

Application of basic zeolites in the decomposition reaction of 2-methyl-3-butyn-2-ol and the isomerization of 3-carene

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Abstract

Basic zeolite catalysts can be generated via ion exchange or via impregnation with alkali metals and alkali metal acetates following different methods. The decomposition of 2-methyl-3-butyn-2-ol and the isomerization reaction of 3-carene to 2-carene have been studied in the gas phase over various basic zeolites to investigate their value as test reactions for basic properties of zeolites. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The replacement of liquid basic catalysts by solid bases in the organic synthesis of fine and intermediate chemicals offers an opportunity to avoid salt formation, corrosion, and other environmental problems. Furthermore, there is a high interest to produce basic materials with a specific pore structure to provide the possibility for shape-selectivity in base-catalyzed reactions. The basic zeolites can be prepared in two ways. The first method is an ion-exchange of the zeolite with alkali metal ions. Alkali cation-exchanged zeolites exhibit basic properties and promote several base-catalyzed reactions [1–4]. Their basic sites are, however, relatively weak.

A possibility for the creation of zeolites with strong basic sites is an impregnation of the zeolite with fine particles of alkali metals or alkali oxides that can act as bases themselves. This can be accomplished, e.g., by the thermal decomposition of sodium azide deposited in dehydrated zeolites [5] or by the impregnation with different alkali or alkaline earth metal salts [6,7]. The salts can then be decomposed by calcination. The active basic sites are supposed to be neutral alkali metal clusters and alkali metal oxides, encapsulated in the zeolite cavities.

The methods used to characterize basic sites can be divided into titration methods, spectroscopic methods using probe molecules and catalytic test reactions. An advantage of an adequate choice of a test reaction is that it can give useful information about the catalyst under reaction conditions.

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The reactions of 2-methyl-3-butyn-2-ol (MBOH) are already known as catalytic test reactions to characterize the acidic and/or basic properties of several metal oxides and alkali-exchanged zeolites with weak basic sites [8,9]. The alcohol gives different reaction products whether reacting on solid acids, solid bases or amphoteric sites (Fig. 1). Acid centers catalyze the dehydration to 3-methyl-3-buten-1-in (mbyne) and the intramolecular rearrangement to 3-methyl-3-buten-2-on (prenal). On basic sites, the molecule decomposes into acetone and acetylene. The formation of 3-methyl-3-butene-2-one (MIBK) and 3-hydroxy-3-methyl-2-butanone (HMB) was observed in the presence of amphoteric sites.

The isomerization of 3-carene to 2-carene (Fig. 2) is reported to take place in basic solutions, e.g., in the presence of ethylenediamino lithium, *tert*-butyl potassium or various other strong bases [10]. Over hydrogenation catalysts such as Raney nickel and Pd on carbon, 2-carene was produced in addition to the hydrogenated products under a hydrogen atmosphere. Tanabe et al. [12] reported that 3-carene undergoes isomerization to 2-carene over solid bases such as MgO, CaO, SrO, and ZrO₂ [11,13]. Poisoning tests with CO₂ as a probe molecule proved that the active sites are basic. Suitable pretreatment temperatures of a MgO catalyst (900°C) increased the selectivity to 2-carene to 96% at a conversion of 3-carene of 46%.

Booth et al. found the utility of 2-carene as a precursor for the production of menthol which is used in fragrance industry. The first step in

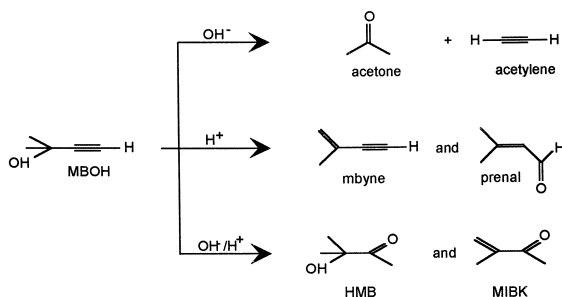


Fig. 1. Reactions of 2-methyl-3-butyn-2-ol (MBOH).

