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Preparation of superbases and their use as catalysts for double-bond isomerization

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Abstract

Solid superbases with basic strength up to $H_- \geq 37$ can be prepared by a treatment of the carriers such as γ-alumina and MgO successively with alkali metal hydroxide and alkali metal under nitrogen or with cesium acetate followed by calcination at 700–750°C in vacuum. The catalytic activity of such superbases was studied in the double bond isomerization of β-pinene. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Materials which possess basic sites stronger than $H_- = 26$ are called superbases (with H_- corresponding to the pK_a value of the indicator). Such materials have been developed by the Sumitomo Chemical Company [1]. They consist of an alkali metal hydroxide and the alkali metal itself supported on γ-alumina, according to the general formula $(MOH)_x / M_y / \gamma\text{-}Al_2O_3$, (M = alkali metal, $x = 5$–15 wt.%, $y = 3$–8 wt.%). Due to their high activity, superbases are applied as catalysts for reactions in the field of intermediates and fine chemicals, such as the isomerization of olefins and the side-chain alkylation of alkylbenzenes [2–4]. Solid superbases are favourable for catalysis of sensitive reactions under mild conditions. An example for the application of a strong solid base catalyst for the fine chemistry in industrial scale is the isomerization of the double bond in 5-vinyl-2-norbornene to 5-ethylidene-2-norbornene, a compound used for vulcanization purposes [2].

The isomerization of β-pinene to α-pinene has been reported to take place over homogeneous catalysts such as *t*-BuOK in DMSO [5], potassium 3-aminopropylamide (KAPA) in 3-aminopropylamine (APA) [6], and over heterogeneous basic catalysts: CaO, SrO or MgO evacuated at 900–1300°C [7]. The disadvantage of this reaction is a very unfavourable reactant/catalyst mass ratio of only 1.04–1.4 g β-pinene/g catalyst.

The aim of our work was the preparation of superbasic heterogeneous catalysts, and characterization of their catalytic properties.

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2. Experimental

The superbases were prepared on two different carriers, i.e., the typical pure basic carrier MgO and γ-alumina with acidic and basic properties. γ-Alumina was prepared from boehmite (Pural SB/Condea) by calcination at 550°C for 12 h. The same pretreatment conditions were applied for MgO (Hopkin & Williams). The carriers were used in powder form. The preparation of the superbases was carried out in an Ni-lined steel reactor. The carriers were first heated to 500–550°C at constant stirring under N_2 for 1 h. Then, the temperature was decreased to the melting point of the used alkali metal hydroxide which was introduced at that stage in portions (8–10 wt.% in relation to the support). After a further stirring at this temperature for 2–3 h, the alkali metal (4–10 wt.%) was added in portions. After stirring for the next 0.5–1 h, the system was cooled down to room temperature. The whole procedure was carried out under N_2.

In the case of γ-alumina treated with cesium acetate, the same pretreatment conditions were used. After the addition of cesium acetate, the mixture was stirred for 2 h. As a final treatment, the material was calcined in vacuum at 700–750°C for decomposition of the acetate (decomposition temperature of cesium acetate is around 330°C [8]) and activation of the catalyst.

The obtained materials were characterized by N_2 adsorption and BET surface areas. The BET surface areas of the catalysts were calculated from nitrogen adsorption at 77 K using the instrument Omnisorb 100.

The amount of basic sites and their strength were measured by benzoic acid titration method using various Hammett indicators under an inert atmosphere. The solid base was suspended in benzene, after which the titration was done with benzoic acid dissolved in benzene [9–11].

The catalytic activity of the superbases was studied in the isomerization reaction of β-pinene to α-pinene. All the catalytic tests were carried out in a batch reactor under an inert atmosphere. The reaction temperature varied between 25 and 150°C. The catalysts were used in the powder form, and the reactant/catalyst mass ratio was within the range of 20 to 50 (g β-pinene/g catalyst). The β-pinene (Fluka) was freshly distilled before use and stored under argon.

3. Results and discussion

Three different types of superbases $Cs_xO/γ$-Al_2O_3 (catalyst A), Na/NaOH/γ-Al_2O_3 (catalyst B) and Na/NaOH/MgO (catalyst C) were prepared. The specific surface area and basicity of those superbases and the carriers are listed in Table 1.

