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Side-chain alkylation of toluene with methanol on Cs-exchanged NaY zeolites: effect of Cs loading

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The side-chain alkylation of toluene with methanol was studied on Cs-exchanged NaY zeolites containing up to 31% Cs (exchange degree, ED, up to 70%). Formation of styrene and ethylbenzene was significant only on Na(Cs)Y zeolites of ED higher than about 40%. Bimolecular side-chain alkylation reaction would require a proper surface geometric configuration of $O^{\delta-}$-Cs^{+} pairs that is achieved only on Cs-rich zeolites. In contrast, the side reaction forming carbon monoxide from methanol increases monotonically with increasing ED because it is essentially controlled by the basicity of the oxygen lattice.

KEY WORDS: side-chain alkylations; toluene alkylation; styrene; basic zeolites.

1. Introduction

The side-chain alkylation of toluene with methanol for producing a mixture of styrene and ethylbenzene offers economical advantages compared with the conventional homogeneously catalyzed Friedel-Crafts process that uses ethylene and benzene as reactants [1] The reaction is catalyzed by solid bases and has been widely studied, particularly on basic zeolites [2–4]. However, both the reaction mechanism and the active site requirements for enhancing the selectivity toward styrene are not completely understood yet. It has been reported that the side-chain alkylation of toluene with methanol requires a cooperative action of acid/base pairs for efficiently promoting the rate-limiting step in the reaction mechanism [5,6] but other authors suggested that catalyst selectivity is essentially governed by the overall acid–base strength as measured by Sanderson electronegativity [7]. In particular, Palomares *et al.* [8] studied by *in situ* infrared spectroscopy the sorption and reaction of toluene and methanol over basic catalysts with the aim of ascertaining the requirements for side chain alkylation.In an attempt to obtain more insight on the active site requirements for the alkylation of toluene with methanol on alkali-exchanged zeolites, we recently explored a new approach for relating the solid surface properties with its catalytic performance based on selective acid–base poisoning [9]. We concluded that active sites involving surface acid–base pairs are required for promoting the rate-limiting step of the reaction mechanism.

Although base oxides such as MgO and CaO have been used for side-chain alkylations [10], several studies indicate that the zeolite pores might be indispensable to efficiently catalyze the reaction [11]. The superior catalytic performance shown for alkali-exchanged zeolites has been explained by considering that the reaction occurs via formation of a benzyl carbanion intermediate that could be stabilized within the restricted micropores of high-aluminum zeolites structure [12]. Recently, it was highlighted the potential role of substrate electrophilicity to stabilize this carbanion intermediate [13].

Previous studies attempting to relate the zeolite basicity with its ability to promote the side-chain alkylation of toluene have employed zeolites of different structure, such as zeolites L, Y, and X, or containing different exchanged cation, such as Cs, K, Rb, or Na [3,6,7]. However, the effect that varying the exchange degree has on the zeolite selectivity has not been investigated. It is expected that the gradual substitution of, for example, Na for Cs in NaY zeolites will gradually decrease the Sanderson intermediate electronegativity of the zeolite. This would provide a practical and fine tuning of the surface basic properties that could be more rigorously related with resulting changes on the zeolite selectivity. In this paper we have prepared a set of Cs-exchanged NaY zeolites with exchange degrees between 0% and 70% and tested them for the gas-phase alkylation of toluene with methanol. Results will show that, in addition to the surface basicity strength, a minimum density of Cs active sites is required on Na(Cs)Y zeolites to catalyze the side-chain alkylation reaction of toluene with methanol. This is explained by considering that bimolecular side-chain alkylation would require a specific $O^{\delta-}$-Cs^{+} pairs configuration for activating both

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toluene and methanol, that is achieved on Na(Cs)Y zeolites only for exchange degrees higher than about 40%.

