Synthesis and characterization of potassium-modified alumina superbases

Ying Wang
Jian Hua Zhu
Wenyu Huang
Synthesis and characterization of potassium-modified alumina superbases

Ying Wang,* Jian Hua Zhu and Wen Yu Huang

Department of Chemistry, Nanjing University, Nanjing 210093, China

Received 2nd January 2001, Accepted 20th April 2001
First published as an Advance Article on the web 22nd May 2001

Novel solid superbases can be prepared by dispersing potassium salts such as K₂CO₃ and KHCO₃ on alumina followed by thermal treatments. The resulting materials show an extremely high activity in the isomerization of cis-but-2-ene at 0 °C and possess base strength of at least H₋ = +26.5. X-Ray diffraction (XRD) and Raman spectra of K₂CO₃ or KHCO₃ modified alumina reveal the formation of potassium hydroalumina carbonate, which is the precursor of active species. Decomposition of potassium salts on alumina has been studied by use of thermal gravimetric differential thermal analysis (TG-DTA) and temperature programmed decomposition-mass spectrometry (TPDE-MS). Two CO₂ evolution processes were observed in the TPDE-MS profile, corresponding to the decomposition of potassium hydroalumina carbonate and bulk potassium salt.

Introduction

The development of clean and economical processes for the production of fine chemicals is becoming an area of growing interest. Solid strong acids and bases are desirable for environmentally benign catalysis because of their advantages in recyclable use and easy separation from liquid reaction mixtures. Although not many studies on superbases have been reported, it is expected that the development of a wide variety of superbases will have an increasing importance in the fine chemical industry, since they can catalyze various reactions under mild conditions and minimize the production of pollutants. However, preparing solid superbase at a low cost is still a developing field, although there has been rapid development over the last 20 years. In general, traditional methods of preparation of solid superbases from natural oxides are difficult and expensive; for instance, alkali earth metal oxides such as CaO or SrO should be evacuated at 850–900 °C and no doubt the surface area of the oxides will inevitably be reduced at such high temperatures. Another type of solid superbases is prepared by loading alkali metal onto an oxide support. Kijenski and Malinowski prepared Na—MgO with a base strength of H₋ = +35 by evaporating metallic sodium onto MgO and this catalyst exhibited a high activity for the isomerization of pent-1-ene. Suzukamo reported a new solid superbase by supporting alkali metal on γ-Al₂O₃, but the Al₂O₃ should be pretreated with alkali metal hydroxides at 200–600 °C. One of the resulting materials, Na/NaOH—Al₂O₃ possessed a superbasicity of H₋ > +37 and catalyzed the isomerization of 5-vinylbicyclo-(2,2,1)-hept-2-ene (VNB) to 5-ethylidenebicyclo-(2,2,1)-hept-2-ene (ENB) with very high conversion and selectivity. Loading potassium onto alumina in liquid ammonia and heating the resulting material under vacuum at 250–300 °C, Baba et al. obtained a superbase K/NH₄—Al₂O₃ that is very active for isomerization of alklenes. However, the complex and time-consuming preparation process would be inconvenient for industrial use, therefore novel preparation methods must be developed.

Recently, we successfully prepared a solid strong base by loading KNO₃ onto γ-Al₂O₃ or KL zeolite and the composites showed a very high activity in cis-but-2-ene isomerization. Moreover, an unusually strong basicity H₋ = +26.5 was found for these materials after decomposition of the supported KNO₃. However, formation of nitrogen oxides during decomposition of the nitrate hinders the application of KNO₃ supported catalysts in industry. This prompted us to study the role anions play in the modification of the potassium salt, and to explore the possibility of loading other potassium salts onto alumina to generate superbasic sites. Potassium carbonate is frequently used as additive or promoter to modify the acid–base properties of alumina. It reacts strongly with surface hydroxy groups and forms Al—OK groups on the alumina by neutralizing the most acidic sites and removing the OH⁻ groups at 3790 cm⁻¹. As a result, introduction of the potassium salt dramatically increases the basicity of γ-Al₂O₃. However, although systematic studies on the basic strength of alumina modified by K₂CO₃ were found in the literature, the mechanism of promotion is not yet fully understood.