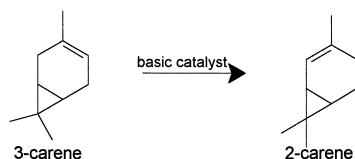


Fig. 2. Double bond isomerization of 3-carene to 2-carene.

this process is the conversion of 3-carene to 2-carene [14].

Over acidic catalysts such as SiO₂-Al₂O₃, Ce₂O₃, and TiO₂, 3-carene is isomerized to various menthadienes and dehydrogenated mainly to *m*- and *p*-cymenes.

We have studied strong basic zeolites in two gas phase reactions to investigate their value as catalytic test reactions: the reactions of 2-methyl-3-butyn-2-ol and the double bond isomerization of 3-carene. The aim of the present study is to compare the results obtained in these two test reactions over basic zeolites prepared by various methods. Furthermore, we aimed in concluding which test reaction is the most suitable for the characterization of strong basicity in zeolites.

2. Experimental

2.1. Catalyst preparation

The NaX zeolite in powder form (Fa. Grace, Si/Al = 1.6) was kneaded with water and a peptizing agent. Next, it was formed into extrudates with a diameter of 2 mm. The extrudates were dried at 110°C for 12 h and calcined at 550°C for 12 h. Crushing and sieving gave a catalyst with the particle size of 1.0–1.6 mm for the fixed bed reactor. The zeolite particles were calcined again at 550°C for 6 h and dried at 150°C for 6 h under inert atmosphere in order to remove water and CO₂.

The dehydrated NaX zeolite was impregnated under inert atmosphere with a methanolic solution of sodium azide containing 0.77–3.85 mmol NaN₃ per gram of zeolite. The volume of the solution filled exactly the pore volume of the support. After removal of the solvent, the sodium

azide was decomposed to nitrogen and sodium clusters in order to form the active species. The activation procedure took place at 400°C (1 h) under a nitrogen stream (4 l/h) in situ in the catalytic reactor.

Alkali oxides containing zeolites were prepared by contacting the zeolite powder with aqueous solutions of various cesium acetate concentrations [0.15 mol (Cs,NaX36), 0.3 mol (Cs,NaX72), 0.6 mol (Cs,NaX146), 0.7 mol (Cs,NaX180), and 1 mol (Cs,NaX 260) of cesium acetate per liter, 3 ml/g NaX]. After drying at 80°C for 12 h, the samples were calcined in air at 550°C for 6 h in order to form the oxide species. The powder was pressed into tablets under reduced pressure (100 bars, 5 s). Crushing and sieving gave a catalyst with the particle size of 1.0–1.6 mm for the fixed bed reactor. Before the catalytic reaction, the catalysts were calcined again at 450°C under reduced pressure (5 h) to avoid water and CO₂.

2.2. General reaction procedure

The catalytic tests were carried out in a continuous flow fixed-bed reactor in form of a coil with an internal diameter of 0.6 cm. The reactor was placed in a heated oven. The apparatus was equipped with a gas dosing system for N₂. Zeolite catalysts in form of small particles (1.0–1.6 mm) in amounts of 3 g were placed in the center of the reactor. The typical reaction temperature was 120°C for the reaction of MBOH and 250°C for the isomerisation of 3-carene. The resulting WHSV was 2/h. Before the reaction, the catalysts were pretreated 1 h under a nitrogen stream (4 l/h) at 400°C (heating rate of 10°C/min) in order to build the active species. After the decomposition of the impregnated salts, the reactor was cooled down to the desired reaction temperature under a stream of nitrogen and the educts were added into the reactor by means of a metric pump. All reaction components were stored under argon atmosphere. The feed evaporated at the reactor inlet

and the vapour was transported in the presence of 4 l N₂/h over the catalyst bed.

2.3. Analysis of the products

GC analysis of the products of the MBOH reaction was done in a Siemens RGC 202 system equipped with a 50-m OV1701 CS column and a flame ionization detector.

The product analysis of the isomerisation of 3-carene was performed in a Siemens RGC 202 using a 50-m column (Carbowax) with nitrogen as carrier gas.

