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Characterization of strong solid bases by test reactions

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The isomerization of 2,3-dimethylbut-1-ene and the decomposition of 2-methyl-3-butyn-2-ol were carried out over a number of solid base catalysts. Rubidium amide supported on alumina was the most active for the isomerization, which proceeds almost to the equilibrium in 10 min at 201 K. The isomerization is a very useful test reaction for determining the relative activities of very strong solid bases. However, weak solid bases such as K^+-exchanged Y zeolite are totally inactive for the isomerization. The decomposition of 2-methyl-3-butyn-2-ol is a suitable reaction to discriminate acidic and basic catalysts. It can be also used for estimating the basic property of weak bases such as lithium hydroxide supported on alumina. However, caution is necessary for strongly basic catalysts because of strong adsorption of the products, acetylene and acetone.

Keywords: solid base, isomerization, 2,3-dimethylbut-1-ene, decomposition, 2-methyl-3-butyn-2-ol, alumina, rubidium amide, alkali metal compound supported on alumina

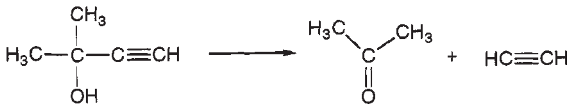
1. Introduction

Though the number of reports on solid bases is still much smaller than that of solid acids, it is increasing year by year. Recently, various strongly basic catalysts have been described. Potassium amide supported on alumina (KNH_2/Al_2O_3) is very effective for a number of base-catalyzed reactions [1–6]. Even toluene ($pK_a = 41$) is activated to react with silanes at 329 K [6], and the isomerization of 2,3-dimethylbut-1-ene smoothly proceeds even at 201 K [1,2]. Potassium fluoride supported on alumina (KF/Al_2O_3) has been used by organic chemists for a long time [7–9], but it has been recently found that this catalyst becomes much more active when treated at 573–673 K under vacuum [6,10,11]. Yamaguchi et al. reported that the catalysts, which were prepared by loading alkali metal compounds such as KNO_3 on alumina, followed by heating at 773–873 K, were very strongly basic catalysts and active for the isomerization of but-1-ene at 273 K [12]. Fu et al. used alkali compounds supported on alumina for the reaction of catechol with dimethyl carbonate and reported that the product distribution depended very much on the catalyst used [13–15]. Oxides of alkaline earth metals have been known to have very strong basic sites [16,17]. MgO and CaO have basic sites stronger than $H_- = 26$. At present, however, no attempts have been made to compare the basic properties of these strongly basic catalysts.

Though a variety of methods are available for characterizing solid acids, methods for characterizing solid bases are rather limited. Infrared study or temperature-programmed desorption of carbon dioxide is often used. The information is, however, not straightforward since carbon dioxide has several different adsorption states [17]. Furthermore, it is difficult to rationalize the desorption temperature of CO_2 with the capability of basic sites for proton abstraction from organic molecules. An indicator method has been used [17]. However, indicators may change the color by a mechanism different from an acid–base interaction.

One way to characterize basic sites is the use of test reactions. In this work, we selected two reactions, namely, the isomerization of 2,3-dimethylbut-1-ene (DB-1) to 2,3-dimethylbut-2-ene in liquid phase and the decomposition of 2-methyl-3-butyn-2-ol (MBOH) in vapor phase and compared the activities of a number of solid base catalysts.

(1)



(2)

The first reaction is selected because the reaction is mechanistically simple. The reaction proceeds through an allylic anion intermediate formed by the abstraction of a proton from the reactant by basic sites. Since the pK_a values of alkenes are high, i.e., $pK_a = 35$ for propene, this reaction may be useful for characterizing strong bases. The decomposition of MBOH proposed by Lauron-Pernot et al. [18] has been used for diagnosis of acid–base properties of solid catalysts [18,19]. Acidic catalysts afford 3-methyl-3-buten-1-yne and/or 3-methyl-2-buten-1-al, and amphoteric catalysts such as zirconia afford 3-hydroxy-3-methyl-2-butanone and/or 3-methyl-3-butene-2-one. Finally, basic catalysts yield acetylene and acetone, as shown in reaction (2). This reaction may be applicable for moderately basic catalysts.

