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Solid state ion exchange of alkali metal cations into zeolite Y: Physicochemical characterization and catalytic tests.

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KY-, RbY- and CsY-zeolites have been prepared from NaY at 100 % exchange level. For RbY and CsY this was only possible by solid state ion exchange. Extensive physical characterizations suggest that the basicity of framework oxygen slightly increases with decreasing cation electronegativity. However, in CsY ion exchange was presumably incomplete and small amounts of CsOH- and/or Cs_2O-clusters were present in addition to retained bridging OH´s. The catalytic properties for the conversion of isopropanol and methanol can be tentatively explained on the basis of these characteristics.

1. INTRODUCTION

Whereas zeolites as acid catalysts have been extensively studied during the last decades, base catalysis in zeolites is still an underdeveloped field. The ultimate goal in this area is perhaps the synthesis of a zeolite analogue with anion exchange capacity which, in its OH-form, could act as a true Brönsted base [1]. So far, this approach was not yet successful, hence current research focusses on the accommodation of basic guests in conventional molecular sieves as hosts. Up to now, essentially four approaches for the generation of basic sites in zeolites have been explored: (i) Exchange of bulky alkali metal cations into the zeolite [2, 3]. IR investigations with probe molecules such as pyrrole seem to indicate that, in such materials, framework oxygens adjacent to the alkali cations act as Lewis base sites [4]. (ii) Isomorphous substitution of silicon by germanium in the zeolite framework [5,6]; (iii) the deposition of ionic alkali metal clusters (e.g. Na_4^{3+}) or of alkali metal clusters, e.g. by controlled thermal decomposition of the corresponding azide [7], and (iv) the preparation of basic oxide guests (i.e. Cs_2O) in the cavities of the zeolite [8]. In the present paper, the first approach was selected because of its straightforward manner. Zeolite NaY was completely exchanged with K^+ (via ion exchange in aqueous suspension) or with Rb^+ and Cs^+, respectively, by solid state ion exchange [9]. The obtained materials were extensively characterized with respect to their acid-base properties, both by sophisticated physicochemical techniques and by catalytic test reactions.

2. EXPERIMENTAL SECTION

2.1. Materials

Zeolite NaY was a commercial product supplied by Union Carbide Corporation, Tarrytown, N.Y., USA. The sodium cations of the starting material were completely replaced by potassium cations via sevenfold ion exchange with 1 M aqueous solutions of KCl at 353 K (m_{KCl} / m_Z = 1). Using this method, a maximum degree of ion exchange of only 70 % can be achieved for the larger cations, viz. Rb^+ and Cs^+ [10] because in aqueous solution they are not able to pass the 6-ring windows of the sodalite cages and exchange with Na^+ cations hidden in this position. Therefore, solid state ion exchange was employed with the intention to completely replace Na^+ by Rb^+ and Cs^+. For this purpose, zeolite NaY was first transferred to NH_4Y by sevenfold ion exchange of NaY with 1 M aqueous solution of NH_4Cl at 353 K (m_{NH_4Cl} / m_Z = 0.5). 5 g of zeolite NH_4Y were then thoroughly mixed with a slight excess of Rb_2CO_3 or $CsOH \cdot H_2O$, respectively (n_{Cs} / n_{NH_4} = n_{Rb} /n_{NH_4} = 1.1). The mixtures were placed in evaporating dishes and heated in air according to the temperature program:

$$293\ K \xrightarrow{4h} 393\ K\ (3h) \xrightarrow{6h} 573\ K \xrightarrow{2h} 773\ K\ (6h).$$

After cooling to room temperature, excess exchange salts were removed by washing with distilled water. As an acidic reference material, zeolite MgNaY was prepared from NaY by repeated ion exchange with $MgCl_2$.