The quality and basicity of the zeolites prepared were checked by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer and temperature-programmed desorption (TPD) of CO₂. The BET surface area of the catalysts were calculated from nitrogen adsorption at 77 K (Omnisorb 100).

3. Results and discussion

3.1. Reactions of 2-methyl-3-butyn-2-ol

3.1.1. Experiments with various alkali-exchanged zeolites

A suitable test reaction for the characterisation of basic zeolites should be highly selective towards the desired reaction products. Table 1 shows the product distribution over four different zeolites.

The only product detected over the NaX and CsX zeolites was acetone, i.e., the product of the base-catalyzed cleavage reaction of methylbutynol. Due to the off-line analysis, the second cleavage product acetylene could not be detected, but it should be formed in equal amounts as acetone. A completely different product distribution over the two ZSM-5 zeolites revealed a different reaction route. Due to the acidic character of these materials, mbyne was the dominant product. In addition, small amounts of prenal were detected. The different product distribution shows that the yield of acetone and

Table 1
Reaction of methylbutynol over different zeolites

Catalyst	Time [h]	Conversion of MBOH [%]	Selectivity [%]		
			Acetone	Mbyne	Prenal
NaX	1	9.8	97.6	0	0
	3	4.0	94.7	0	0
	5	1.1	82.1	0	0
CsX	1	21.5	99.4	0	0
	3	13.6	99.4	0	0
	5	10.8	99.1	0	0
Na-ZSM-5	1	12.4	0	92.1	7.9
	2	4.5	0	80.5	13.3
	3	3.3	0	100	0
H-ZSM-5	1	24.8	0	91.9	4.4
	2	6.8	0	90.6	9.4
	3	4.9	0	91.0	8.7

Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, T = 120°C.

acetylene can be taken as a measure of basicity and the yield of mbyne and prenal as a measure of acidity.

3.1.2. NaX zeolite impregnated with different amounts of NaN₃

Simple ion-exchanged faujasites are known as relatively weak basic catalysts. To compare the reaction results of stronger basic sites, standard reaction conditions (reaction temperature = 120°C, WHSV = 2/h) were determined.

A NaX zeolite has been impregnated with methanolic solutions of sodium azide of various concentrations. After removal of the solvent, the zeolite adducts were activated by thermal decomposition at 400°C in situ in the catalytic reactor. The decomposition of sodium azide results in the formation of metallic sodium and nitrogen [6]. After the activation procedure, the MBOH reaction was carried out. Samples of the reaction mixture were taken after 1 h, 3 h, and 5 h on stream. Under these conditions, the only products are acetone and acetylene which originate from the base-catalyzed cleavage reaction of 2-methyl-3-butyn-2-ol. Fig. 3 and Table 2 show the results obtained at 120°C and at a WHSV of 2/h.

The pure NaX zeolite shows only very low conversion since it is less than 10% (Table 1). The conversion of the base-catalyzed reaction pathway increases with increasing amounts of sodium azide impregnated on the zeolites. The best results were achieved with the highest loading of 3.85 mmol NaN₃/g NaX. Approximately 100% selectivities to both products and a conversion of 95% could be achieved. A slight deactivation with time is attributed to condensation reaction of acetone and adsorption of such products as well as the adsorption of the reactant.

3.1.3. Different zeolites and alumina impregnated with NaN₃

Fig. 4 shows the results of the MBOH decomposition reaction over several alkali exchanged zeolites and alumina after 3 h on stream. The samples have been impregnated with the same amount of sodium azide (2.3 mmol NaN₃/g carrier material). It should be examined if the different carrier materials exert an influence on the activity in the MBOH reaction.