The ordering of various base catalysts by these test reactions is of practical importance in selecting suitable catalysts for desired reactions.

2. Experimental

2.1. Catalyst preparation

Various catalysts were prepared as follows. The loading amount of the compounds on the support and pretreatment temperature of catalysts were optimized as much as possible based on literature and our own experience.

$NaNH_2/Al_2O_3$, KNH_2/Al_2O_3, $RbNH_2/Al_2O_3$: These catalysts were prepared according to [1,2]. γ-alumina (130 $m^2\,g^{-1}$) which had been calcined at 773 K, and a small amount of Fe_2O_3 (a catalyst for converting alkali metal into the corresponding amide) were heated in the reactor under vacuum at 773 K for 3 h. A piece of alkali metal was then put into the reactor under nitrogen. After evacuation, ammonia was liquefied in the reactor to dissolve the metal. After 1 h, the reactor was warmed to room temperature for removing most of ammonia and then heated at 523 K ($NaNH_2/Al_2O_3$), 573 K (KNH_2/Al_2O_3), or 633 K ($RbNH_2/Al_2O_3$) for 1 h.

$Na(NH_3)/Al_2O_3$, $K(NH_3)/Al_2O_3$: These catalysts were prepared in the same way as $NaNH_2/Al_2O_3$ and KNH_2/Al_2O_3 except that Fe_2O_3 was not added. The active species are amides of these metals, which are formed during heat treatment [1].

$Eu(NH_3)/Al_2O_3$, $Yb(NH_3)/Al_2O_3$, $Eu(NH_3)$/KY: These catalysts were prepared in the same way as $K(NH_3)/Al_2O_3$. The active sites are supposed to be amide or imide of the rare earth metals [20–24].

KNO_3/Al_2O_3, K_2CO_3/Al_2O_3, $NaOH/Al_2O_3$, KOH/Al_2O_3, $RbOH/Al_2O_3$, $CsOH/Al_2O_3$, KF/Al_2O_3: The alkali compounds are supported on alumina by an impregnation method from their aqueous solutions and then dried at 393 K for 12 h. The catalysts were heated under vacuum in the case of the isomerization of DB-1 or in a flow reactor under a nitrogen stream prior to reactions in the case of the decomposition of MBOH.

MgO, CaO, SrO: MgO was prepared by heating $Mg(OH)_2$ under vacuum at 773 K. The oxides of alkaline earth metals were prepared by heating calcium carbonate or strontium hydroxide under vacuum at 1073, 1023, and 773 K, respectively.

Mixed oxides: Mixed oxides with compositions of $4MgO{\cdot}Al_2O_3$ and samples of $4CaO{\cdot}Al_2O_3$ were prepared by heating hydrotalcite, $Mg_2Al(OH)_6NO_3{\cdot}nH_2O$ at 773 K, $3CaO{\cdot}Al_2O_3{\cdot}Ca(NO_3)_2{\cdot}nH_2O$ at 873 and 1073 K, and $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}nH_2O$ at 1073 K.

Zeolites: KY and KX were prepared by ion exchange from NaY ($SiO_2/Al_2O_3 = 5.6$) and NaX ($SiO_2/Al_2O_3 = 3.1$), respectively. CsX was prepared by ion exchange from NaX according to the procedures by Hattori and coworkers [35]. NaX was soaked in a 0.4 M cesium acetate solution, and stirred for 24 h at 333 K. The ion-exchange procedures were repeated three times. The ion-exchange degree was 50% (37.8 Cs atoms per unit cell). CsOAc-loaded CsX was prepared as follows. Cesium acetate was impregnated into CsX. After stirring for 3 h at 298 K, the slurry was dried in a rotary evaporator. The solid was then dried at 383 K for 12 h. Two samples were prepared and the supported amounts of cesium acetate were 4.2 and 10.2 wt%, respectively. These amounts correspond to 3.1 and 7.5 Cs atoms per unit cell of NaX in addition to 37.8 Cs atoms per unit cell in original CsX.

