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Michael addition of ethyl acrylate and acetone over solid bases

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The catalytic behaviour of the superbases Na/NaOH/γ-Al_2O_3 and Cs_xO/γ-Al_2O_3 as well as of the basic zeolites Na/NaX and Cs_xO/CsX were investigated in the Michael addition of ethyl acrylate and acetone. The reactions were carried out in the liquid phase at catalyst loadings varying from 0.05 to 0.1 mol ester/g catalyst.

Keywords: solid base, superbase, basic zeolites, Michael addition, ethyl acrylate, heterogeneous catalysis

1. Introduction

The replacement of liquid basic catalysts by solid bases in the synthesis of fine and intermediate organic chemicals allows one to avoid corrosion and environmental problems.

Solid basic catalysts are potentially favourable for organic syntheses involving carbon–carbon bond formation such as addition and condensation reactions. Michael additions are conjugate additions of carbanions to α,β-unsaturated carbonylic compounds and are catalyzed by homogeneous catalysts such as sodium hydroxide, sodium ethoxide and piperidine [1].

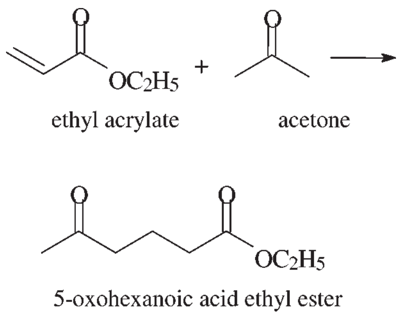
Only a few heterogeneous catalysts have been used for Michael additions, thereby basic sites are responsible for the formation of the carbanion by abstracting a proton from the molecule having an α-hydrogen. Recently, partially dehydrated $Ba(OH)_2$ has been reported as a useful solid basic catalyst for the Michael addition of chalcones to active methylene compounds such as ethyl malonate, ethyl acetoacetate, acetylacetone and nitromethane [2]. Potassium fluoride supported on alumina (KF–Al_2O_3) is active in the Michael additions of nitromethane to 3-buten-2-one and 1,3-diphenyl-2-propen-1-one as well as dimenone to methyl vinyl ketone. In the Michael self-addition of methyl crotonate, a high activity is exhibited by MgO [3]. Recently, mesoporous MCM-41 materials impregnated with cesium acetate proved to be active as catalysts in the Michael addition of diethyl malonate and neopentylglycol diacrylate [4,5].

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 Chem. Comp. [6]. They consist of an alkali metal hydroxide and the alkali metal itself supported on γ-alumina, according to the general formula $(MOH)_x/M_y/\gamma$-Al_2O_3 (M = alkali metal, x = 5–15 wt%, y = 3–8 wt%). Due to a 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 [7–12]. The solid superbases are profitable as they catalyze sensitive reactions under mild conditions.

The basic zeolites can be prepared with two methods. The first of them is an ion exchange of the zeolite with alkali metal ions and the other is an impregnation of the zeolite with fine particles able to act themselves as bases [13,14]. For example, the clusters of sodium metal can be generated in the pores and cavities of faujasites using various techniques. Interaction of zeolites with alkali metals in vapour form or as solid generates red and blue products of basic properties. A detailed catalytic study showed that the active sites in basic catalysis are the framework oxygen close to neutral sodium clusters entrapped in the large zeolite cages [15–18].

Hathaway and Davis performed impregnation of faujasites with cesium acetate followed by decomposition of the acetate at 450 °C in air. The active sites of such catalysts are supposed to be cesium oxides [19].

In this work, various prepared solid superbases and basic zeolites were applied for the process of Michael addition expressed by equation (1):



(1)

Such esters of 5-oxohexanoic acid are conventionally generated by the liquid-phase Michael addition of acetone and

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acrylic ester by using a primary amine or a Schiff base as the catalyst [20,21]. The esters can be ring transformed and dehydrogenated to resorcines which are valuable components for the production of rubber and synthetic materials [20].

2. Experimental

2.1. Catalyst preparation

2.1.1. Superbases on basis of γ-alumina

All carriers were used in powder form and were calcined at 550 °C for 12 h. 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. This catalyst has been designated as **A**.

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. The final treatment was calcination at 700–750 °C in vacuum in order to decompose the acetate (catalyst **B**).