The surface area of both superbases based on γ-alumina are above 120 $m^2 \ g^{-1}$, whereas the surface area of the MgO based superbase is much smaller (9.5 $m^2 \ g^{-1}$).

Table 1
Basicity and surface area of the investigated superbases and the supports γ-Al_2O_3 and MgO

Catalyst	Loading mmol/g carrier	Surface area (m^2/g)	Base strength H_	Basicity H_ $\geq$ 33[a] (mmol/g catalyst)
γ-Al_2O_3	–	219	9.3 ≤ H_ < 15	0.0
MgO	–	–	9.3 ≤ H_ < 15	0.0
Cs_xO/γ-Al_2O_3 (A)	2.0 CsOAc	129	H_ ≥ 37	1.0–1.2
Na/NaOH/γ-Al_2O_3 (B)	2.9 NaOH 2.0 Na	135	35 ≤ H_ < 37	0.9–1.05
Na/NaOH/MgO (C)	2.5 NaOH 2.3 Na	9.5	35 ≤ H_ < 37	0.4–0.55

[a]The indicator employed is triphenylmethane ($pK_a = 33$). No accurate result was obtained using the indicator 4-chloroaniline (H_ = 26.5) because of the indistinct colour change, therefore only superbasic sites of H_ ≥ 33 were determined.

In addition to it the results by means of titration, a valuable information about basic properties came from the TPD measurement of CO_2 (Fig. 1).

The CO_2 desorption was observed over a wide temperature range for both superbases A and B. A distinct peak at 200°C indicates that both superbases possess a high amount of weak basic sites. The maximum of the CO_2 desorption at a higher temperature indicates stronger basic sites. The peak appearing at 750°C for catalyst A is not appreciable for the system B which shows a less intensive desorption peak at 680°C. This indicates that, in the case of catalyst A, stronger basic sites are generated. The TPD experiments correlate with the basic strength measured with Hammett indicators (Table 1). The catalyst A possesses basic sites stronger than $H_- \geq 37$, whereas the superbase B shows slightly weaker superbasic sites with $35 \leq H_- < 37$. The carrier $\gamma\text{-Al}_2O_3$ has only little amounts of basic sites.

3.1. Isomerization of β-pinene

The isomerization of β-pinene was carried out in the liquid phase in a batch reactor at 25–150°C. No solvent was used. All the prepared superbases revealed extremely high selectivities for the formation of α-pinene.
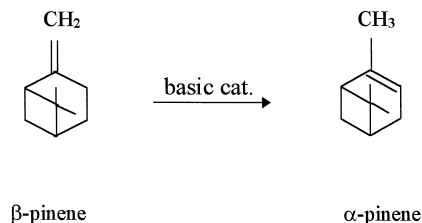
The comparison of the activity of the three catalysts A, B and C and the carriers are summarized in Table 2.

Here, the superbases A and B showed the highest activity as well. Almost complete conversion of β-pinene was achieved after 30 min. In contrast, superbase C was less active. At a reactant/catalyst mass ratio of 20 g β-pinene/g catalyst and a reaction temperature of 150°C, a similar conversion was obtained only after 24 h. The catalyst showed no activity at room temperature.

The catalyst C has about half of the amount of superbasic sites ($H_- \geq 33$) in relation to the superbase $Cs_xO/\gamma\text{-Al}_2O_3$ (A) and Na/NaOH/
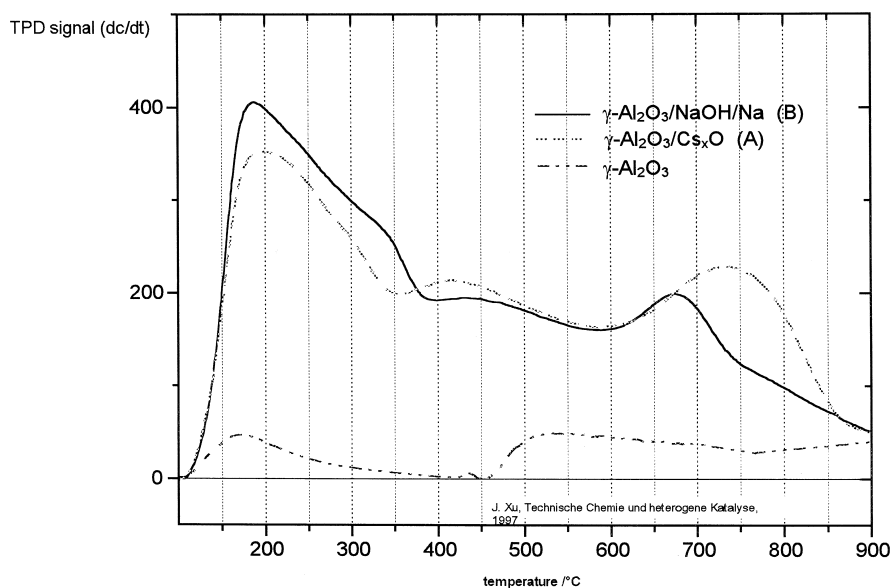