2.2. Characterization

The structural integrity of the produced materials was checked by X-ray powder diffraction, scanning electron microscopy and ^{27}Al MAS NMR spectroscopy. Elemental analysis was done by atomic absorption spectroscopy (AAS). Adsorption capacities for water were determined by thermogravimetric analysis. The following nuclei were studied using MAS NMR spectroscopy (Bruker MSL 400 spectrometer): ^1H (400.13 MHz), ^{27}Al (104.26 MHz), ^{29}Si (79.49 MHz) and ^{133}Cs (52.48 MHz); the MAS frequencies used were 10 kHz for ^1H and ^{27}Al MAS NMR and 5 kHz for ^{29}Si and ^{133}Cs MAS NMR. Spectra simulations were performed with the PC program WINFIT. For XP spectroscopy a VSW ESCA-Lab 100 spectrometer equipped with a hemispherical energy analyzer type HA 100 was applied using MgK_α radiation (1253.6 eV). Spectra were recorded in the FAT mode (pass energy 22 eV) with a step width of 0.06 eV and data accumulation times of 0.3 s per channel. Binding energies were referenced to the C1s signal at 284.4 eV. The maximum pressure in the UHV system during data acquisition was 5×10^{-6} hPa. Fourier transform IR spectra were recorded on a Bruker IFS 66 spectrometer using a low temperature in situ cell which was described previously [11]. Typically, 256 scans were accumulated at a spectral resolution of 0.7 cm^{-1}. The samples were pressed into thin self-supporting wafers (15 mg/cm^2) and heated in situ in an O_2 atmosphere at 773 K for 1 h and then evacuated (10^{-3} Pa) at 773 K for 1h prior to the adsorption of CO, $CDCl_3$ and CO_2 probe molecules.

2.3. Catalytic Reactions

The catalytic experiments were conducted in a flow-type apparatus equipped with saturator, fixed bed reactor, on-line sampling and product analysis by capillary gas chromatography. For the conversion of isopropanol, nitrogen was used as carrier gas, and the partial pressure of isopropanol amounted to 7.3 kPa. The reaction temperature was adjusted to 473 K or 673 K, respectively. Gas chromatographic separation of the reaction products was performed using a

fused silica CARBOWAX column (FID detection). Methanol conversion experiments were carried out with helium as carrier gas, with a partial pressure of methanol of 14.3 kPa and a reaction temperature of 673 K. A PORAPLOT Q column and a TC detector were used for product analysis of this reaction. Prior to the catalytic experiments, each catalyst was activated in a stream of nitrogen at 773 K. Activities and selectivities of the catalysts are generally reported after 5 hours time-on-stream after which period constant conversion was reached.

3. RESULTS AND DISCUSSION

3.1 Characterization

The X-ray powder pattern of the parent NaY zeolite and the ion-exchanged materials prepared from it are depicted in Figure 1. It can be seen that significant changes in the relative intensities of the diffraction lines and a strong decrease in the signal-to-noise ratio occurs with increasing size of the exchanged cation. This is particularly evident for the CsY zeolite. Both observations, the change in relative intensities and the strongly reduced peak intensities are at present attributed to the changes in structure factors and X-ray absorption behavior with increasing size of the cation. That the integrity of the zeolite Y framework is still preserved can be deduced from the results of ^{27}Al and ^{29}Si MAS NMR spectroscopy: The ^{27}Al MAS NMR spectra of all samples consist of a single line at a chemical shift of ca. 59 ppm which is attributed to tetrahedrally coordinated aluminum in lattice positions. In no case a band around 0 ppm could be observed which would indicate the presence of extra-framework aluminum. From the ^{29}Si MAS NMR spectrum of CsY (Figure 2) the existence of amorphous siliceous species (broad signal at ca. -110 ppm [12]) can also be excluded. However, in comparison to the spectra of samples with lower degrees of cesium exchange (CsNaY-45 and CsNaY-70,

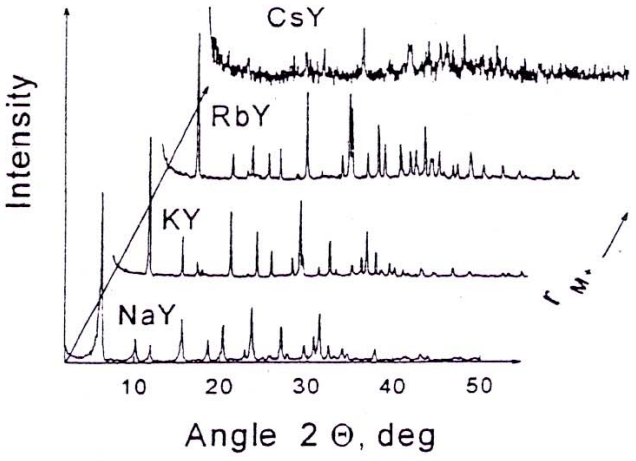


Figure 1. X-ray diffraction pattern of zeolites NaY, KY, RbY and CsY (CuKα-radiation).