2. Experimental

Catalysts were prepared by exchanging a commercial NaY zeolite (UOP Y-54, Si/Al: 2.65) with Cs acetate (Sigma, 99.8%). Ion exchanges were carried out either at 353 K and 1 atm (Method A) or in an autoclave at 413 K (Method B), using different Cs acetate concentration, contact time (θ_i) and number of exchanges (N_i). Following each individual exchange step, the zeolites were washed with hot water, dried at 393 K, and calcined in air at 723 K for 4 h. The exchange degree (ED) was determined by measuring elemental compositions by atomic absorption spectroscopy (AAS), using a Perkin Elmer 3110 spectrometer. Details of the samples and the preparation method are given in table 1.

The solid structure in zeolite samples was characterized by X-ray diffraction (XRD) methods, in the range of $2\theta = 0$–70°, using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu Kα radiation ($\lambda = 1.540$ Å). Total surface areas (S_g) were measured by N_2 physisorption at 77 K using a Quantachrome Nova-1000 sorptometer and BET analysis methods.

The structure of CO_2 chemisorbed on the samples was determined by infrared spectroscopy (IR). Data were obtained using a Shimadzu 8101 M Fourier transform spectrometer after CO_2 adsorption at room temperature and sequential evacuation at 298 and 373 K. The spectral resolution was 4 cm^{-1} and 40 scans were coadded. Samples were pressed into thin self-supporting wafers (15 mg/cm^2) and heated in vacuum at 773 K for 2 h; spectra were taken at room temperature. An inverted T-shaped Pyrex cell containing the sample wafer was used. The two ends of the short arm of the T were fitted with CaF_2 windows. Brönsted and Lewis surface acid sites were determined by recording the IR spectra of adsorbed pyridine. Sample wafer was heated in vacuum up to 773 K and held for 2 h at this temperature. After cooling to room temperature, the sample IR spectrum was recorded. Excess pyridine was then adsorbed at room temperature on the sample and allowed to equilibrate for 15 min. Spectra were taken after evacuation at 298 and 423 K. The IR spectrometer and cell equipment were the same described above for studying CO_2 chemisorption.

Gas-phase alkylation of toluene with methanol was carried out in a differential fixed-bed tubular reactor at 1 atm. Samples were sieved to retain particles with 0.35–0.42 mm diameter for catalytic measurements and treated in air at 723 K for 2 h before reaction in order to remove H_2O, hydrocarbons, and CO_2. A mixture of toluene (EM Science, 99.5%) and methanol (Merck, 99.8%) of 1:1 molar ratio was vaporized in a preheating section and delivered to the reactor. The reaction was carried out at in N_2 at 708 K and 101.3 kPa, employing a space velocity (WHSV) of 2 h^{-1}. Reaction products were analyzed by on-line gas chromatography using an Hewlett-Packard 5890 chromatograph equipped with a Supelcowax 10^{TM} column. Data were collected every 0.5 h during 6 h. Toluene conversion (X_{tol} mol of toluene reacted/mol of toluene fed) was calculated as: X_{tol} (%) = [T Y_j/(T Y_j + Y_{Tol})]·100, where T Y_j is the molar fractions of aromatic products, including benzene, and Y_{Tol} is the outlet molar fraction of toluene. The selectivity to product j (S_j, mol of product j/mol of toluene reacted) was determined as:$S_j(\%) = [Y_j/\Sigma Y_j]\cdot 100$.