In this paper, the procedure of loading K₂CO₃ and KHCO₃ as well as KOH on alumina to obtain strong solid basic catalysts is studied. TPDE-MS combined with TG-DTA is employed to examine the decomposition of the potassium salt on the alumina, while XRD and Raman spectroscopy are utilized to investigate the interaction between the promoter and the support. Additionally, titration with Hammett indicator and the cis-but-2-ene isomerization reaction are used to evaluate the basicity of the potassium modified alumina.

Experimental

Two samples of γ-Al₂O₃, with surface areas 179 m² g⁻¹ (JRCALO-4) and 150 m² g⁻¹ (AKPG-015, Sumitomo Chem. Int. Ltd.) respectively, denoted as A and A*, were used as the starting material for the preparation of potassium salt-modified catalysts. The alumina support was first ground with K₂CO₃ or KHCO₃ at a given weight ratio, then mixed with an appropriate amount of water. The paste was dried at 110 °C overnight, and finally crushed and sieved to particles of 20–40 mesh. To distinguish the resulting materials, these samples without calcination were denoted as e.g. 20KCA-110,
in which 20 stands for the loading amount in wt.% of K$_2$CO$_3$, KC represents K$_2$CO$_3$, KHC represents KHCO$_3$ and KOH represents KOH respectively. A means the support is Al$_2$O$_3$ (JRCALO-4) and A* is Al$_2$O$_3$ (AKPG-015), while 110 indicates the drying temperature. For the calcined samples e.g. 20KCA-600 was used to indicate that the samples have been calcined at 600 ºC in air for 5 h. Unless otherwise noted the term 110 is omitted.

A closed recirculation system (285 cm$^3$) connected to a U-shaped quartz reactor was used to follow isomerization of cis-but-2-ene at 0 ºC. The reactor was purified by repeated freeze–thaw cycles and passing through 5A zeolites. A catalyst sample of about 5 mg was evacuated at a given temperature for 2 h prior to contact with the reactant (50 torr) at 0 ºC. The reaction mixture was separated by a 5 m column packed with VZ-7 operated at room temperature and analyzed by an on-line gas chromatograph equipped with thermal conductivity detection (TCD). In cis-but-2-ene isomerization the conversion level after 3 min is chosen to represent the initial rate. The relative rate of double bond isomerization from cis-but-2-ene to but-1-ene was compared with that of rotational isomerization from cis-but-2-ene to trans-but-2-ene, and represented as the ratio of R-B/1-B in the reaction products.

The strength of the basic sites was measured by the cyclohexane titration method. The indicators employed are 4-nitroaniline (H$_t$ = 18.4) diphenylamine (H$_t$ = +22.3), 4-chloroaniline (H$_t$ = +26.5) and triphenylmethylene (H$_t$ = +33). Each indicator was dissolved in benzene (Wako Pure Chem. Ind. Ltd.) to form a 0.1 wt.% solution for measurement. Cyclohexane (Wako Pure Chem. Ind. Ltd.) was the non-polar solvent in the experiment and was purified by repeated freeze–pump–thaw cycles and passing through activated molecular sieves, and was finally transferred into a glass reservoir by vacuum distillation. A sample of 50 mg was evacuated at a given temperature for 2 h and then cooled to room temperature, then 2.5 mL of purified cyclohexane was added to the pretreated sample by vacuum distillation. The sample tube was removed from the vacuum apparatus, two drops of indicator solution were added to the suspension, and the color change of the indicator at the solid surface was monitored visually.