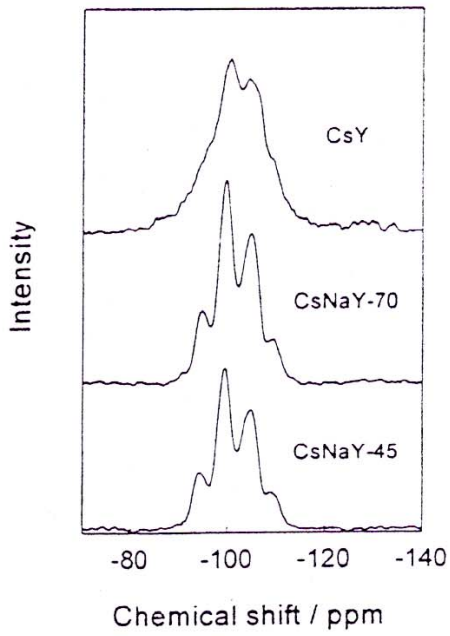


Figure 2. ^{29}Si MAS NMR spectra of Cs^+ exchanged Y-zeolites with different Cs^+-contents.

prepared by ion exchange in aqueous solution) the lines are significantly broadened. This line broadening indicates that probably some framework distortion occurred, which is caused by the incorporation of the large amount of cesium cations. Such a framework distortion could also explain the distortions in the X-ray powder pattern of CsY.

The results of the chemical analyses and the adsorption capacities for water are summarized in Table 1. For all samples, the molar amount of alkali metal equals the amount of aluminum present in the zeolite framework. This suggests that complete ion exchange was achieved. In addition, the linear correlation between the $Cs3d_{5/2}$/Si2p XP intensity ratio and the number of Cs atoms in the unit cell (Figure 3) clearly shows that these are homogeneously distributed throughout the crystallites after solid state ion exchange in CsY, and deposition on the external surface is excluded. The quantitative disappearance of the Na1s emission is also consistent with 100 % ion exchange. The adsorption capacities for water decrease with increasing size of the exchanged cation. Under the assumption that the structural integrity of the zeolite framework was virtually preserved, the decrease in adsorption capacity is at present tentatively attributed to (i) an increase in the volume of the cation which results in a reduced intra-zeolitic void volume, and (ii) a blockade of the six-membered ring windows in the faujasite structure by the larger alkali metal cations so that water has no longer access to the void volume inside the sodalite cages.

