as effective catalysts as CaO for the isomerization.

While $Na/NaOH/Al_2O_3$ is a highly active catalyst for the isomerization,[6–8] it is far more difficult to prepare than $K(NH_3)/Al_2O_3$ or KNH_2/Al_2O_3.

Conclusions

It was found that $K(NH_3)/Al_2O_3$ had a much greater catalytic activity for the isomerization of alkenes than alkali metals loaded on supports by vapour deposition. The catalytic activity was strongly influenced by the evacuation temperature and the amount of potassium species. The active species of $K(NH_3)/Al_2O_3$ is the KNH_2-like species formed on Al_2O_3. Alumina loaded with KNH_2 (KNH_2/Al_2O_3) was more active than $K(NH_3)/Al_2O_3$. Both catalysts are superbasic and the basic strength of $K(NH_3)Al_2O_3$ is at least $H_- = 37$.

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Paper 3/05142K; *Received* 25*th August*, 1993