Table 1
Samples obtained by exchanging NaY zeolite with Cs acetate

Sample	Exchange method	θ_i[a] (h)	N_i[b]	Cs acetate concentration (mol/L)	Cs content[c] (%)	ED (%)	S_g (m^2/g)	E_{int}[d]	δ_O[e]
NaY	–	–	–	–	0	0	700	3.53	−0.354
CsY1	A	0.5	1	0.03	8	18.2	580	3.47	−0.365
CsY2	A	1.0	1	0.03	13	29.6	560	3.44	−0.372
CsY3	B	2.0	1	0.10	11	24.3	580	3.46	−0.369
CsY4	A	0.5	1	0.20	15	35.3	565	3.43	−0.376
CsY5	A	1.0	2	0.03	16	36.4	520	3.42	−0.377
CsY6	A	1.5	1	0.20	22	50.0	500	3.38	−0.385
CsY7	B	2.0	2	0.10	18	41.0	530	3.41	−0.379
CsY8	B	2.0	3	0.10	22	50.0	550	3.38	−0.385
CsY9	A	1.0	3	0.03	24	54.6	370	3.37	−0.387
CsY10	B	2.0	4	0.10	23	52.3	550	3.38	−0.386
CsY11	A	2.0	2	0.20	28	64.3	408	3.34	−0.393
CsY12	A	2.0	4	0.40	30	68.3	456	3.33	−0.396
CsY13	A	2.0	4	0.20	31	69.6	370	3.33	−0.396

[a] Contact time.
[b] Number of exchanges.
[c] Determined by AAS.
[d] Sanderson intermediate electronegativity.
[e] Oxygen charge.

The $S_{St\text{-}E}$ selectivity is the sum of ethylbenzene and styrene, which are the side-chain alkylation products. In toluene basis, the product yields (η_j, mol of product j/mol of toluene fed) were calculated as $\eta_j = S_jX_{tol}$.

3. Results and discussion

3.1. Catalyst characterization

Results in table 1 show that the value of ED was increased from 0 up to about 70% by varying the experimental parameters (Cs acetate concentration, contact time, and number of consecutive exchange operations) involved in methods A and B used for exchanging Na by Cs in the parent NaY zeolite. As previously stated [14, 15], the maximum ED value expected to be achieved by ion exchange for Cs in NaY is about 70% because in aqueous solution large Cs cations are not able to pass the 6-ring windows of the sodalite cages and exchange with Na cations hidden in this position

Figure 1 shows the X-ray diffraction patterns of zeolites NaY, CsY1, CsY5, CsY11, and CsY13. The diffractograms show solely reflections corresponding to faujasite. However, significant changes in the relative diffraction line intensities are observed by comparing the XRD patterns of NaY with those of Cs-exchanged zeolites, probably because the incorporation of alkaline metal cations bigger than Na^+ changes the structure factors and X-ray absorption coefficients of the parent NaY zeolite [16].

On the other hand, in figure 2 we have plotted the sample surface area as a function of ED. It is observed that S_g decreases monotonically with increasing ED, irrespective of the preparation method used in this work. The surface area of parent NaY zeolite (700 m^2/g) diminishes, in fact, to about 370 m^2/g for ED ≅ 70%.

The structure of chemisorbed CO_2 species on zeolites NaY and CsY12 was determined by FTIR measurements of preadsorbed CO_2. Figure 3 presents the IR spectra obtained on the catalysts after CO_2 adsorption and sequential evacuation at 298 and 373 K. The parent NaY zeolite exhibited infrared bands at around 1710, 1690, 1645 and 1370 cm^{-1}. Adsorption of CO_2 on CsY