The highest MBOH conversion of about 72% is obtained with the sodium impregnated NaX zeolite. The impregnated sodium mordenite yields conversions of about 62% indicating a high activity of the catalyst. Under the same conditions, the impregnated NaL zeolite reaches conversions of only 23%. Alumina was even

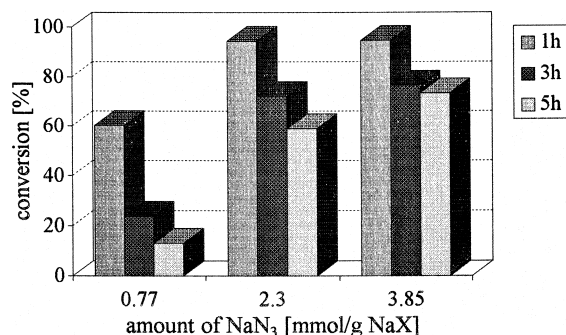


Fig. 3. Decomposition of methylbutynol over NaX impregnated with NaN₃. Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, T = 120°C.

Table 2
Decomposition of methylbutynol over NaX impregnated with NaN₃

NaN ₃ [mmol/g NaX]	Time on stream					
	1 h		3 h		5	
	S _{acetylene} [%]	S _{acetone} [%]	S _{acetylene} [%]	S _{acetone} [%]	S _{acetylene} [%]	S _{acetone} [%]
0.77	42.6	53.4	44.6	53.9	45.5	51.5
2.30	44.5	54.6	44.2	55.1	46.0	53.0
3.85	44.4	54.0	44.5	55.1	44.9	52.2

Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, T = 120°C.

less active as only 16% alcohol was converted. The selectivities of the five catalysts to the product of base-catalyzed reaction is in the same range of about 97–99%.

The high activity of the impregnated zeolites NaX and NaY can be correlated with their high basicity due to their low Si/Al ratio of the framework. The application of Al₂O₃ as carrier material using the azide method leads to lower conversions in the MBOH reaction as compared with the impregnated zeolites. On the basis of this activity behaviour, it can be stated that zeolites, especially zeolite X, are the most appropriate support for the stabilization of sodium clusters and therefore, for the generation of strong basic catalysts via the azide method.

3.1.4. NaX zeolite impregnated with cesium acetate

Hathaway and Davis reported that the decomposition of cesium acetate occluded in al-

kali-exchanged faujasites results in the generation of active cesium oxide basic sites [7]. In this work, a sodium exchanged X zeolite was impregnated with aqueous solutions of various amounts of cesium acetate. The residual solids were dried at 80°C for 12 h. The samples were calcined in air at 550°C for 7 h leading to the formation of the oxide species. Before the characterisation, they were calcined again at 500°C for 5 h under reduced pressure in order to avoid moisture and CO₂. The compositions of the solids are listed in Table 3.

The adsorption and desorption isotherms of the parent and modified zeolites obtained after activation of the solids are depicted in Fig. 5. The adsorption isotherms belong to type I without hysteresis loop indicating the absence of mesopores. The micropore volume and specific area of the modified X zeolites decreases monotonously with increasing cesium loading (Table 3). Taking into account that no

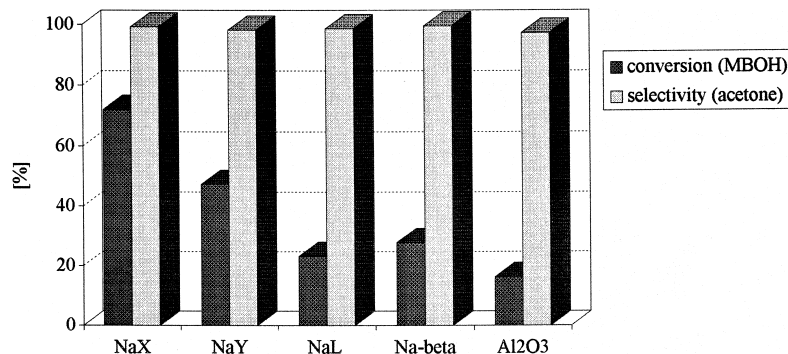


Fig. 4. Decomposition of methylbutynol over different zeolites and alumina impregnated with NaN₃. Reaction conditions: 2.3 mmol NaN₃/g NaX; activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, 120°C, T = 3 h.