In TG-DTA, about 10–20 mg of sample was heated in a platinum crucible at a rate of 20 °C min$^{-1}$ under nitrogen flow in a meter thermal-analyzer SDT 2960. For the TPDE-MS experiments about 50 mg of sample were first outgassed at 300 ºC for 3 h in order to remove the physically adsorbed water. The sample was then cooled to room temperature in vacuum and the TPDE-MS experiment was started, the evolutions were analyzed by using an AQA-200 quadrupole mass spectrometer using a flow of argon as an internal standard. The sample was heated to 900 ºC at a heating rate of 10 ºC min$^{-1}$.

XRD patterns of the samples were recorded on a Rigaku Diffractometer with Cu-Kx radiation using an acceleration voltage of 40 kV and a current of 20 mA. The detector range of 29 is from 5 to 75°. Raman spectra were measured on a RFS-100 spectrometer equipped with a microscope, multi-channel detection and a laser source (Spectra-Physics model, 514.5 nm argon line). Spectra were obtained with a laser power of 50 mW at the source, while the cell current was recorded, presenting sharp and strong increases followed by decays.

Results and discussion

1. Isomerization of but-1-ene and cis-but-2-ene

Fig. 1 displays the time course of cis-but-2-ene (c-B) isomerization on 20KCA at 0 ºC. c-B isomerization is a well-known model reaction for probing the strong basicity of solid bases. The catalyst showed a very high activity for the isomerization at the reaction temperature of 0 ºC and no skeletal isomerization could be observed. A selectivity (the ratio of trans-but-2-ene to but-1-ene) of more than 10 was obtained in the initial stage (3 min), higher than that reported by Izuka et al. on CaO evacuated at 700–900 ºC. The yield of but-1-ene, which is the product of double bond migration, was rather low (ca. 3%) and stable during the reaction time. This high R-B/1-B value is contrary to those reported on common solid bases but similar to those reported on CaCO$_3$ evacuated at 900 ºC, which is a superbase catalyzing the direct cis-trans isomerization of butene.$^{15}$ These facts imply two different active sites; one "unusually strong basic site" and another common basic site$^{15}$ formed on potassium modified Al$_2$O$_3$ by evacuation at 500 ºC.

Catalysts derived from K$_2$CO$_3$ or KHCO$_3$ supported on Al$_2$O$_3$ were compared with MgO, the typical solid base used in cis-but-2-ene isomerization, in order to study the function of the potassium cation. All samples were evacuated at 500 ºC prior to use and the results are summarized in Table 1. Alumina gave a trace of activity in this reaction while two kinds of neat potassium salts were inactive, probably resulting from their small surface area. Loading of K$_2$CO$_3$ or KHCO$_3$ dramatically enhanced the activity of the alumina, being higher than that of MgO in most cases. The rate of isomerization on Al$_2$O$_3$-supported potassium salts increased with the increase in K$^+$ density and reached a maximum at K$^+$ density of 12 ion nm$^{-2}$, then decreased when the loading amount exceeded this density. According to Stork and Pott,$^{13}$ on the surface of fully hydroxylated alumina, K$^+$ ions replaced the protons of isolated hydroxy groups to form O–K groups, which were considered to be the active species of this catalyst, so the density of the hydroxy groups on the surface of γ-Al$_2$O$_3$ was more likely related to the maximum in activity. The alumina used in our study is an activated γ-Al$_2$O$_3$ with a high surface area of ca. 179 m$^2$ g$^{-1}$, which has maximum surface hydroxyl coverage of 11 OH$^{-}$ nm$^{-2}$. These values represent the estimated total number of surface lattice sites considering the alumina surface to be comprised of the (100), (111), and (110) planes of its defective spinel structure.$^{17}$ Jordan$^{18}$ reported the maximum uptake of K$^+$ on alumina by deprotonation of surface OH$^{-}$ to be 13 K$^+$ nm$^{-2}$, this is very close to the corresponding K$^+$ concentration at the highest activity of our catalyst, 12 K$^+$ nm$^{-2}$, which is slightly more than that of a monolayer coverage (ca. 10 Å$^2$ per K$^+$).$^{18}$ When the amount of potassium cations loaded on alumina was below the saturation uptake of K$^+$, it could be well dispersed. As a result, the number of basic sites together with the activity of the sample would increase with the potassium
content. However, if the amount of potassium salt exceeded the saturation uptake of K\(^+\), residual bulk potassium salt would cover the basic sites on the surface of the catalyst, resulting in a lowered catalytic activity. The selectivity of the samples is also listed in Table 1. The initial t-B/1-B ratio was below unity on MgO and the sample with lower K\(^+\) content, coinciding with that observed by Foster and Cvetanovic on common solid base; \(^{19}\) however, the ratio was above unity on the samples loaded with K\(_2\)CO\(_3\) or KHCO\(_3\), more than 10 wt.% or 12 wt.% respectively, similar to that reported by Iizuka \textit{et al.} on the CaO evacuated at 900 °C which is known as a superbase for this reaction. \(^{15}\) A high initial t-B/1-B ratio of around 10 in the products of the reaction was found in our samples, higher than that reported by Iizuka \textit{et al.} \(^{15}\) Based on these results it is very likely that > 10 wt.% K\(_2\)CO\(_3\) or > 12 wt.% KHCO\(_3\) more on alumina can generate superbasic sites, but the true reason for the formation of such unusually strong basic sites needs to be explored.