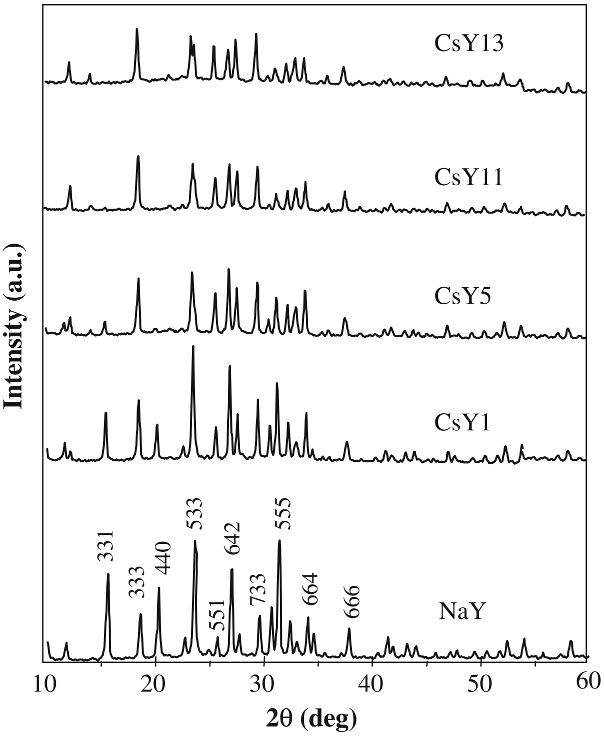

Figure 1. XRD diffraction patterns of NaY and Cs-exchanged NaY zeolites.

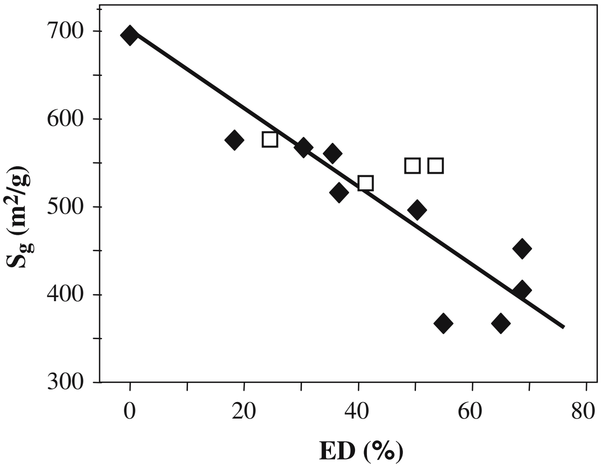

Figure 2. BET surface areas of Cs-exchanged NaY zeolites as a function of the exchange degree (ED). Zeolite NaY exchanged by method A (◆) and method B (□).

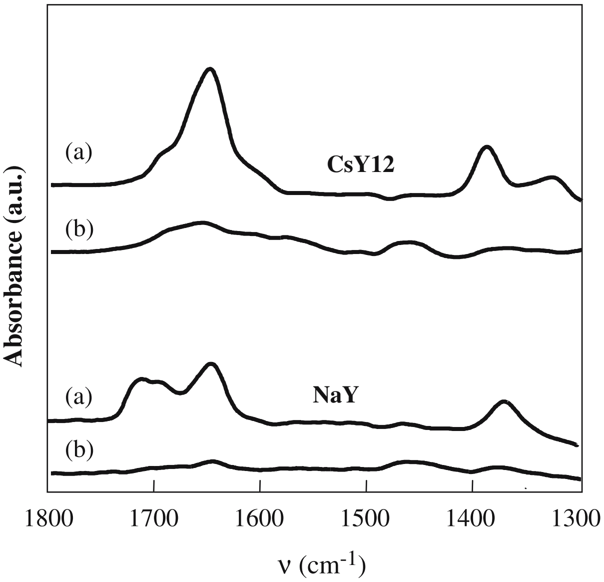

Figure 3. IR spectra of CO_2 adsorbed on zeolites NaY and CsY12 at 298 K and evacuated at: (a) 298 K; (b) 373 K.