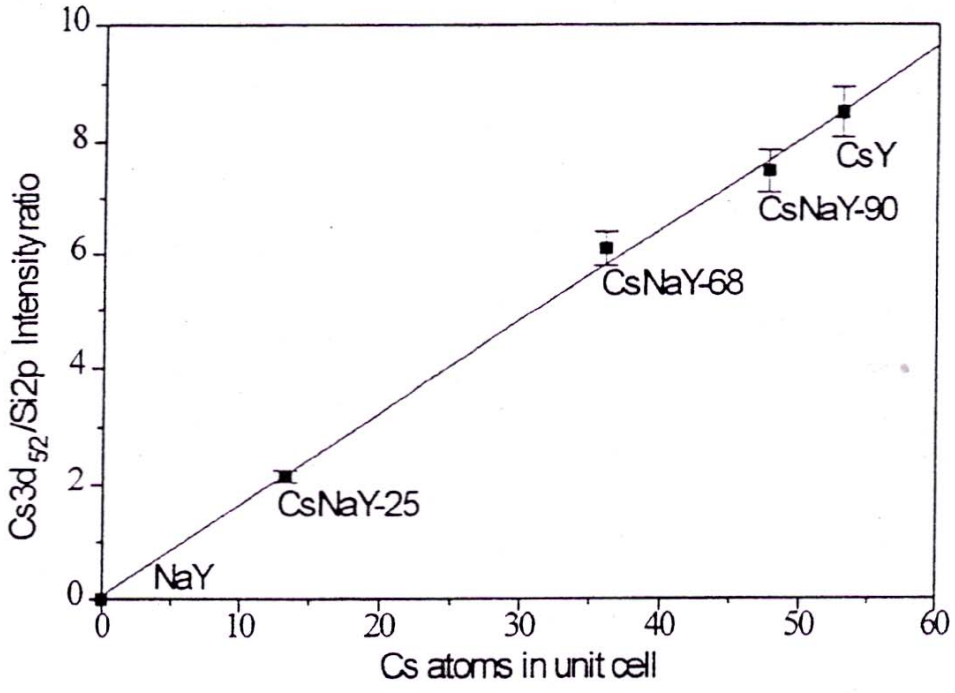


Figure 3. $Cs3d_{5/2}$/Si2p XP intensity ratio as a function of number of Cs atoms in unit cell.

It has been shown previously [13] that the cesium population of the different cation sites in Y-type zeolites can be derived from ^{133}Cs MAS NMR measurements. Figure 4 shows the actual ^{133}Cs MAS NMR spectrum of the CsY zeolite prepared in the present study (a), the simulated spectrum (b), and the individual components derived from deconvolution (c). The spectrum consists of four lines at -78 ppm, -66 ppm, -61 ppm and +57 ppm. Based on earlier

results [13], the lines at -78 ppm, -66 ppm and -61 ppm can be assigned to cesium cations on sites I' (in the sodalite cages), III and II (both in the large supercages). The assignment of the line at +57 ppm, which occurs only in the completely exchanged CsY-type zeolite is based on analogies with earlier NMR investigations related to the positions of lanthanum in zeolite LaNaY [14]. At present, it is tentatively assumed that this line results from CsOH species located in the sodalite (β-) cages of the faujasite structure. Quantitative data on the cation population as derived from ^{133}Cs MAS NMR spectroscopy are given in Table 2.

Table 1:
Chemical compositions and sorption capacities for water

	NaY	KY	RbY	CsY
n_{Si} / n_{Al}	2.62	2.62	2.62	2.62
n_{M^+} / n_{Al}	1.0 ± 0.03	0.98 ± 0.03	0.96 ± 0.06	1.01 ± 0.03
formula	$M_{53}[(AlO_2)_{53}(SiO_2)_{139}]$, M: alkali metal			
m_{H2O} / m_Z, %	34	25	18	15

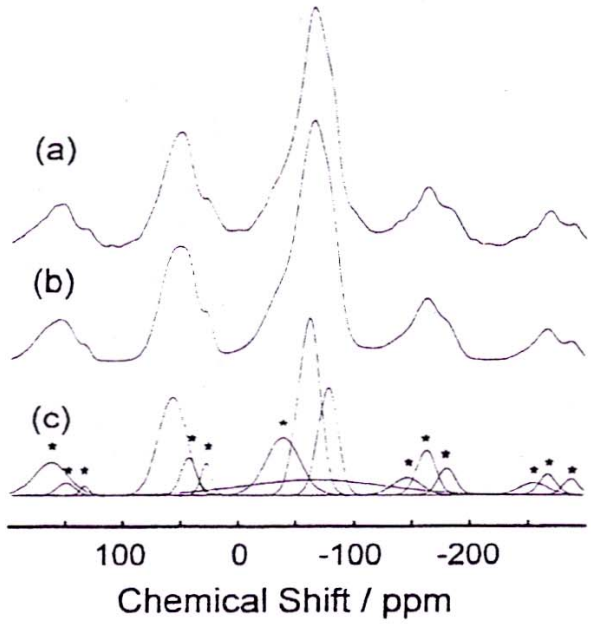


Figure 4. ^{133}Cs MAS NMR spectrum of zeolite CsY prepared in the present study (a), the simulated spectrum (b) and the individual components (c). The asterisks denote spinning side bands.