KY and KX were heated under vacuum at 773 K for 3 h for the isomerization of DB-1. KX, CsX and CsOAc-loaded CsX were heated under nitrogen stream at 773 K for the decomposition of MBOH. CsOAc was decomposed into Cs_2O at this stage in the case of Cs_2O-loaded CsX.

2.2. Catalytic reactions

2.2.1. Isomerization of 2,3-dimethylbut-1-ene

The reaction was carried out in the same reactor where the catalysts had been prepared. The reactant was introduced from the side arm of the reactor to avoid the exposure of the catalysts to air, since the strongly basic catalysts are very sensitive to carbon dioxide or water vapor. Reaction temperature and reaction time were adjusted depending on the catalytic activity of the catalyst used. The catalyst suspended in the reactant was stirred and the product, 2,3-dimethylbut-2-ene was determined by a gas chromatograph.

2.2.2. Decomposition of 2-methyl-3-butyn-2-ol

The reaction of MBOH was carried out in a continuous flow reactor operating at atmospheric pressure at 453 K. The catalysts were packed into a reactor of silica tubing (8 mm i.d.) and heated in a nitrogen stream in a vertical furnace. The reactant was delivered by means of a motor-driven syringe and vaporized in the preheating zone of the reactor. The partial pressure of MBOH was 39 kPa. The effluent from the reactor was analyzed with a gas chromatograph. Propane was used as an internal standard.

3. Results and discussion

3.1. Isomerization of 2,3-dimethylbut-1-ene

The catalytic activities of a variety of solid base catalysts for the isomerization of DB-1 were tested. The reaction was performed at 313 K for 20 h and the results were listed in table 1, which shows that a great range of catalytic activity was manifested depending on the catalyst used.

3.1.1. Alkali amides supported on Al_2O_3 or KY

Very high conversions were obtained with KNH_2/Al_2O_3 and $K(NH_3)/Al_2O_3$. We have shown that the active species in $K(NH_3)/Al_2O_3$ is KNH_2 formed on Al_2O_3 during evacuation at 423 K [1]. The active species on $Na(NH_3)/Al_2O_3$

Table 1
The catalytic activities of solid base catalysts for the isomerization of 2,3-dimethylbut-1-ene at 313 K.[a]

Catalyst[b]	Pretreatment		Conversion (%)
	Temperature (K)	Time (h)	
Metals supported from liquid NH_3			
KNH_2/Al_2O_3(2.6)	573	1	91.3
$K(NH_3)/Al_2O_3$(2.0)	423	1	89.4
$Na(NH_3)/Al_2O_3$(3.5)	423	1	89.3
$Eu(NH_3)/Al_2O_3$(0.5)	523	1	83.4
$Yb(NH_3)/Al_2O_3$(0.5)	473	1	29.4
$Eu(NH_3)$/KY(0.5)	423	1	2.3
$Yb(NH_3)$/KY(0.5)	473	1	1.0
Alkali metal compounds/Al_2O_3			
KNO_3/Al_2O_3(5.0)	873	3	90.7
KOH/Al_2O_3(5.0)	673	3	86.0
KF/Al_2O_3(5.0)	623	3	25.6
Metal oxides			
CaO	1073	3	89.8
MgO	773	3	84.9
SrO	1023	3	1.6
BaO	1073	3	0.4
Sm_2O_3	773	3	1.2
Eu_2O_3	923	3	1.0
Yb_2O_3	923	3	0.9
Al_2O_3	773	3	3.9
Mixed oxides			
$4CaO\cdot Al_2O_3$[c]	1073	1	11.9
$4CaO\cdot Al_2O_3$[c]	873	1	10.3
$4MgO\cdot Al_2O_3$	773	4	1.3
$4CaO\cdot Al_2O_3$[d]	1073	3	0.6
Zeolite			
KY	773	3	<0.1