12 revealed similar IR bands: 1690, 1650, and 1390 with shoulders at 1600, and 1330 cm^{-1}. According to the literature [17–19], bidentate carbonates form on Lewis acid-Brönsted base pairs (M^{n+}-O^{2-}, where M^{n+} is the metal cation), and shows a symmetric O–C–O stretching at 1320–1340 cm^{-1} and an asymmetric O–C–O stretching at 1610–1630 cm^{-1}. Unidentate carbonate formation requires stronger basic sites and exhibits an asymmetric O–C–O stretching at 1510–1560 cm^{-1} and a symmetric O–C–O stretching at 1360–1400 cm^{-1}. The IR spectra of figure 3 show therefore that zeolites NaY and CsY12 form essentially bidentate carbonate species. Nevertheless, the IR bands on CsY12 were slightly shifted toward the positions of unidentate carbonate species, suggesting an increase of the surface oxygen basicity [20]. Bidentate carbonates species on NaY zeolite disappear after evacuation at 373 K; in contrast, a fraction of the bidentade carbonate species remains adsorbed on the CsY12 surface after outgassing at 373 K. This confirms that zeolite CsY12 contains stronger basic sites than NaY, and is consistent with an increase in the basicity of framework oxygens upon exchange of Na by a cation of lower electronegativity.

The IR spectra in the hydroxyl-stretching region (not shown here) of zeolites CsY12 and NaY were obtained after sample evacuation at 773 K for 4 h. No absorption bands were detected for both samples, thereby indicating that the hydroxyl group concentration on these zeolites is negligible.

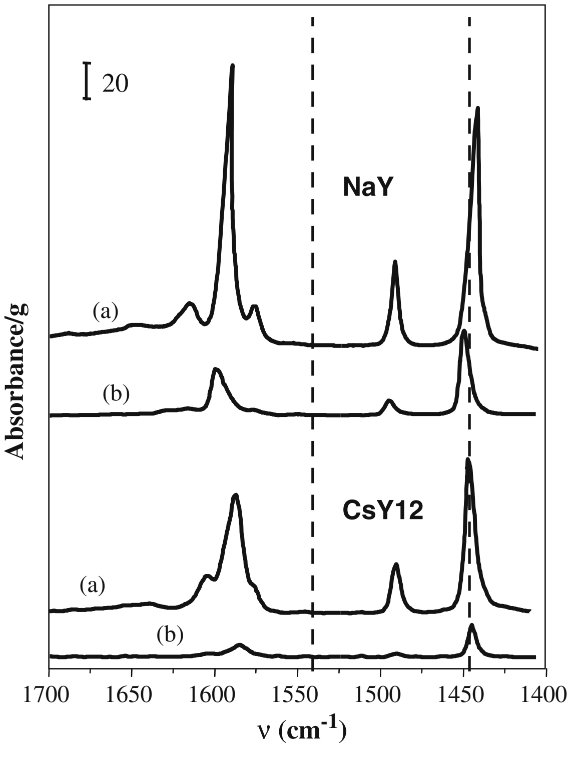

Figure 4. IR spectra of pyridine adsorbed on zeolites NaY and CsY12 at 298 K and evacuated at: (a) 298 K; (b) 423 K.

The density and nature of surface acid sites were determined from the IR spectra of adsorbed pyridine. Figure 4 shows the spectra obtained on zeolites CsY12 and NaY after admission of pyridine, adsorption at room temperature, and sequential evacuation at 298 and 423 K. The peaks at about 1450 y 1540 cm^{-1} arise from pyridine adsorbed on Lewis and Brönsted acid sites on zeolites [21–23]. Pyridine absorption spectra in figure 4 do not reveal any Brönsted acidity on zeolites CsY12 and NaY, which is consistent with FTIR results showing that the concentration of hydroxyl groups on both samples is negligible. The band representing Lewis acid centers appears on NaY at about 1440–1444 cm^{-1} after evacuation at 298 and 423 K, a frequency considerable lower as compared to those determined for similar bands on non-zeolitic Al-MCM-41 and SiO_2–Al_2O_3 samples [24]. This frequency shift has been interpreted by considering that the pyridine is adsorbed on NaY by a polarization of the molecule in the field due to cation [22], i.e. the interaction is associated with Na rather than to Al. Figure 4 shows that the FTIR bands accounting for coordinately bound pyridine on CsY12 appear at similar frequencies than on NaY, but pyridine was more easily eliminated on CsY12 than on NaY by evacuating the samples at 423 K. This result showed that sample CsY12 contains weaker Lewis acid sites than NaY, as expected taking into account the lower electronegativity of Cs than Na on Sanderson electronegativity estimates.