Table 3
Surface areas and basicities of the solids

Zeolite	Cesium acetate [mmol/g NaX]	BET surface area [m ² /g]	Micropore volume [ml/g]	Basicity H_-
NaX	0	738	0.4	$7.2 \leq H_- < 9.3$
Cs ₃ NaX36	0.36	569	0.3	$17.2 \leq H_- < 18.4$
Cs ₃ NaX72	0.72	519	0.2	$17.2 \leq H_- < 18.4$
Cs ₃ NaX146	1.46	375	0.2	$17.2 \leq H_- < 18.4$
Cs ₃ NaX180	1.80	250	0.1	$17.2 \leq H_- < 18.4$
Cs ₃ NaX260	2.60	216	0.1	$18.4 \leq H_- < 26.5$

loss of crystallinity is noticed for the zeolites Cs₃NaX36, Cs₃NaX72 and Cs₃NaX146, the decrease of surface area and micropore volume can be assigned to a decrease in the free void volume due to the formation of cesium oxide in the zeolite cavities.

Fig. 6 and Table 4 show the activities of NaX zeolite catalysts impregnated with various amounts of cesium acetate in the MBOH reaction. The reaction was carried out at 120°C and WHSV of 2/h.

The cesium acetate-impregnated NaX zeolites are quite active in the cleavage reaction of 2-methyl-3-butyn-2-ol to form acetylene and acetone. The conversion of methylbutynol increases with increasing loadings of cesium acetate and passes through a maximum. The catalyst Cs₃NaX36 with a loading of 0.36 mmol cesium acetate/g zeolite reaches a conversion of 25% after 2 h on stream. With the faujasite X

impregnated with 1.8 mmol cesium acetate/g zeolite, a conversion of 82% could be obtained after the same time. After 3 h on stream, a conversion of 81% is obtained with a zeolite loaded with 1.46 mmol cesium acetate/g. The sample having a higher amount of 1.8 mmol cesium acetate/g zeolite reaches only 71% conversion.

Due to the increasing loading with basic particles, the basic strength of the materials increases as well. A qualitative information on the basic strength could be obtained with the help of Hammett indicators (Table 3). For instance, the H_- function is < 9.3 in NaX. It rises up to 17.2 for the impregnated zeolites. Only the catalyst with the highest loading of 2.6 mmol cesium acetate/g NaX reaches a higher basicity of $18.4 \leq H_- < 26.5$. At low cesium acetate loadings, the increase of the conversion with the amount of deposited basic particles is assumed to result from a higher basicity of the materials than before impregnation.

A better explanation of the observed activity behaviour can be drawn from the results of TPD measurements (Fig. 7).

The TPD plots show the same activity pattern with a maximum as already observed in the MBOH reaction. As the loading of cesium acetate increases, the activity goes through a maximum. Thus, the whole amount of cesium oxide seems to be accessible for the catalytic reaction resulting in high conversions of MBOH. As can be concluded from the TPD measurements, the zeolite impregnated with 1.46 mmol cesium acetate/g zeolite X possesses the highest

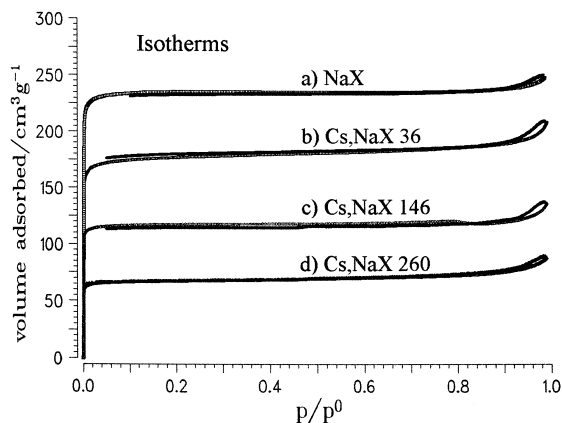


Fig. 5. Adsorption and desorption isotherms of NaX and the modified zeolites.