2.1.2. Basic zeolites

The cesium-containing zeolites X were prepared by ion exchange of NaX with 1 N cesium chloride solution (solid/solution ratio = 1 g/5 ml) at 70 °C for 24 h with stirring. The ion exchange was repeated three times. Thereby the cesium-containing zeolites were slurried in aqueous solutions of 1 mol/l (solid/solution = 1 g/3 ml) at room temperature for 24 h under agitation. After drying at 80 °C, the solids were calcined at 550 °C in air for 6 h in order to form the oxide species. Before the catalytic reaction, the catalysts were calcined again at 450 °C under reduced pressure for 5 h in order to remove moisture and CO_2 (catalyst **C**).

Generation of sodium cluster by mixing dry NaX with solid sodium was done according to the method by Yoon et al. [22,23]. A dehydrated NaX was dried at 200 °C in vacuum. Next, the zeolite powder was mixed with small pieces of sodium at room temperature. The preparation steps were carried out under an inert atmosphere. Typically, 1 g zeolite was mixed with 2.8 mmol sodium. During mixing, the colorless zeolite turned into red (catalyst **D**).

2.2. Characterization of the catalysts

Characteristic features of the prepared basic zeolites and superbases on basis of alumina are given in table 1. The basicity has been measured with Hammett indicators. In the catalysts **A** and **B**, the superbasic centers with basic strength higher than $H_- \geqslant 35$ were created. In the case of catalyst **C**, basic strength of $17.2 \leqslant H_- < 18.4$ could be obtained. It was not possible to determine the basicity of the purple, sodium-impregnated NaX (catalyst **D**) because the application of the Hammett indicator method is restricted to colorless solids.

The BET surface areas of the catalysts were calculated from nitrogen adsorption at 77 K (Coulter, Omnisorb 100). The adsorption isotherms of the modified zeolites belonged to type I without any hysteresis, which indicated absence of mesopores. The X-ray diffractograms of the impregnated zeolites indicated that the structure was not damaged during the modification procedure.

Valuable information about basic properties is given by the TPD measurement of CO_2. Figure 1 shows the TPD profiles of CO_2 for the catalysts **A** and **B**.

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 **B** is not appreciable for the system **A** which shows a less intensive desorption peak at 680 °C. This indicates that, in the case of catalyst **B**, stronger basic sites are generated. The TPD experiments correlate with the basic strength measured with Hammett indicators (table 1). The catalyst **B** possesses basic sites stronger than $H_- \geqslant 37$, whereas the superbase **A** shows slightly weaker superbasic sites with $35 \leqslant H_- < 37$.

Table 1
Basicity and surface area of the solid bases.

Catalyst		Catalyst loading	Surface area (m^2/g)	Base strength H_-
Na/NaOH/γ-Al_2O_3	**A**	2.9 mmol NaOH/g γ-Al_2O_3 2 mmol Na/g γ-Al_2O_3	135	$35 \leqslant H_- < 37$
Cs_xO/γ-Al_2O_3	**B**	2 mmol CsOAc/g γ-Al_2O_3	129	$H_- \geqslant 37$
Cs_xO/CsX	**C**	1.7 mmol CsOAc/g CsX	519	$17.2 \leqslant H_- < 18.4$
Na/NaX	**D**	2.6 mmol Na/g NaX	328	– [a]

[a] The basicity could not be determined with Hammett indicators because of the colour of the solid; the catalyst is assumed as a superbase due to the presence of sodium clusters.

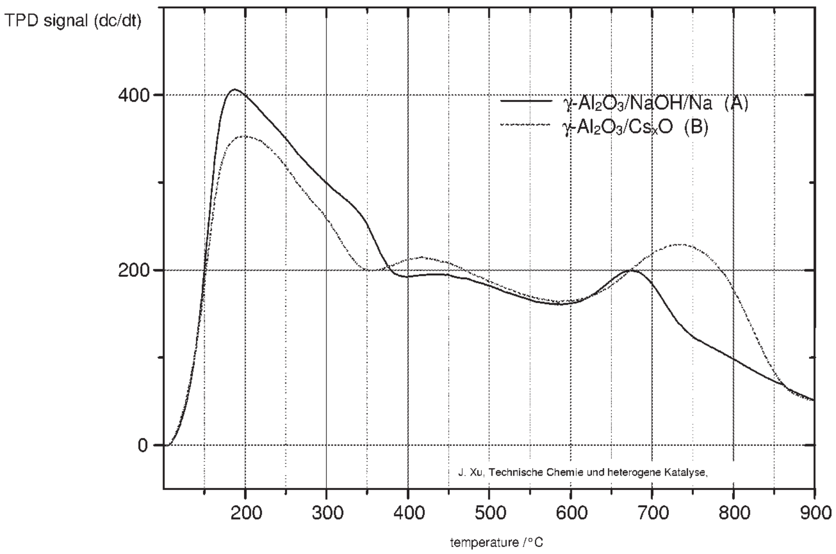


Figure 1. TPD desorption of CO_2 for catalysts **A** and **B**.