Fig. 1. TPD desorption of CO_2 for catalyst A, B and the carrier $\gamma\text{-Al}_2O_3$.

Table 2
Isomerization of β-pinene

Catalyst	T (°C)	Ratio β-pinene/ catalyst (g/g)	Conversion (%)		
			0.5 h	2 h	24 h
MgO	150	20	0	0	0
$Cs_xO/\gamma\text{-}Al_2O_3$ (A)	150	20	97	97	97
$Na/NaOH/\gamma\text{-}Al_2O_3$ (B)	150	20	97	97	98
$Na/NaOH/MgO$ (C)	150	20	14	51	97
$\gamma\text{-}Al_2O_3$	25	30	0	0	0
MgO	25	30	0	0	0
$Cs_xO/\gamma\text{-}Al_2O_3$ (A)	25	30	92	98	99
$Na/NaOH/\gamma\text{-}Al_2O_3$ (B)	25	30	99	99	99
$Na/NaOH/MgO$ (C)	25	30	0	0	0

$\gamma\text{-}Al_2O_3$ (B). Probably the lower amount of superbasic sites as well as the small BET surface area of 9.5 m^2 g^{-1} are the reasons for this effect. Catalysts B and C contain a similar amount of sodium but were prepared on various carriers. The carrier materials may also be responsible for that different catalytic behavior. The treatment of the two various carriers with NaOH and Na leads to the formation of superbasic sites in a different way. In the case of catalyst B, the γ-alumina reacts with sodium hydroxide to form sodium γ-aluminate with a distorted structure. This aluminate reacts with sodium and generates superbasic sites. The formation of these extremely strong sites was proposed to result from an electron transfer from the alkali metal to the aluminate followed by ionization of the alkali metal [2,4]. In the case of MgO treatment with sodium or sodium hydroxide, it was supposed that the mechanism of sodium interaction (sodium cation and metallic sodium) consists of its reaction with the surface oxygen atoms groups (framework anions and the oxygen atoms from adsorbed water). Various oxygen anions O^{2-} of low coordination number occur on the MgO surface. They are considered to be responsible for the strong basicity. In contrast to γ-alumina, the introduction of sodium onto the MgO surface results also in the formation of one-electron-donator centres [7].

In all the cases, the observed selectivities to α-pinene were about 100%.

The carriers MgO and $\gamma\text{-}Al_2O_3$ showed no activity for the reaction of β-pinene to α-pinene under the applied reaction conditions.

Fig. 2 shows the effect of reactant/catalyst mass ratio (g β-pinene/g catalyst) on the conversion of β-pinene over the superbases $Cs_xO/\gamma\text{-}Al_2O_3$ (A) and $Na/NaOH/\gamma\text{-}Al_2O_3$ (B).

The conversion of β-pinene over both superbases A and B decreases with increasing reactant/catalyst mass ratio from 30 to 50 g β-pinene/g catalyst. The selectivity to α-pinene remains always about 100%. At a reactant/catalyst mass ratio (g β-pinene/g catalyst) of 20 and 30, both superbases A and B show very high conversion of β-pinene of about 98%. With a higher reactant/catalyst mass ratio of 40 and 50, the conversion over catalyst B decreases to 78 and 41%, respectively, whereas the system A shows furthermore high activity with 98 and 61% conversion, respectively.