A physical characterization of the basic properties of the alkali Y zeolites was attempted by XPS and FTIR spectroscopy of CO, $CDCl_3$ and CO_2 probe molecules. O1s binding energies (accuracy ± 0.2 eV) of 531.8, 531.1, 531.3 and 530.9 eV were measured for the Na^+, K^+, Rb^+ and Cs^+ forms, respectively, at 100 % exchange level of the Y-zeolite. For the partially Cs^+-exchanged NaY, a continuous shift of the O1s binding energies from 531.8 to 530.9 eV was

Table 2:
Cs^+ population of the cation sites in zeolite CsY

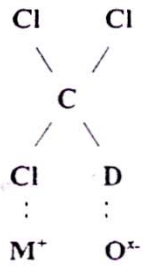
site	I'	III	II	CsOH/β-cage
chemical shift / ppm	-78	-66	-61	+57
n_{Cs+} / uc	9	6	17	21

observed when the Cs content is varied between 0 and 100 %. The interpretation of O1s binding energy shifts in terms of variations of basic strength is by no means straightforward. However, since the present samples have identical Si/Al ratios and since the effect of the cation identity on the Madelung potentials at the sites in the framework is negligible [15], the decreasing O1s binding energy with decreasing electronegativity of the alkali ion may in fact be interpreted in terms of increasing charge density and hence, base strength at the framework oxygens. The experimental values seem to suggest that the most significant enhancement of the base strength occurs from NaY to KY ($\Delta E_b \approx 0.7$ eV), while only comparably small additional changes should be expected when going to RbY and CsY.

CO is coordinated to the alkali cations at 88 K. The carbonyl stretching frequency is very close to the gas phase frequency (2143 cm^{-1}) in CsY (2145 cm^{-1}) and increases with the electronegativity of the alkali cation, as shown in Figure 5.

Cl_3CD is a CH-acid and is expected to probe basic surface sites [16]. Figure 6 shows FTIR spectra of Cl_3CD adsorbed on CsY at room temperature in the C-D streching region. There are two bands at 2239 and 2173 cm^{-1} suggesting the presence of two types of adsorbed species, namely type A and B (M^+= alkali cation):

A:



2239 cm^{-1}

B: $O^{x-} \ldots D - CCl_3$

2173 cm^{-1}

The low-frequency component is attributed to a C_{3v} species type B adsorbed through an acid-base interaction. Hence, the frequency shift of the C-D stretching mode relative to the gas phase frequency at 2253 cm^{-1} should be a measure of the basic strength of the O^{x-} framework site. For the series of alkali Y-zeolites NaY, KY, RbY and CsY frequencies of 2225, 2220, 2205 and 2173 cm^{-1} were observed, respectively. Consistent with the O1s binding energies, this suggests increasing basic strength of the zeolite framework oxygen atoms as the electronegativity of the exchangeable cations decreases.

CO_2 is frequently used to probe basic surface sites [17]. When CO_2 is adsorbed in CsY at room temperature, the antisymmetric stretching mode was observed at 2345 cm^{-1}, and the symmetric stretching mode was weakly activated due to symmetry reduction. The corresponding species is most probably interacting with the Cs^+ cations and is very weakly adsorbed, as it is quantitatively desorbed on evacuation at room temperature. Weak bands of

surface carbonates were also detected for KY, RbY and CsY. These carbonates might perhaps be formed on alkali oxide clusters which might be present in minute quantities. Although the present data do not permit a quantitative determination of the basic strength of the Y-zeolites under study, the CO_2 adsorption results suggest that the basic strength is quite moderate even in the most basic CsY material.