[a] Catalyst = 0.25 g, 2,3-dimethylbut-1-ene = 3 ml (24 mmol).
[b] Numbers in parentheses = loading ($mmol\,g^{-1}$).
[c] Prepared from $3CaO\cdot Al_2O_3\cdot Ca(NO_3)_2\cdot nH_2O$.
[d] Prepared from $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot nH_2O$.

was not studied, but it is also likely that the active species is not metallic sodium but the amide. Separate experiments showed that KNH_2/Al_2O_3 or $K(NH_3)/Al_2O_3$ is much more active for pentane isomerization than K/Al_2O_3, which was prepared by deposition of potassium vapor.

3.1.2. $Eu(NH_3)/Al_2O_3$, $Yb(NH_3)/Al_2O_3$, $Eu(NH_3)$/KY

We have shown that Eu or Yb metal supported on alumina or zeolites from the ammoniacal solution is a strong base catalyst, and that the active species are amide or imide forms of these metals [20–24]. $Eu(NH_3)/Al_2O_3$ and $Yb(NH_3)/Al_2O_3$ were very active, for the isomerization but $Eu(NH_3)$/KY and $Yb(NH_3)$/KY showed much lower activities. Strong support effect was manifested in accord with a previous work [24].

3.1.3. Potassium compounds supported on Al_2O_3

Yamaguchi et al. reported that potassium compounds supported on Al_2O_3 are very basic catalysts [12]. The present work confirms their conclusion. KNO_3/Al_2O_3 and KOH/Al_2O_3 gave high conversion values. KF/Al_2O_3 is also active for the isomerization.

3.1.4. Metal oxides

Among the metal oxides studied, only CaO and MgO are highly active. Other alkaline earth oxides (SrO, BaO) and rare earth metal oxides are also basic.

3.1.5. Mixed oxides

Calcined hydrotalcites are very often used as basic catalysts [25–30]. Corma et al. concluded that calcined hydrotalcite has basic sites with pK_a up to 16.5, most of them being in the range of 10.7–13.3 from the catalytic activities for Knoevenagel condensation [30]. For DB-1 isomerization, the activity of $4MgO\cdot Al_2O_3$, which was prepared by decomposition of hydrotalcite ($Mg_2Al(OH)_6NO_3\cdot nH_2O$), is not high (conversion of DB-1, 1.3%), reflecting the large difference in the pK_a values of the reactants between alkene isomerization and Knoevenagel reactions. The mixed oxide with the composition of $4CaO\cdot Al_2O_3$, which was prepared by decomposition of hydrocalmeite ($3CaO\cdot Al_2O_3\cdot Ca(NO_3)_2\cdot nH_2O$) showed much higher activity than the decomposition product of hydrotalcite.

3.1.6. Zeolites

Alkali-ion-exchanged zeolites are basic catalysts [2,31]. For example, they are active for ring transformation of γ-butyrolactone into γ-butyrothiolactone [32] and methylation of phenylacetonitrile with methanol or dimethyl carbonate [33]. The decomposition of MBOH on alkali-exchanged faujasite indicates that these materials are basic [19]. Corma et al. carried out the Knoevenagel reactions and concluded that the basic sites of alkaline faujasites have $pK_a < 10.3$ [34]. As shown in table 1, potassium-exchanged Y zeolites (KY) have no activity for the isomerization of DB-1 at 313 K, indicating that the basic strength of KY is weak.

Table 1 shows that there are groups of catalysts which have very high activities for the isomerization of DB-1. They are alkali amides on Al_2O_3, alkali compounds on Al_2O_3, CaO and MgO. Since the conversions over these catalysts are close to the equilibrium value, it is hard to know the relative ranking of activities from table 1. Therefore, we conducted the isomerization at much lower temperature (201 K) and shorter reaction time. The results are given in table 2. In this table, we added $RbNH_2/Al_2O_3$ and a series of alkali hydroxides supported on Al_2O_3.