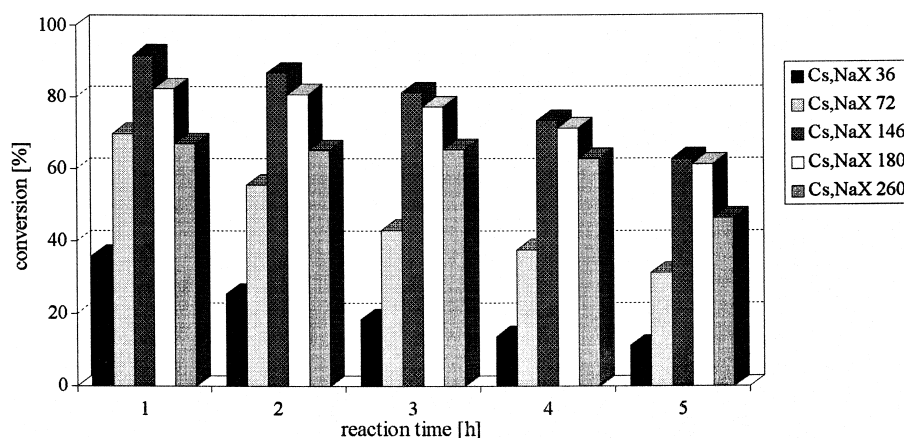


Fig. 6. Decomposition of methylbutynol over NaX impregnated with cesium acetate. Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, T = 120°C.

amount of basic sites. In comparison, the two zeolites with higher loadings, Cs,NaX180 and Cs,NaX260, show lower signal intensities. This decline in basicity of the highest loaded zeolites can also be observed in decreasing conversions in the MBOH reaction. The loss of basicity may be due to the destruction of the zeolite structure at higher cesium acetate loadings. Furthermore, not all cesium oxide may be accessible for the reacting molecules because at higher loadings, cesium oxide may form larger aggregates with a smaller external surface.

3.1.5. Impregnation with different alkali acetates

A NaX zeolite has been ion-exchanged with different alkali metal salts. Each alkali-ex-

changed zeolite has been impregnated with an aqueous solution of the parent alkali metal acetate. After drying and calcination in air, the zeolite catalyst was calcined again under reduced pressure to remove water and CO₂. The catalytic activities of the ion-added samples are depicted in Fig. 8 and Table 5.

All these modified zeolites favour the base-catalyzed cleavage reaction of methylbutynol to acetylene and acetone. The resulting activities agree with the expected behaviour of the different alkali metals used considering their different electropositivities. The sodium-added NaX zeolite shows the lowest activities in the MBOH reaction. The conversion is 33% after 1 h reaction time and decreases to 10% after 6 h. The potassium-added KX zeolite shows a slight increase in activity. The best results were ob-

Table 4
Decomposition of methylbutynol over NaX impregnated with cesium acetate

Catalyst	Time on stream					
	1 h		3 h		5 h	
	S _{acetylene} [%]	S _{acetone} [%]	S _{acetylene} [%]	S _{acetone} [%]	S _{acetylene} [%]	S _{acetone} [%]
Cs,NaX36	44	56	45	55	45	55
Cs,NaX72	44	56	46	54	45	55
Cs,NaX146	45	55	45	55	44	56
Cs,NaX180	44	56	48	53	44	56
Cs,NaX260	43	57	46	54	46	54

Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, T = 120°C.