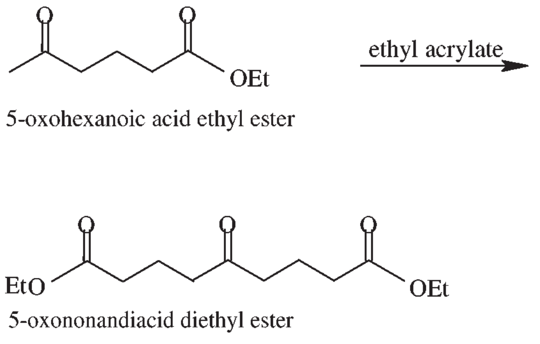
2.3. General reaction procedure

The reactions were carried out in a batch reactor. 1 g catalyst powder, 50–100 mmol acrylic ethyl ester and 100–200 mmol acetone (ratio acrylic ester : acetone = 1 : 2) were introduced in this sequence into a 100 ml glass autoclave. Small amounts of the inhibitor, 2-hydroxyanisole, were added to avoid polymerization reactions. All the reaction steps were carried out under an inert atmosphere. The reaction mixture was heated in an oil bath under stirring. The temperature of the oil bath was in the range of 50–110 °C. Samples were taken from the reactor in regular intervals.

3. Results and discussion

3.1. Solid base catalysts in the Michael addition of ethyl acrylate with acetone

Table 2 shows the results of the Michael addition carried out over the catalysts **A**, **B**, **C** and **D**. Ethyl acrylate reacts with acetone yielding 5-oxohexanoic acid ethyl ester as the main product. The main by-product is 5-oxononandiacid diethyl ester, which is formed by the double Michael addition of acrylic ester and 5-oxohexanoic acid ethyl ester according to equation (2):



(2)

Table 2
Results of Michael addition reaction in dependence on reaction time.[a]

Catalyst	Ester/acetone (mol/mol)	Time (min)	Conversion (%)	Selectivity (%)
Na/NaOH/γ-Al_2O_3 (**A**)	1/1	2	27	67
		6	31	69
		24	46	68
Cs_xO/γ-Al_2O_3 (**B**)	1/2	2	36	71
		6	37	72
		24	51	70
Cs_xO/CsX (**C**)	1/2	2	9	75
		6	13	74
		24	21	69
Na/NaX (**D**)	1/2	2	76	55
		6	78	55
		24	84	57

[a] Conditions: reactant/catalyst ratio = 0.05 mol acrylic ethyl ester/g catalyst, $T = 90\,^\circ C$, $t = 24$ h.

The reaction temperature was 90 °C. Samples were taken after 2, 6 and 24 h. The conversions described in table 2 refer to the converted amount of acrylic ethyl ester whereas the selectivities refer to the desired product 5-oxohexanoic acid ethyl ester.

With catalyst **A** an increase of conversion from 27 to 46% has been observed at increasing the reaction time from 2 to 24 h. The selectivities to 5-oxohexanoic acid ethyl ester were about 67–69%. Catalyst **B** led to a selectivity to 5-oxohexanoic acid ethyl ester of 71% at a conversion of 34% after 2 h. No significant change of activity occurred after 6 h reaction time. After 24 h, the conversion increased to 51% while the selectivity was maintained at 70%. That means catalyst **B** has higher basic strength than catalyst **A** resulting in somewhat higher conversion.

Table 2 also shows the results obtained over the CsX zeolite loaded with cesium acetate (catalyst **C**). After the impregnation procedure, the zeolite was calcined in air at

550 °C for 6 h leading to the formation of the oxide species. Before the catalytic reaction, the zeolite was calcined again at 450 °C for 5 h under reduced pressure in order to remove moisture and CO_2. After 2 h, a conversion of acrylic ester of 9% was achieved. It increased to 21% after 24 h. The selectivity of the main product, 5-oxohexanoic acid ethyl ester, was 69–74%. With the reaction time a slight decrease of the selectivity to 5-oxohexanoic acid ethyl ester could be observed. It resulted most likely from increasing reaction between 5-oxohexanoic acid ethyl ester and acrylic ester. For comparison, the catalytic tests were carried out with pure CsX zeolite and without any catalyst under the same conditions. The tests yielded no conversion of acrylic ester. The catalyst proved to be reusable in further reactions. After filtration and calcination in air and under reduced pressure the catalyst retained its basicity and could be used in further reactions.