2. Effect of evacuation temperature

The influence of the evacuation temperature on the activity of 20KCA and 23KHCA* can be seen from Fig. 2. The evacuation temperature seemed to be crucial for the generation of catalytic activity on the composite, because the sample evacuated at 300 °C was inactive for cis-but-2-ene isomerization. Moreover, the activity change profiles are almost the same although the decomposition temperature differs in each salt. KCA and KHCA samples showed catalytic activity when they were evacuated at 400 °C while the highest activity was observed on those uncalcined composites after evacuation at 500 °C. However, evacuation at 700 °C led to a loss in activity. Since K\(_2\)CO\(_3\) or KHCO\(_3\) are inactive for this isomerization, the activity variation of the catalyst evacuated at different temperatures should be attributed to the different decomposition extent and distribution of potassium salts on the alumina support. For example, deactivation of the composite at high temperature probably resulted from the loss of potassium species, by sublimation and/or penetration into the subsurface or bulk by solid–solid reaction leading to formation of spinels such as K\(_2\)Al\(_2\)O\(_4\).

3. Basic strength of KCA and KHCA

Table 2 summarizes the base strengths of KCA, KHCA and MgO. The parent alumina was acidic and converted the color of dimethylaminooazobenzene (H\(_o\) = 3.3) from yellow to red. After the loading of potassium salts and their evacuation at 500 °C, all of the modified alumina samples exhibited a high base strength regardless of the kinds of potassium salt. They could change the color of 4-chloroaniline (H\(_o\) = 26.5) from colorless to pink very quickly, but failed to convert triphenylmethane (H\(_o\) = 33.0) to its conjugate base form, therefore their base strength could be tentatively denoted as +33.0 > H\(_{o}\) > +26.5. According to Tanabe’s definition, \(^{20}\) these sites are superbasic sites. Although the superbasic property of dispersed K\(_2\)CO\(_3\) was expected, \(^{21}\) this is the first observed evidence on KCA and KHCA samples. The base strength of MgO is found to be +26.5 > H\(_{o}\) > +18.4, in good agreement with the report of the take.\(^{22}\) and mirroring the results of isomerization in which potassium-modified catalysts show a higher activity than MgO. On the other hand, calcination at high temperature is proved to lower the basicity of the sample. After calcination at 900 °C prior to evacuation at 400 °C.