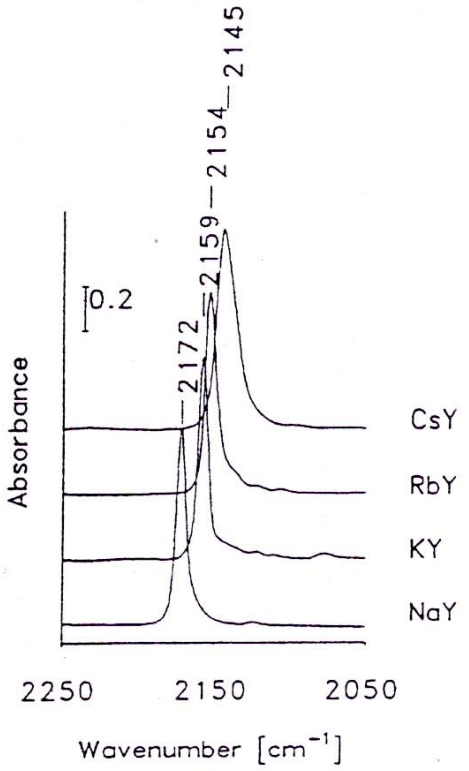


Figure 5. FTIR spectra of 0.6 hPa CO adsorbed at 88 K on alkali Y-zeolites.

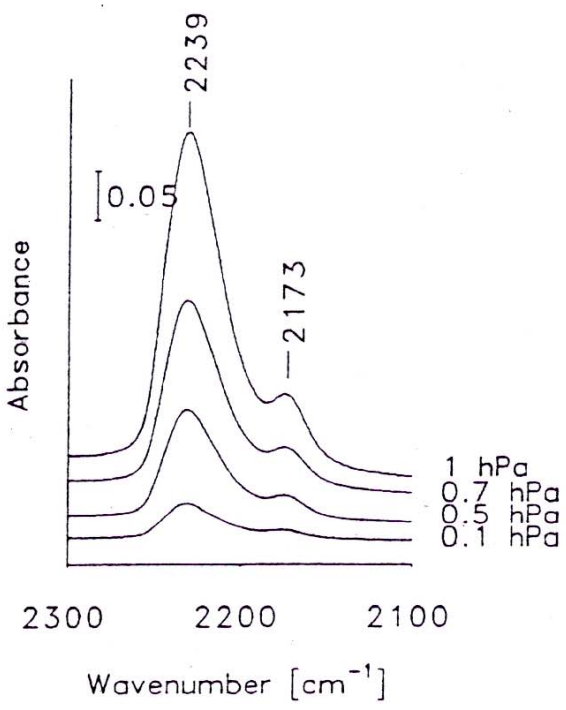


Figure 6. FTIR spectra of Cl_3CD adsorbed on CsY at room temperature.

3.2. Conversion of Isopropanol and Butan-2-ol

Isopropanol (iProl) conversion is a frequently used test reaction in acid-base catalysis. In this context, it is generally accepted that acid sites catalyze the formation of propene or diisopropylether, while over basic sites isopropanol is converted to acetone [8]. However, mechanisms for the dehydration of secondary alcohols over basic sites have been discussed as well [17-19]. The results of isopropanol conversion at 473 and 673 K over the alkali metal exchanged Y-type zeolites are presented in Table 3. For comparison, data obtained with a typical Brönsted-acid faujasite-type zeolite (viz. MgNaY) are also included.

Already at a reaction temperature of 473 K, isopropanol dehydration occurs over the acid reference catalyst (MgNaY). For the alkali cation exchanged zeolites, the activity is generally much lower and decreases with increasing size of the cation. In no case the product of the base catalyzed reaction (acetone) was observed. Upon increasing the reaction temperature to 673 K, acetone formation does occur over the K^+- and Rb^+-exchanged zeolites. Unexpectedly, however, zeolite CsY clearly behaves like an acid catalyst. In order to elucidate in more detail the source of this acidity, CsY was characterized by ^1H MAS NMR spectroscopy, both directly after the solid state ion exchange and after the activation procedure at 775 K. In general, the obtained spectra consist of two major resonance lines identified as bridging OH-

groups (Brönsted-acid sites, chemical shift of 4.0 ppm) and OH^--groups associated to Cs^+ cations (CsOH, chemical shift of 6.7 ppm due to its location in the sodalite cages and the development of hydrogen bonds to lattice oxygens). After the activation, however, the intensity of the resonance line attributed to Brönsted-acid sites (at 4.0 ppm) is considerably reduced, most probably due to the occurrence of dehydroxylation at the relatively high activation temperature. From these data, it is tentatively concluded that, under the conditions applied in the present study, solid state ion exchange of zeolite NH_4Y with CsOH does not proceed in a quantitative manner. Therefore, although the chemical analysis suggests complete ion exchange, the final catalyst contains some CsOH species as well as residual Brönsted-acid sites, hence the unexpected behavior of CsY in the catalytic tests. From CsOH deposited in pores, the formation of small amounts of Cs_2O could be envisaged which explains the occurrence of surface carbonates upon CO_2-adsorption (vide supra).