3.2. Catalytic results

Figure 5 shows toluene conversion and product selectivities obtained at 708 K on zeolites CsY1 (ED = 18%) and CsY13 (ED = 69.6%), and typically illustrates the time-on-stream behavior of the catalysts during the reaction. Low-Cs content CsY1 zeolite was poorly active for converting toluene ($X_{tol} \cong 3.6\%$) and formed exclusively xylenes ($S_{Xy} = 89\%$) and heavy alkylated compounds (C_9^+), such as tri and tetramethylbenzenes. In contrast, zeolite CsY13 yielded essentially styrene and ethylbenzene ($S_{St\text{-}E} = 94\%$), and minor amounts of xylenes, benzene, and C_9^+ compounds. Moreover, CsY13 converted toluene at high rates ($X_{tol} \cong 8.2\%$) as compared to CsY1. No significant activity decay was observed on both zeolites during the catalytic runs. Results of figure 5 clearly show that the activity and selectivity of Cs-exchanged NaY zeolites for toluene conversion reactions greatly depend on the Cs loading. Zeolite CsY1 that contains 8% of Cs does not display any activity for the side-chain alkylation of toluene with methanol while on zeolite CsY13 containing 28% of Cs the selectivity to side-chain alkylation products is higher than 90%.

In order to obtain more insight on the effect of Cs loading on toluene/methanol conversion reactions, we carried out additional catalytic tests using all the samples of table 1. In figure 6 we have represented the evolution of the selectivity to the main products resulting from ring (xylenes) and side-chain (styrene/ethylbenzene) alkylations with the exchange degree of Cs-exchanged NaY zeolites. Samples containing up to about 18% of Cs (ED $\cong$ 40%) form exclusively ring alkylation products, in particular xylenes. Product selectivities do not change significantly with Cs loading on these low-content Cs samples, producing all of them about 90% of xylenes. However, and because low-content Cs samples were poorly active, the yield to xylenes was lower than 4%. Increasing the sample Cs concentration further drastically changes the product selectivity, and side-chain alkylation products, specifically styrene and ethylbenzene, become the predominant reaction products. For example, $S_{\text{St-E}}$ was 88% on sample CsY6 that contains 22% of Cs (ED = 50%), and 94% on samples containing about 30% Cs (ED = 64–70%). Results of figure 6 clearly shows therefore that Cs-exchanged NaY zeolites require a minimum concentration of surface Cs sites for promoting the side chain alkylation of toluene with methanol that is reached when the exchange degree is about 40%. Figure 6 also shows that the yield to chain alkylation products ($\eta_{\text{St-E}}$) increases monotonically with ED for samples of ED greater than about 40%. In other words, on high-content Cs samples the conversion of toluene to styrene/ethylbenzene increases proportionally to the Cs loading.

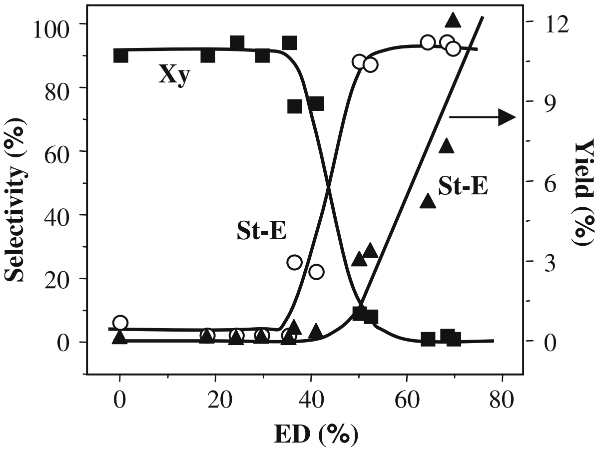

Figure 6. Product selectivities and yields as a function of the exchange degree on Cs exchanged NaY zeolites. T = 708 K, P = 101.3 kPa, $P_{\mathrm{CH_3OH}}$ = 3.85 kPa, WHSV = 2 h^{-1}, toluene:methanol = 1.