The reason for this behaviour can be explained by a higher basic strength as well as a higher amount of basic sites with the strength $H_- \geq 33$ of the superbase $Cs_xO/\gamma\text{-}Al_2O_3$ (A). Only this material possesses basic sites stronger than $H_- \geq 37$. In the case of superbase B, only the superbasic sites of the strength $H_- \geq 35$ are determined. The TPD experiments and the re-
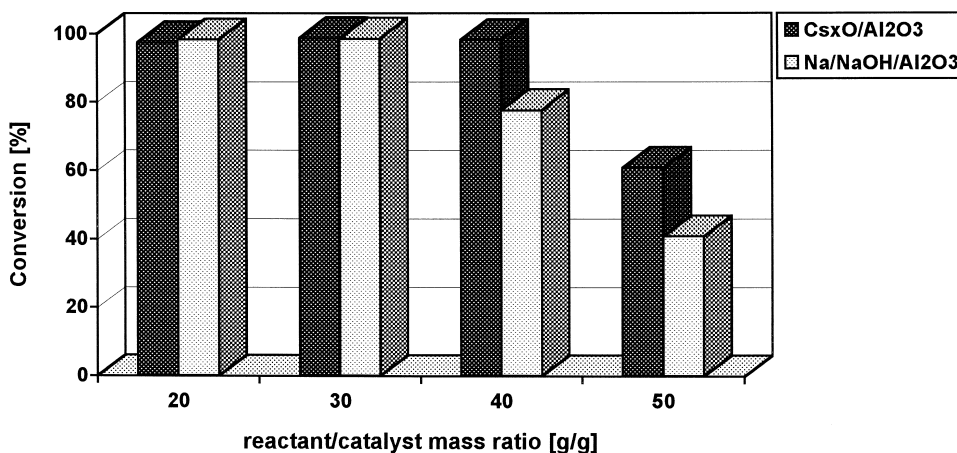
Fig. 2. Influence of reactant/catalyst mass ratio on β-pinene conversion, $T = 25°C$, $t = 24$ h.

sults of titration correlate with the catalytic results.

The superbases showed a better catalytic performance than the evacuated CaO or SrO catalysts published until now [7]. As the almost complete conversion of β-pinene reported in the literature was achieved with a reactant/catalyst mass ratio of only 1.04–1.4 (g β-pinene/g catalyst), the superbases showed considerably higher conversions at much higher reactant/catalyst mass ratios up to 40 g β-pinene/g catalyst. That means the superbases are much more effective than CaO and SrO.

3.1.1. Lifetime of the catalysts

It is necessary for an industrial application, that the catalysts reveal a high service time. In the present investigations, all the catalysts were deactivated after the reaction and their colours turned from white or pale yellow to pale brown. This may be caused by organic deposits. The formed 'coke' or its precursor could be adsorbed irreversibly on the basic sites and thus prevent the reaction. Furthermore, the organic deposits could hinder the diffusion or accessibility of the pores for the substrates. The degree of the deposit formation was determined using the TG/DSC and C–H elemental analysis. Accord-

ing to the C–H analysis of the organic deposit, the carbon-to-hydrogen ratio varied between 0.43–0.60. This small carbon-to-hydrogen ratio indicates that those organic deposits could very well be waxy-like compounds. Solid acid catalysts favor the formation of aromatic compounds as deactivating deposits, which is resembled by C:H ratios > 1. Thus, no formation of aromatic residues on superbasic catalysts could be concluded.

The TG/DSC analysis confirmed the C–H analysis and showed a distinct exothermic peak at 300°C which most likely corresponds to the removal of the organic deposits at a weight loss in the range of 8 to 12 wt.%.

For the external regeneration after the use in the batch reactor, the catalyst has to be separated from the products. The regeneration of the superbases was carried out under pure oxygen at 500°C for 3 h in a quartz tube. Thereby, the organic deposits were oxidized and removed. This treatment was followed by the calcination at 550–600°C for 5 h in vacuum. The regeneration experiments were performed for the two superbases A and B. The basicity of the regenerated catalysts was measured by means of Hammett indicators. The BET surface area of the regenerated catalysts was determined as well. The results are given in Table 3.