Table 2 shows that $RbNH_2/Al_2O_3$ and KNH_2/Al_2O_3 are the most active catalysts for the isomerization. $RbNH_2/Al_2O_3$ gave almost equilibrium conversion at 201 K just in 10 min with a very small amount of the catalyst (0.063 g or 0.16 mmol Rb). In contrast, $NaNH_2/Al_2O_3$ is not active at this temperature. KNO_3/Al_2O_3 is much more active than K_2CO_3/Al_2O_3. Among alkali hydroxides supported on Al_2O_3, $CsOH/Al_2O_3$ is far more active than other hydroxides. $RbOH/Al_2O_3$ and KOH/Al_2O_3 are also quite active, while $NaOH/Al_2O_3$ and $LiOH/Al_2O_3$ have no activity under the reaction conditions. CaO and MgO are also very active.

Table 2
The catalytic activities of solid base catalysts for the isomerization of 2,3-dimethylbut-1-ene at 313 K.[a]

Catalyst[b]	Pretreatment temperature[c] (K)	Reaction time (min)	Conversion (%)
$RbNH_2/Al_2O_3(2.6)$[d]	633	10	90.2
$KNH_2/Al_2O_3(2.6)$[d]	573	10	87.3
		30	93.8
$KNH_3/Al_2O_3(3.1)$[d]	573	10	59.0
$NaNH_2/Al_2O_3(2.6)$[d]	623	10	0.1
$KNO_3/Al_2O_3(2.6)$	873	30	49.4
$K_2CO_3/Al_2O_3(2.6)$	873	30	4.2
$CsOH/Al_2O_3(2.6)$	873	30	67.8
$RbOH/Al_2O_3(2.6)$	873	30	36.4
$KOH/Al_2O_3(2.6)$	873	30	34.1
$NaOH/Al_2O_3(2.6)$	873	30	0
$LiOH/Al_2O_3(2.6)$	873	30	0
CaO	1025	10	63.0

[a] Catalyst = 0.25 g.
[b] Numbers in parentheses = loading (mmol g^{-1}).
[c] Pretreatment time = 1 h.
[d] 0.063 g 2,3-dimethylbut-1-ene = 3 ml (24 mmol).

The order of the activities for the most active class of solid base catalysts is as follows:

$$RbNH_2/Al_2O_3 > KNH_2/Al_2O_3 > CaO > MgO > CsOH/Al_2O_3 > KNO_3/Al_2O_3 > RbOH/Al_2O_3 > KOH/Al_2O_3$$

Tanabe defined a solid superbase as a solid which has basic strength of $H_- > 19$ [17]. The pK_a value of propene is 35 and we can assume that the pK_a value of DB-1 is not far from this value. Therefore, all of these catalysts can be assigned to being solid superbases. We have shown that KNH_2/Al_2O_3 develops a purple color when isopropylbenzene ($pK_a = 37$) is adsorbed [1]. CaO was reported to have basic sites stronger than $H_- = 26$ [17]. These facts suggest that all of the catalysts in this series are solid superbases.

It should be noted, however, that the activities of the catalysts are very sensitive to the preparation conditions, especially heat treatment temperature. The dependence of the catalytic activity of $RhNH_2/Al_2O_3$ for DB-1 isomerization on the evacuation temperature is shown in figure 1. A similar dependence of the activity of KNH_2/Al_2O_3 has been reported previously [2].

3.2. Decomposition of 2-methyl-3-butyn-2-ol

The decomposition of MBOH was carried out with a series of alkali compounds supported on alumina. The contact time was selected to get the conversion levels of 10–30%. The conversions at 5 and 35 min of time on stream are listed in table 3. The conversions, x^t, at time t were converted to the reaction rates, r^t, by using the following equation:

$$r^t = 1/(W/Fy)x^t,$$

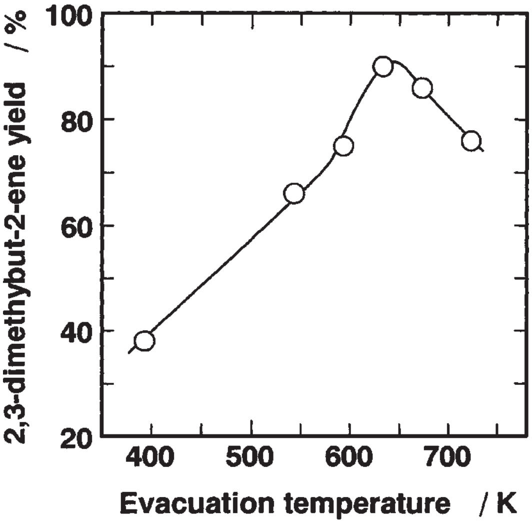


Figure 1. The influence of the evacuation temperature on the catalytic activity of $RbNH_2/Al_2O_3$ for the isomerization of 2,3-dimethyl-1-butene at 201 K. Catalyst weight = 0.063 g, 2,3-dimethyl-1-butene = 3 ml (24 mmol), reaction time = 10 min, amount of Rb loaded = 2.6 mmol/g, Al_2O_3 pretreatment temperature = 673 K.

where W is the weight of the catalyst; F, the flow rate ($MBOH + N_2$) in mol h^{-1}; y, the mole fraction of MBOH in the feed; r^t, the rate at running time t, 5 or 35 min.

All the catalysts studied gave acetylene and acetone as reaction products in the ratio very close to unity, indicating that all the catalysts are basic in nature.

The values of r^5 in a series of alkali hydroxides supported on Al_2O_3 are in the following order:

$$LiOH/Al_2O_3 < NaOH/Al_2O_3 < KOH/Al_2O_3 < RbOH/Al_2O_3 \approx CsOH/Al_2O_3$$

The order of the activities is the same as that found in the isomerization of 2,3-dimethylbut-1-ene. However, the relative activities among the catalysts are quite different for the two reactions. For the alkene isomerization at 201 K, $NaOH/Al_2O_3$ is totally inactive and $CsOH/Al_2O_3$ is very active. On the other hand, the ratio of activities (r^5) of the two catalysts is only 2.5 in the case of MBOH decomposition. The difference in r^5 values among KOH/Al_2O_3, $RbOH/Al_2O_3$, and $CsOH/Al_2O_3$ is very small, 8.5, 9.5, and 9.7, respectively, and furthermore, the difference in r^{35} is very trivial, 7.3, 7.5, and 7.8, respectively.

Other strongly basic catalysts, KNO_3/Al_2O_3, K_2CO_3/Al_2O_3, $KHCO_3/Al_2O_3$, and KF/Al_2O_3 gave the r^5 values in the range of 5.3–12, the first two being the most active. The activities of the three catalysts for the two reactions exhibit the similar order (tables 1 and 3):

$$KNO_3/Al_2O_3 > KOH/Al_2O_3 > KF/Al_2O_3$$

There are, however, some obvious discrepancies in the reaction orders determined by the two reactions. $CsOH/Al_2O_3$ is more reactive than KNO_3/Al_2O_3 for alkene isomerization while the order (r^5) is reverse for MBOH decomposition, r^{35} being almost the same. KNO_3/Al_2O_3 is much more

Table 3
The catalytic activities of solid base catalysts for the decomposition of 2-methyl-3-butyn-ol over alkali compounds supported on alumina.[a]