### Table 1 Isomerization of cis-but-2-ene at 0 °C over potassium-modified alumina

<table>
<thead>
<tr>
<th>Sample</th>
<th>K(^+) density /nm(^2)</th>
<th>Loading amount (wt.%a)</th>
<th>Initial activity /mmol g(^{-1}) min(^{-1})</th>
<th>Selectivity (t-B/1-B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(_2)CO(_3)</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>KHCO(_3)</td>
<td>—</td>
<td>—</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>—</td>
<td>—</td>
<td>trace</td>
<td>—</td>
</tr>
<tr>
<td>MgO</td>
<td>—</td>
<td>—</td>
<td>3.0</td>
<td>0.3</td>
</tr>
<tr>
<td>3KCA</td>
<td>1.5</td>
<td>3.0</td>
<td>0.25</td>
<td>0.1</td>
</tr>
<tr>
<td>5KCA</td>
<td>2.6</td>
<td>5.0</td>
<td>5.35</td>
<td>5.8</td>
</tr>
<tr>
<td>10KCA</td>
<td>5.5</td>
<td>10.0</td>
<td>15.77</td>
<td>7.1</td>
</tr>
<tr>
<td>14KCA</td>
<td>8.0</td>
<td>13.97</td>
<td>23.65</td>
<td>10.4</td>
</tr>
<tr>
<td>20KCA</td>
<td>12.0</td>
<td>20.0</td>
<td>31.11</td>
<td>13.15</td>
</tr>
<tr>
<td>30KCA</td>
<td>21.0</td>
<td>30.0</td>
<td>19.90</td>
<td>8.47</td>
</tr>
<tr>
<td>4KHC(_A)*</td>
<td>1.5</td>
<td>3.56</td>
<td>0.06</td>
<td>0.23</td>
</tr>
<tr>
<td>7KHC(_A)*</td>
<td>3.0</td>
<td>6.87</td>
<td>0.79</td>
<td>0.82</td>
</tr>
<tr>
<td>12KHC(_A)*</td>
<td>5.5</td>
<td>12.07</td>
<td>3.93</td>
<td>5.29</td>
</tr>
<tr>
<td>16KHC(_A)*</td>
<td>8.0</td>
<td>16.44</td>
<td>5.00</td>
<td>9.78</td>
</tr>
<tr>
<td>23KHC(_A)*</td>
<td>12.0</td>
<td>23.00</td>
<td>16.67</td>
<td>12.07</td>
</tr>
<tr>
<td>33KHC(_A)*</td>
<td>20.0</td>
<td>32.98</td>
<td>10.54</td>
<td>10.60</td>
</tr>
<tr>
<td>26KHC</td>
<td>12.0</td>
<td>26.50</td>
<td>32.30</td>
<td>14.75</td>
</tr>
</tbody>
</table>

### Table 2 Base strength of solid bases after evacuation at 400 and 500 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>K(_2)CO(_3)</td>
<td>—</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>—</td>
</tr>
<tr>
<td>MgO</td>
<td>—</td>
</tr>
<tr>
<td>20KCA-110</td>
<td>33.0 &gt; H(_{o}) &gt; 26.5</td>
</tr>
<tr>
<td>26KHC(_A)-110</td>
<td>33.0 &gt; H(_{o}) &gt; 26.5</td>
</tr>
<tr>
<td>16KOHA-110</td>
<td>33.0 &gt; H(_{o}) &gt; 26.5</td>
</tr>
<tr>
<td>20KCA-900</td>
<td>18.4 &gt; H(_{o}) &gt; 15</td>
</tr>
</tbody>
</table>
400 °C, 20KCA completely lost its basicity, and only a medium basicity could be recovered when the evacuation temperature was raised to 500 °C. This is also in agreement with the result of the activity test for the isomerization of cis-but-2-ene.