Table 3.
Activities and selectivities in the conversion of isopropanol over alkali cation exchanged Y-type zeolites and over MgNaY (data taken after 5 h time on stream).

		MgNaY	NaY	KY	RbY	CsY
	$\frac{W/F_{iProl}}{g \cdot h/mol}$	22	55	55	55	55
T = 473 K	X_{iProl} / %	5	0.5	0.005	0.001	0
	$S_{acetone}$ / %	0	0	0	0	0
	$\frac{W/F_{iProl}}{g \cdot h/mol}$	2.4	0.6	6	6	0.6
T = 673 K	X_{iProl} / %	100	2	2	10	3
	$S_{acetone}$ / %	0	0	60	12.5	0

It should be noted that the selectivity in the conversion of butan-2-ol was also shifted from dehydration towards dehydrogenation as the cation electronegativity decreased. Among the dehydration products, the but-1-ene percentage was considerably higher than that in the equilibrium composition at reaction temperature (423 K), this observation being characteristic for base-catalyzed dehydrations [17].

3.3. Conversion of Methanol

Over Brönsted-acid sites, methanol is known to be converted to dimethylether (DME) and further to hydrocarbons (HC), whereas over basic sites, methanol is decomposed to carbon monoxide (and hydrogen) [20]. The results obtained with the materials prepared in this study are summarized in Table 4.

As expected, methanol is completely converted to hydrocarbons (and water) over the acid reference catalyst (MgNaY). Over the alkali cation exchanged zeolites, both conversion of methanol to dimethylether (acid-catalyzed) and CO-formation (base-catalyzed) are observed. These results suggest that residual Brönsted-acid sites (probably of low acid strength which suffices for dimethylether formation) as well as mildly basic sites are present. However, no clearcut tendency of the influence of the alkali cation on the basic properties of the zeolite could be observed, most probably due to the interference of (different) residual amounts of acid OH-groups in the different catalysts.

Table 4.
Conversion of methanol (MeOH) over MgNaY and the alkali cation exchanged Y-type zeolites (data taken after 5 h time on stream).

	MgNaY	NaY	KY	RbY	CsY
$\frac{W/F_{MeOH}}{g \cdot h/mol}$	290	290	140	140	140
X_{MeOH} / %	100	15	9	33	19
S_{CO} / %	0	63	68	27	24

4. CONCLUSIONS

100% cation exchanged KY-, RbY- and CsY-zeolites have been prepared from NaY as starting material. This was achieved for KY by exchange in aqueous solution, whereas solid state ion exchange had to be applied for the Rb- and Cs-forms using NH_4Y as the starting material. As shown by XRD and ^{29}Si MAS NMR, the zeolite framework remained intact although some lattice distortions were evident for the materials containing the larger cations. O1s XP binding energies and the adsorption of Cl_3CD as a probe for basic sites suggested that the basic strength of lattice oxygen slightly increases as the alkali cation electronegativity decreases. Carbon dioxide adsorption on KY, RbY and CsY indicated the formation of small amounts of alkali hydroxide and/or oxide clusters. This suggests that - although the stoichiometry of the materials was consistent with 100 % exchange within the limits of experimental accuracy - the cation exchange was not complete. Consequently, an equivalent number of charge-compensating protons must have been retained in the zeolites. The corresponding bridging OH groups were in fact detected by ^{1}H MAS NMR. The catalytic behavior of the synthesized materials in the conversion of secondary alcohols and methanol were tentatively interpreted on the basis of their physicochemical properties. The ion exchange procedures will be further optimized such as to prepare homogeneous materials avoiding the deposition of alkali hydroxide/oxide cluster formation.

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