Catalyst	W/F ($\mathrm{g\,h\,mol^{-1}}$)	MBOH conversion[b] (%) 5 min	MBOH conversion[b] (%) 35 min	Rate[b] $\times 10^{-1}$ ($\mathrm{mol\,h^{-1}\,g^{-1}}$) 5 min	Rate[b] $\times 10^{-1}$ ($\mathrm{mol\,h^{-1}\,g^{-1}}$) 35 min
$LiOH/Al_2O_3$	0.78	10.3	7.4	0.51	0.37
$NaOH/Al_2O_3$	0.26	26.3	20.9	3.9	3.1
KOH/Al_2O_3	0.13	26.9	24.5	8.5	7.3
$RbOH/Al_2O_3$	0.094	22.8	18.1	9.5	7.5
$CsOH/Al_2O_3$	0.088	21.8	17.7	9.7	7.5
KNO_3/Al_2O_3	0.12	34.8	23.1	12	7.8
K_2CO_3/Al_2O_3	0.12	36.7	16.9	12	5.6
$KHCO_3/Al_2O_3$	0.12	23.1	18.0	7.5	6.0
KF/Al_2O_3	0.20	26.5	25.5	5.3	4.9
$4MgO\cdot Al_2O_3$[c]	2.07	20.8	19.0	0.39	0.36
$4CaO\cdot Al_2O_3$[d]	1.89	15.4	9.1	0.32	0.19
$4CaO\cdot Al_2O_3$[d,e]	1.89	12.0	5.3	0.25	0.11
KX	0.78	0.1	0.1	0.0055	0.0049
KX[f]	1.56	6.1	3.9	0.152	0.097
CsX	0.78	0.1	0.1	0.0055	0.0055
CsX[f]	1.56	0.6	0.4	0.0150	0.010
4.2[g]CsOAc/CsX	0.78	0.47	0.23	0.023	0.012
10.2[g]CsOAc/CsX	0.78	7.10	4.61	0.35	0.230

[a] Reaction conditions: 453 K, MBOH = 39.3 kPa, pretreatment temperature of the catalyst = 673 K, supported amount on alumina = 5 $\mathrm{mmol\,g^{-1}}$.

[b] Time on stream.

[c] Prepared from $Mg_2Al(OH)_6NO_3\cdot nH_2O$.

[d] Prepared from $3CaO\cdot Al_2O_3\cdot Ca(NO_3)_2\cdot nH_2O$ at 873 K.

[e] Prepared from $3CaO\cdot Al_2O_3\cdot Ca(NO_3)_2\cdot nH_2O$ at 1073 K.

[f] Reaction temperature = 483 K.

[g] Supported amount of CsOAc.

active than K_2CO_3/Al_2O_3 for the isomerization, but the activities of the two catalysts are almost the same for MBOH decomposition.

In any case, it is worthy of note again that the difference in activities for MBOH decomposition among strongly basic catalysts is rather small; all merge in between 5.3 and 12.0 for r^5 and between 5.6 and 7.8 for r^{35}. Therefore, it is concluded that MBOH decomposition is not a sensitive test reaction for estimating the nature of very strong solid bases. The plausible reason may be assigned to the effect of the products, acetylene and acetone. The $\mathrm{p}K_\mathrm{a}$ values of these two products are 25 and 20, respectively. As described above, H_- values of very strong bases are much higher than these values. Therefore, both of the products of MBOH decomposition must be strongly adsorbed on the active sites of the strongly basic catalysts. This should result in the retardation of the rate of the MBOH decomposition. This effect may be stronger for stronger bases. It is very plausible that the poisoning effect of the products such as acetylene compresses appreciably the difference of intrinsic basicities of the strongly basic catalysts. On the other hand, in the case of the isomerization, the acidity of the product is not different from the reactants and there will be no effect of the product adsorption.

Table 2 shows that $LiOH/Al_2O_3$ is the weakest among alkali metal hydroxides supported in alumina. The activity of $LiOH/Al_2O_3$ is similar to these of mixed oxides, $4CaO\cdot Al_2O_3$ or $4MgO\cdot Al_2O_3$. The zeolites KX and CsX are more weakly basic than these catalysts. These general trends are in accord with the order of the activities determined by the isomerization of DB-1. CsX loaded with Cs_2O and especially CsX with 10.2 wt% cesium acetate were much more active than CsX in conformity with the results by Davis and Hattori and their coworkers [35–39]. But, they are still less active than $LiOH/Al_2O_3$.

In conclusion, alkene isomerization is a more effective measure to estimate the nature of strongly basic catalysts. The decomposition of MBOH is a good test reaction to classify acid, amphoteric, basic catalysts. However, this reaction is not suitable for characterizing strong bases, though the reaction may be useful for mild or weak bases.

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