4. Dispersion and location of potassium on Al₂O₃

Fig. 3 displays the XRD patterns of KCA-110. With a loading amount of K₂CO₃ below 10 wt.% (Fig. 3B, C and D), the composite only showed XRD patterns of alumina without any bulk K₂CO₃ or new species, indicating the high dispersion of guest material. On the patterns of 10KCA (Fig. 3E) new diffraction lines appeared at 2θ of 15.8, 21.3, 26.5, 31.9 and 41.9°, which are assigned to KAl(OH)₂CO₃ referring to the JCPDS file number 22-791. Montagnet et al. also found this compound on their catalyst with a K content of 8 wt.%. As the amount of potassium salt increased to 20 wt.% (Fig. 3F), other diffraction lines appeared at 2θ of 12.8, 24.2 and 30.1° representing a crystal phase of K₂CO₃. When the loading amount of K₂CO₃ increases to 30 wt.% (Fig. 3G), the peak intensity of was obviously enhanced. Different dispersions of the potassium salt on alumina depend on the K⁺ content of the composite, because of the existence of a dispersion threshold, as reported in the dispersion of MoO₃ or KCl on alumina. There are many defects or vacancies in the structure of alumina, resulting from the dehydration of surface hydroxy groups, so that dispersion of oxide or salt on the alumina is actually the incorporation of cations into the vacancies by strong salt-support interaction or oxide-oxide interaction. In the case of KCA, the more potassium salt that was loaded on the alumina, the more the number of free vacancies decreased. When the loading amount of K₂CO₃ closely matches the amount of surface hydroxy groups, an optimum interaction between K₂CO₃ and the support results in the formation of a stoichiometric KAl(OH)₂CO₃ phase. Higher loading amounts will hinder the dispersion of K⁺ and lead to agglomeration of bulk carbonate.

For further understanding of the dispersion behavior of potassium salts, the 26KHC sample with the same K⁺ content as 20KCA was examined and the XRD patterns are shown in Fig. 4. No crystalline KHCO₃ was observed in the composite, indicating a perfect dispersion, but similar to the data of 20KCA, characteristics of KAl(OH)₂CO₃ emerged in the patterns near 2θ = 15.8, 21.3, 26.5, 28.4 and 31.9°. It is obvious that the same compound KAl(OH)₂CO₃ formed on the alumina supports from both K₂CO₃ and KHCO₃. This fact allows us to assume that potassium salts react with the alumina support to form a stoichiometric compound KAl(OH)₂CO₃ during preparation, especially in wet mixing:

\[
\text{Al}_2\text{O}_3 + 2\text{KHCO}_3 + \text{H}_2\text{O} = 2\text{KAl(OH)CO}_3
\]

\[
\text{Al}_2\text{O}_3 + \text{K}_2\text{CO}_3 + \text{CO}_2 + 2\text{H}_2\text{O} = 2\text{KAl(OH)CO}_3
\]

This gives an important clue for the interpretation of the similar catalytic activity of the different catalysts derived from K₂CO₃ or KHCO₃ in cis-but-2-ene isomerization. A crystalline KAl(OH)₂CO₃ species is formed on both composites as the product of host-guest interaction and this probably leads to a precursor of the same active species.

Fig. 5 shows the Raman spectra of KCA samples measured by the use of 515.5 nm excitation with high sensitivity. The spectral feature obviously depends on the K⁺ concentration of the composite, coinciding with that observed in the XRD experiment. 3KCA (Fig. 5D) showed almost the same spectrum as the parent alumina, but new bands near 1097 and 728 cm⁻¹ with a weak intensity could be detected on 5KCA (Fig. 5E). The intensity of the 1097 cm⁻¹ band increased, as the K⁺ content of the composite increased, probably due to the formation of KAl(OH)₂CO₃, because this band was absent in the spectrum of alumina and of unsupported K₂CO₃. Characteristic bands of carbonate emerged at 1060 and 1026 cm⁻¹ in...
the spectrum of 10KCA (Fig. 5F), but their intensities were relatively weak. As the loading amount of K$_2$CO$_3$ increased to 30 wt.% (Fig. 5H), the carbonate bands became stronger, representing bulk potassium salt on the composite.