In previous works [7,25], the ability of different zeolites for selectively alkylating the methyl group of toluene to form styrene and ethylbenzene has been relating with the Sanderson intermediate electronegativity (E_{int}). Specifically, it was pointed out that zeolites with an intermediate electronegativity less than about 3.6 form essentially styrene and ethylbenzene. In contrast, acid-catalyzed alkylation of the aromatic ring to produce xylenes preferentially would occur over zeolites with an intermediate electronegativity greater than 3.6. We calculated here the E_{int} values for our sample set following the method described in [26] and using the electronegativity value of atom i, E_{i}, proposed by Sanderson in [27]; results are shown in table 1. From the obtained E_{int} values, we calculated also the oxygen charge in the zeolite framework (δ_{O}) by equation 1 considering for oxygen electronegativity a value of $E_{\text{O}} = 5.21$ [27] (table 1).

$$\delta_{\text{O}} = \frac{E_{\text{int}} - E_{\text{O}}}{2.08\sqrt{E_{\text{O}}}} \tag{1}$$

Results in table 1 show that the intermediate electronegativity of our Na(Cs)Y zeolite decreases monotonically with increasing Cs content, from 3.53 (NaY) to 3.33 (CsY13, ED = 69.6%), while the oxygen charge concomitantly increases from −0.354 (NaY) to −0.396 (CsY13). In spite of that the oxygen charge, and consequently the sample basicity, increases when NaY zeolite is gradually exchanged with Cs, the side-chain alkylation of toluene remains negligible up to reaching an ED value of about 40% (figure 7), that correspond to a E_{int} value of approximately 3.4. Increasing the ED value further dramatically changes the zeolite selectivity, forming almost exclusively styrene and ethylbenzene. This result clearly suggests that, in addition to the surface basicity strength, a minimum density of Cs active sites is required on Na(Cs)Y zeolites to catalyze the

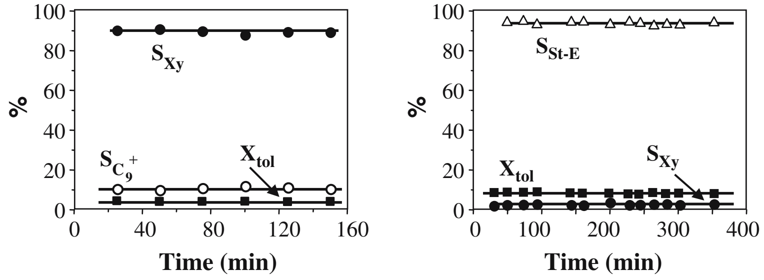

Figure 5. Toluene conversion and product selectivities as a function of time on: (a) CsY1; (b) CsY13. T = 708 K, P = 101.3 kPa, $P_{\mathrm{CH_3OH}}$ = 3.85 kPa, WHSV = 2 h^{-1}, toluene:methanol = 1.

side-chain alkylation reaction of toluene with methanol. Bimolecular side-chain alkylation reaction would require proper acid–base pair sites for activating both reactants, toluene and methanol. Specifically, $O^{\delta-}$ surface basic sites are needed for activating the carbon atom in the methyl group of toluene and also for dehydrogenating methanol to formaldehyde, which is generally believed to be the actual alkylating agent to form styrene [11]. But Cs^+ Lewis acid sites are also required to bound toluene via its aromatic ring [6]. Thus, a specific $O^{\delta-}$-Cs^+ pair configuration is needed to promote the adjacent adsorption of C_1 species and bulkier toluene-derived species. Our results suggest that in terms of catalytic activity this surface geometric configuration becomes significant only when the ED value reaches about 40%. The number $O^{\delta-}$-Cs^+ pair sites increases by increasing ED further thereby explaining the resulting increase of the styrene/ethylbenzene yield on Cs-rich zeolites observed in figure 7.