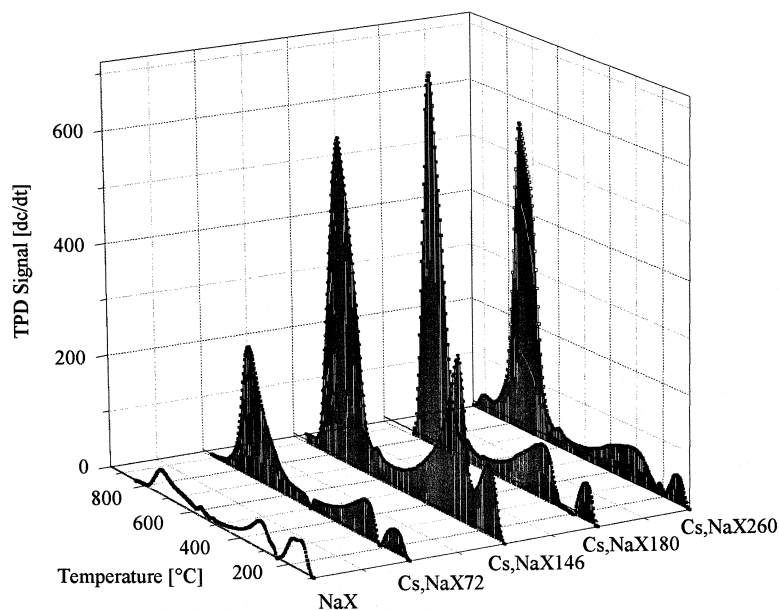


Fig. 7. TPD plots of CO_2 adsorbed on NaX and the modified zeolites.

tained with a cesium-added CsX zeolite. After 1 h reaction time, conversion of 71% is obtained. In conclusion, the activity of the ion-added zeolites increases with a decrease of the electronegativity of the corresponding alkali metal cations.

3.2. Double bond shift of 3-carene to 2-carene

The influence of basic zeolites in the isomerization reaction of 3-carene to 2-carene was

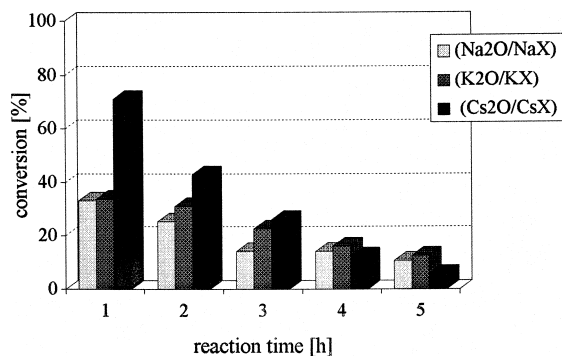


Fig. 8. Decomposition of methylbutynol over NaX impregnated with cesium acetate. Reaction conditions: activation: 1 h at 400°C under a N_2 -stream (4 l/h), WHSV = 2/h, $T = 120^\circ\text{C}$.

examined with regard to a possible application as a catalytic test reaction.

Table 6 shows the results in the isomerization reaction of 3-carene to 2-carene obtained over faujasites impregnated with sodium azide and cesium acetate. Before carrying out the catalytic tests, the materials were activated at a temperature of 400°C for 1 h to form the active basic sites. The experiments were carried out at 200°C and 250°C and a WHSV of 2/h.

It can be seen that the pure zeolites X and Y show almost complete conversion with the formation of various unidentified products. The selectivity to 2-carene lies in the range of 3–14%. This product spectrum seems to result from remaining Brønsted acid sites within the zeolite which are responsible for a high conversion of 3-carene.

The sodium-loaded NaX zeolite showed the best results for the isomerisation of 3-carene to 2-carene. At 200°C , a selectivity to 2-carene of 78% and a conversion of 36% with regard to 3-carene could be achieved after 1 h reaction time. The increasing formation of side products such as terpinolene, terpinene, and *p*-cymene is probably responsible for the increasing deactivation with the reaction time. After 5 h, the selec-

Table 5
Decomposition of methylbutynol over different alkali-added zeolites

Catalyst	Alkali acetate [mmol/g M ^I X]	Time on stream					
		1 h		3 h		5 h	
		S _{acetylene} [%]	S _{acetone} [%]	S _{acetylene} [%]	S _{acetone} [%]	S _{acetylene} [%]	S _{acetone} [%]
Na ₂ O/NaX	0.36	44	56	45	55	45	55
K ₂ O/KX	0.36	45	55	45	55	45	55
Cs ₂ O/CsX	0.36	45	55	45	55	45	55

Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h, T = 120°C.

M^I = alkali metal.

tivity declines to 19% at a conversion of 9%. A removal of sodium with the product stream was not observed. In experiments carried out at a higher temperature of 250°C, the selectivity to 2-carene decreases down to 51% at 1 h time on stream, while the conversion increases to 43%.