Table 3
Basicity and surface area of the regenerated superbases

Catalyst	Surface area (m^2/g)		Base strength H_		Basicity H_ ≥ 33 (mmol/g catalyst)	
	Original	Regenerated	Original	Regenerated	Original	Regenerated
$Cs_xO/\gamma\text{-}Al_2O_3$ (A)	129	129	H_ ≥ 37	H_ ≥ 35	1.0–1.2	0.25
$Na/NaOH/\gamma\text{-}Al_2O_3$ (B)	135	115	H_ ≥ 35	H_ ≥ 26.5	0.9–1.05	0.00

A great difference is seen between the regenerated and the original samples in the superbase properties. The surface area of the regenerated superbase A is similar to their original, whereas that of the regenerated B catalyst is reduced from 135 to 115 m^2 g^{-1}.

Considering the basic strength, the regeneration has appeared to be inefficient. In the case of the system A, the superbasic sites of the strength H_ ≥ 37 cannot be regenerated and only superbasic sites of H_ ≥ 35 were found. As results from the titration, the amount of basic sites H_ ≥ 33 was reduced from about 1.2 to ca. 0.25 mmol/g catalyst. In comparison to that, the superbase B was not possible to be regenerated. Using the Hammett indicator 4-chloroaniline (H_ $= 26.5$), only a weak colour change was observed; this indicated a small number of the sites H_ ≥ 26.5.

The above results are reflected in the catalytic behavior of the regenerated superbases.

The results of isomerization of β-pinene over the regenerated superbase A in comparison to the original catalyst are presented in Fig. 3.

The regenerated superbases show distinctly reduced activities. A very low conversion of 1.2% was observed at the reaction temperature of 25°C. At temperature increased to 100°C, a somewhat higher conversion of 23% was observed but a not complete activity could be regained.

For the superbase B which has no stronger basic sites (H_ ≥ 27) as well as a smaller surface area in comparison to the original catalyst, no conversion was obtained.

Furthermore, leaching tests were carried out. After filtering the catalyst, β-pinene was added to the solution after which the solution was reheated to the reaction temperature. No further conversion could be found. Making unlikely that the active species is being washed out and is present as a homogeneous catalyst.
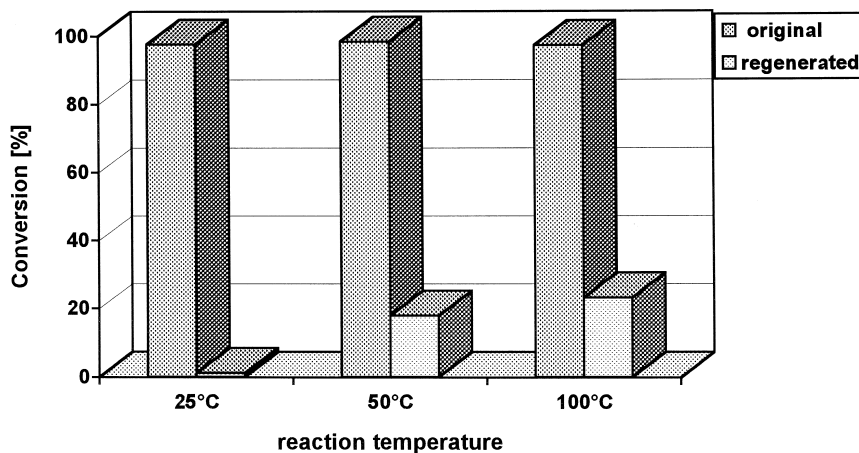

Fig. 3. The β-pinene conversion over the original and regenerated $Cs_xO/\gamma\text{-}Al_2O_3$ reactant/catalyst mass ratio = 20 (g/g), $t = 24$ h.

To summarize, the original activity of the catalysts cannot be regained. The reduced activity of the regenerated superbases could be explained by the deposition of coke on the active sites, and/or by a transformation of the active sites and their interactions during the reaction or the regeneration.

The reduced basicity as well as the strongly reduced number of the superbasic sites are a reason for the changes in activity. The regeneration can likely lead to sintering, thus decreasing the surface area and pore volume, which results in a loss of activity.

4. Conclusion

The superbase catalysts are very efficient for the isomerization of double bond of β-pinene to α-pinene. $Na/NaOH/\gamma$-Al_2O_3 and Cs_xO/γ-Al_2O_3 shows the highest catalytic activity for the isomerization of β-pinene. The reaction at room temperature attains 98% conversion in 30 min at a reactant/catalyst mass ratio of 30.

All catalysts were deactivated after this reaction. The original activity of the catalysts could not be regained under the applied conditions of regeneration.

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