5. The decomposition of potassium salt on alumina

Fig. 6 shows the TG (rhs)-DTA (lhs) curves of KCA. There is only one endotherm centered at about 90 °C for the starting alumina (Fig. 6A). The TG-DTA results for K$_2$CO$_3$ (Fig. 6B) show two endotherms with accompanying weight loss, centered at about 144 and 1158 °C, corresponding to the evolution of water of crystallisation and decomposition of K$_2$CO$_3$, respectively, whereas the small endotherm at 914 °C may be due to the transmutation of crystalline K$_2$CO$_3$. TG-DTA curves of the KCA sample show two peaks centered at about 90 and 225 °C in the spectrum of 5KCA, three endothermal peaks were found for 20KCA and 30KCA. The temperature corresponding to the first two endotherm shifts to higher range as the loading amount of K$^+$ is increased. Additionally, the weight loss corresponding to the second endotherm on 20KCA is higher than that on 30KCA (Fig. 6E, rhs), which probably corresponds to the isomerization activity of these samples. Since KAI(OH)$_2$CO$_3$ was reported to decompose at about 320 °C, it is reasonable to conclude that the weight loss from 225–347 °C on KCA samples is related to the decomposition of KAI(OH)$_2$CO$_3$. The final weight loss occurred at about 700 °C followed by a nearly continuous evolution up to 1110 °C on 20KCA and 30KCA (Fig. 6E and F) being the result of decomposition of the crystalline K$_2$CO$_3$.

As seen in Fig. 7, there is only one evolution of CO$_2$ accompanied by a small peak of water desorption on the TPDE
profile of K$_2$CO$_3$ (Fig. 7A). It appeared around 800 °C and continued even at 900 °C, in good agreement with the reported data:

$$\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2, \ 890 \degree\text{C}$$

Two evolutions of CO$_2$ were observed on the profile of KHCO$_3$ (Fig. 7B), the first one took place in the range 100–200 °C and the second occurred at over 800 °C indicating the two step-decomposition of KHCO$_3$:

$$2\text{KHCO}_3 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2, \ 100 \sim 200 \degree\text{C}$$

$$\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{O} + \text{CO}_2, \ 890 \degree\text{C}$$

Fig. 8 shows the TPDE profiles of 20KCA and 26KCHA, the composite derived from either alumina supported K$_2$CO$_3$ or KHCO$_3$, respectively, but with the same K$^+$ density of 12 nm$^{-2}$. Two evolutions of CO$_2$ were found on both profiles. The first emerged above 300 °C and continued up to 600 °C, followed by the second peak appearing at about 780 °C. As the XRD results revealed, KAl(OH)$_2$CO$_3$ forms on both 20KCA and 26KCHA and this compound is known to decompose at 320 °C. Therefore the first evolution of CO$_2$ in TPDE can be tentatively assigned to the decomposition of KAl(OH)$_2$CO$_3$. The second evolution of CO$_2$ may result from the decomposition of bulk potassium carbonate or bidentate carbonate containing K$^+$, because similar observations have been reported on samples with high K$^+$ content. Considering the fact that pure K$_2$CO$_3$ starts to decompose at 890 °C, it is reasonable to infer that the carbonate loaded on 20KCA and 26KCHA decomposes at a much lower temperature.