Regarding the results obtained with a NaY zeolite impregnated with different amounts of sodium azide, it can be observed that the conversion of 3-carene does not follow the increase of alkali metal salt loading. After only 1 h reaction time that the zeolite impregnated with a higher amount of sodium azide shows a remarkably higher conversion of 59% as compared to 27% over the zeolite impregnated with a smaller amount. Furthermore, the selectivities to 2-carene are very low with values of about 16–20%. Neither the amount of the impregnated

metal nor reaction time show a meaningful influence on the selectivity to 2-carene. The formation of a higher amount of basic sites results in an increasing production of by-products.

Basic zeolites prepared by impregnation of NaX with low amounts of cesium acetate are also active in the reaction of 3-carene. Conversions of 31–51% were obtained using NaX zeolite impregnated with 0.36 mmol cesium acetate per gram. Nevertheless, the selectivities to 2-carene are relatively low (15–18%). Higher cesium acetate loadings lead to low activities with conversions of about 8%.

Comparing the results obtained over NaX impregnated with sodium azide, the NaX zeolite modified with cesium acetate do not show significant basic properties in the isomerization of 3-carene. Only the materials impregnated with a

Table 6
Isomerization of 3-carene to 2-carene in the gas phase

Catalyst	T [°C]	Reaction time [h]					
		1		3		5	
		Conversion [%]	S _{2-carene} [%]	Conversion [%]	S _{2-carene} [%]	Conversion [%]	S _{2-carene} [%]
NaX	250	97.0	3.1	93.2	2.7	87.8	3.8
Na/NaX (3.85 mmol NaN ₃ /g NaX)	200	36.3	78.4	18.3	60.4	8.7	19.1
Na/NaX (3.85 mmol NaN ₃ /g NaX)	250	42.5	50.5	18.6	31.3	27.7	15.3
NaY	250	98.5	7.5	76.4	6.6	54.0	13.7
Na/NaY (0.77 mmol NaN ₃ /g NaY)	250	26.8	19.5	38.3	16.8	27.2	18.4
Na/NaY (2.3 mmol NaN ₃ /g NaY)	250	58.7	15.8	38.1	16.4	21.4	16.5
Cs ₂ O/NaX 36	250	51	15	43	16	31	18
Cs ₂ O/NaX 260	250	8	< 2	7	< 2	7	< 2

Reaction conditions: activation: 1 h at 400°C under a N₂-stream (4 l/h), WHSV = 2/h.

lower amount of alkali metal salt revealed activities in this reaction. Considering the results of the MBOH reaction, the decomposition of sodium azide leads to the formation of stronger basic sites. The low activity of faujasites impregnated with cesium acetate in the double bond isomerization may arise from the fact that the basicity of the materials is not high enough. Furthermore, the impregnation with cesium acetate leads to a decrease of the pore volume from 738 m²/g to 216 m²/g. The reduced pore volume of the modified zeolite may have an influence on the diffusion possibilities of educt molecules into the zeolite resulting in low activities.

4. Conclusions

Basic sites can be generated in zeolites by introduction of alkali metals and alkali metal oxides. The decomposition of 2-methyl-3-butyn-2-ol in the gas phase proved to be a valuable method for the comparison of basic zeolites with various basic strengths. The selectivities to the products of the base-catalyzed reaction pathway are high, so that the yield of acetone and acetylene can be taken as a measure of basicity. Differences in basic character could be displayed with simple ion-exchanged zeolites having weak basic sites as well as with stronger basic zeolites. The course of activity and the degree of basicity obtained with NaX impregnated with different amounts of cesium acetate could be correlated with the TPD results of adsorbed CO₂.

The isomerization of 3-carene to 2-carene is less suitable as standard test reaction for basic zeolites. Only sodium containing zeolites with strong basic sites were able to achieve high activities. A suitable test reaction should be highly selective towards the reaction products. Over strong basic catalysts, the reactions of 3-carene resulted in the formation of several by-products. The basic zeolites prepared did not show any tendency and selectivity to 2-carene with the reaction time and different metal salt loading. That reaction is not suitable as standard test for the characterisation of such materials.

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