Catalyst **D** has been assumed as a superbase due to the presence of sodium clusters. A slight increase of the conversion from 76 to 84% could be observed within the range from 2 to 24 h. The selectivity to 5-oxohexanoic acid ethyl ester was found to be about 55%. Due to a high sensitivity of the catalyst to air and moisture which led to destruction of the sodium clusters, it was not possible to use it again in further reactions.

Comparison tests with the carrier materials γ-Al_2O_3 as well as with the zeolites NaX and CsX applied under standard reaction conditions did not result in any conversion of ethyl acrylate.

3.2. *Influence of the reaction temperature*

The influence of temperature on the reaction has been investigated within the range from 50 to 110 °C. The results obtained for the superbase Na/NaOH/γ-Al_2O_3 (catalyst **A**), Cs_xO/γ-Al_2O_3 (catalyst **B**) and zeolite Na/NaX (**D**) are presented in table 3.

As shown in table 2, the optimum temperature found is 90 °C. At this temperature, the highest activities of all the catalysts have been observed. A decrease of temperature to 50 °C as well as an increase to 110 °C led to a loss of activity. All three catalysts show the same tendencies regarding the reaction temperature.

Table 3

Conversion and selectivity in dependence on reaction temperature.[a]

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)
Na/NaOH/γ-Al_2O_3 (**A**)	50	24	75
	70	27	71
	90	44	70
	110	32	72
Cs_xO/γ-Al_2O_3 (**B**)	50	42	73
	70	43	70
	90	51	70
	110	41	71
Na/NaX (**D**)	60	73	50
	90	84	57
	110	64	56

[a] Conditions: reactant/catalyst ratio $= 0.05$ mol acrylic ethyl ester/g catalyst, ester/acetone $= 1:2$ (molar ratio), $t = 24$ h.

3.3. *Comparison of the solid bases at different catalyst loadings*

The catalytic behaviour of the four catalysts was compared under the same reaction conditions. Figure 2 shows the results obtained at the reaction time of 24 h.

At a catalyst loading of 0.05 mol acrylic ester/g catalyst, the superbasic catalyst Cs_xO/γ-Al_2O_3 shows selectivity to 5-oxohexanoic acid ethyl ester of 70% at the conversion of ethyl acrylate of 51%. In comparison, the superbase Na/NaOH/γ-Al_2O_3 is slightly less active. A selectivity of 65% and a conversion of 44% were achieved. The reason for this behaviour is the higher basic strength and a higher amount of basic sites of the superbase Cs_xO/γ-Al_2O_3, as measured with both the Hammett indicators (table 1) and the TPD experiments of CO_2 (figure 1).

At the test temperature of 90 °C, the catalyst **C** showed a selectivity of 69% to 5-oxohexanoic acid ethyl ester. The

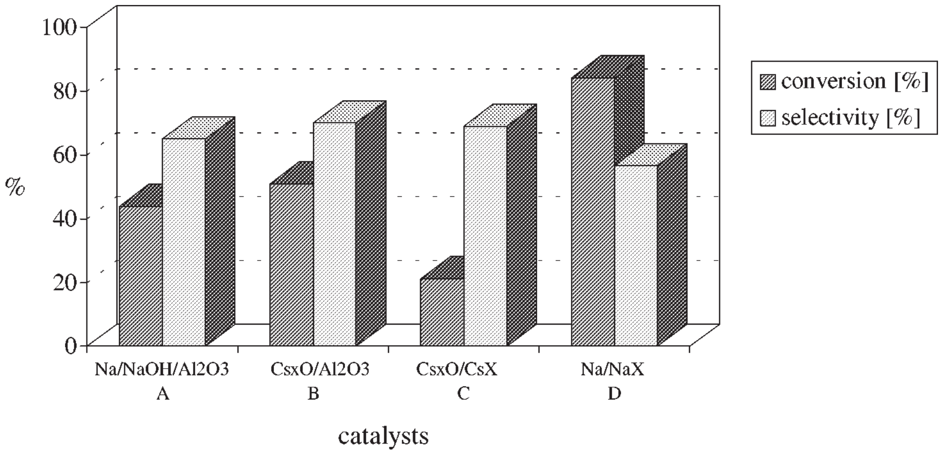


Figure 2. Comparison of the Michael addition results over different solid bases.