In order to check the assignment of the two CO$_2$ evolutions in the TPDE spectra, a series of samples with a K$_2$CO$_3$ loading of 5–30 wt.% were examined and Fig. 9 shows the TPDE profiles. One CO$_2$ evolution occurred in the range 300–780 °C in the spectrum of the composite with low K$^+$ content such as 5KCA, while two appeared at 420 and 750 °C in that of 10KCA. As the loading of K$_2$CO$_3$ increased, the intensity of the second evolution increased but the first remained constant. Furthermore, the first evolution of CO$_2$ was accompanied by water evolution while the second peak showed no relation with H$_2$O. Based on the XRD results mentioned above, it is obvious that only crystalline KAl(OH)$_2$CO$_3$ is formed when the K$_2$CO$_3$ content is around 5 wt.%, while the K$_2$CO$_3$ phase appears when the loading of K$_2$CO$_3$ exceeded 10 wt.%. Thus the first evolution of CO$_2$ is related to decomposition of KAl(OH)$_2$CO$_3$:

$$\text{KAl(OH)}_2\text{CO}_3 \rightarrow \text{KAlO}_2 + \text{H}_2\text{O} + \text{CO}_2$$

The origin of the second evolution of CO$_2$ is not so certain, but it seems to be related to the decomposition of bulk K$_2$CO$_3$ because its intensity is proportional to the amount of K$_2$CO$_3$ loaded on the alumina:

$$\text{K}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{K}_2\text{O}$$

Most of the K$_2$CO$_3$ or KHCO$_3$ can be dispersed on alumina in the case of a loading amount below the threshold of spontaneous dispersion and KAl(OH)$_2$CO$_3$ is thus formed as the result of salt–support interaction and can be decomposed at above 300 °C giving the basic active sites necessary for cis-but-2-ene isomerization, so that the KCA and KHCA samples become active in the reaction after evacuation at above 300 °C. Since the optimum temperature for decomposition of KAl(OH)$_2$CO$_3$ is about 420 °C, both KCA and KHCA samples reach their maximum activity after evacuation at around 500 °C. For those loaded with potassium salt at more than the threshold of spontaneous dispersion, the residual bulk of the guest such as K$_2$CO$_3$ remains on the composite and starts to decompose at around 700 °C. Since the catalytic
activity of KCA or KHCA decreases rapidly after evacuation at 700 °C, the decomposition of bulk K$_2$CO$_3$ on the modified alumina, represented by the second CO$_2$ evolution in the TPDE profile, may cause deactivation of the catalyst.

Conclusions

(1) Dispersing K$_2$CO$_3$ or KHCO$_3$ on alumina combined with thermal treatment at elevated temperatures resulted in a series of novel solid basic catalysts exhibiting a high activity for the isomerization of cis-but-2-ene at 0 °C. An optimum in activity is obtained at the K$^+$ surface density of 12 nm$^{-2}$, close to the threshold of spontaneous dispersion. In addition, these catalysts showed superbasic properties with a base strength of at least H$_n = 26.5$.

(2) Alumina shows a strong interaction with K$_2$CO$_3$ or KHCO$_3$ forming a new species KAl(OH)$_2$CO$_3$, and this species was tentatively shown to be the precursor of strong basic sites. Dispersion of on alumina depends strongly on the potassium content: a high dispersion state appears in the case of a loading below 10 wt.%, KAl(OH)$_2$CO$_3$ forms, when the loading is higher than 10 wt.%, and crystalline K$_2$CO$_3$ remains, if the amount of K$_2$CO$_3$ exceeds 20 wt.%. A threshold of spontaneous dispersion. In addition, these catalysts showed superbasic properties with a base strength of at least H$_n = 26.5$.

(3) Two CO$_2$ evolutions are observed in the TPDE profile of K$_2$CO$_3$ or KHCO$_3$ modified alumina samples. The first, at relatively low temperatures, is assigned to the decomposition of KAl(OH)CO$_3$ forming active sites, while the second results from the decomposition of bulk or crystalline potassium salt at high temperature related to deactivation of the catalyst.

Acknowledgements

We are grateful to the Chinese Education Ministry and the International Rotary Society (Japan) as well as the Analysis Center of Nanjing University for their financial support, and to Professor T. Yamaguchi, Ehime University (Japan) for his help.

References