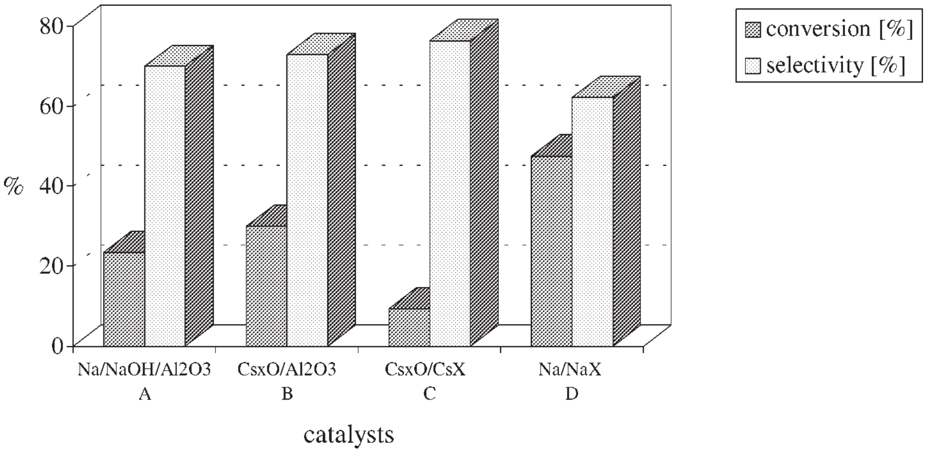


Figure 3. Comparison of the Michael addition results over different solid bases at higher catalyst loading.

conversion of ethyl acrylate was relatively low at about 21%. In comparison to the results obtained for the superbase **B** which is impregnated with a smaller amount of cesium acetate than the catalyst **C**, the conversion decreased by about 60%. The determination of the basic strength with the Hammett indicators showed a lower basicity of the modified zeolite ($17.2 \leqslant H_- < 18.4$) than those of the catalysts **A** and **B**. The lower basicity seems to be responsible for the lower activity. This result may suggest that the impregnation of the two different carrier materials with cesium acetate followed by calcination leads to the formation of different cesium species with different basic strengths. This idea has to be clarified by further investigations.

The use of the NaX zeolite impregnated with sodium resulted in the highest conversion of the ester equal to 84%. At the same time, the selectivity was about 57%. As the main by-product, the product of the Michael addition of two molecules of acrylic ester and acetone was formed. It could be stated that zeolite X was an appropriate support for the stabilisation of sodium clusters and, therefore, for the generation of a highly basic catalyst.

Some experiments were made with NaOH to compare the performance of the investigated solid catalyst with that homogeneous one. The molar content of NaOH was the same as the content of basic compound deposited on the carrier materials. The reaction conditions were the same as with the heterogeneous catalysts. In all the cases, the activity of NaOH was much lower as compared to the solid bases with conversion of only 3%.

Figure 3 shows the results of the reaction over the solid catalysts investigated under the same standard reaction conditions but a higher catalyst loading of 0.1 mol acrylic ester/g catalyst.

The higher catalyst loading (mol acrylic ester/g catalyst) led to a decrease of the conversions of ethyl acrylate after 24 h reaction time. This corresponds to the fact that for each ester molecule a smaller amount of active sites are present to abstract a proton from the active methylene compound. A slight increase of the selectivities could be observed. The different solid base catalysts show the same behaviour considering their basic activity as already observed at the lower catalyst loading.

4. Conclusions

It could be shown that different solid bases are efficient catalysts in the Michael addition of ethyl acrylate and acetone to 5-oxohexanoic acid ethyl ester. The highest activity for such a Michael addition has been observed over NaX impregnated with sodium (catalyst **D**). At a temperature of 90 °C and a catalyst loading of 0.05 mol ester/g catalyst a selectivity of 57% was obtained at a conversion of 84%. Under the same conditions, the two superbasic catalysts show better selectivities (65–70%) but lower conversions (44–51%). For all catalysts, the most favorable temperature proved to be 90 °C. Furthermore, more favorable is a not too high catalyst loading of 0.05 mol ester/g catalyst in order to achieve high conversions. In the case of impregnation with cesium acetate followed by calcination to the corresponding oxides, the impregnated Al_2O_3 showed better results as a superbasic catalyst in the Michael addition reaction than the impregnated zeolite. It could be demonstrated that the applied basic solid catalysts can replace liquid basic homogeneous catalysts, even though the results are not as good as in the case of the homogeneous systems.

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