On the other hand, the major side reaction during toluene alkylation with methanol over solid bases is usually the formation of carbon monoxide by methanol decomposition. On our samples, we observed that in addition to the reaction with toluene, methanol forms significant amounts of CO and dimethylether (DME). In figure 7 we have represented the methanol conversion and product yields on methanol basis as a function of ED for our Cs exchanged NaY zeolites. The conversion of methanol (X_M) was about 80% over the entire zeolite composition range; i.e. X_M does not change significantly by increasing the amount of Cs in the Na(Cs)Y zeolite. In contrast, figure 7 shows that the CO yield increases monotonically with ED at expenses of the formation of DME, reaching a value of $\eta_{CO} \cong 71\%$ on sample CsY13 (ED = 69.6%). Such an increase of η_{CO} probably reflects the stronger basicity of the oxygen lattice with increasing ED, according to the oxygen charge calculated in table 1; it has already been noted, in fact, that strongly basic sites catalyze rupture of CH bonds in the alkylating agent [28]. It has to be noted here that in contrast with formation of styrene and ethylbenzene, methanol decomposition to CO parallels the change in the Sanderson intermediate electronegativity of the zeolite.

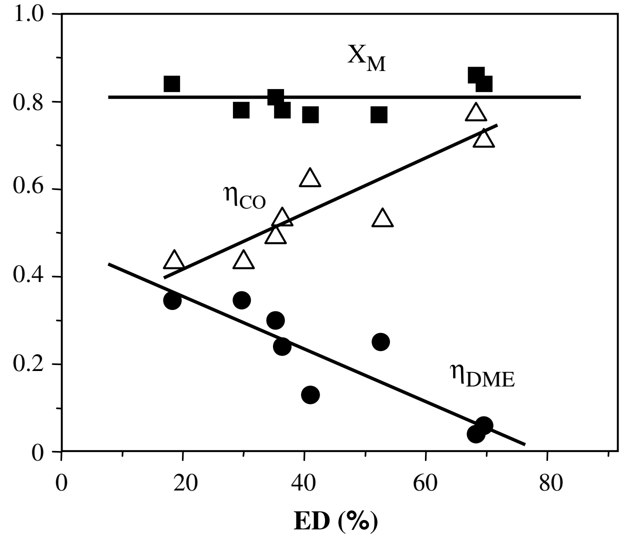

Figure 7. Methanol conversion and product yields on methanol basis as a function of ED for Cs exchanged NaY zeolites. T = 708 K, P = 101.3 kPa, P_{CH_3OH} = 3.85 kPa, WHSV = 2 h^{-1}, toluene:methanol = 1.

Dimethylether formation rate decreases with increasing ED and becomes negligible for Cs-rich zeolites (figure 7). Alcohol dehydration to ethers is a second-order reaction that involves the adsorption of two alcohol molecules on neighboring active sites offering different acid–base properties [29,30]. One alcohol molecule adsorbs through the oxygen of the OH group on a Lewis acid site whereas the other alcohol molecule adsorbs on a basic site via the hydroxylic hydrogen. On our Na(Cs)Y zeolites, the strength of the interaction between methanol and the catalyst is mainly determined by the coordinatively bonding between the metal cation and the lone pair of the oxygen of the OH group [6]. The strength of methanol sorption is therefore stronger on more electronegative, and consequently more acidic, metal cations. The substitution of Na for less electronegative Cs atoms decreases the Lewis acidity of the zeolite, as stated here by using FTIR of pyridine, and will diminish the strength of methanol to the solid. The decrease of DME formation rate with ED in figure 7 is probably explained then by a diminution of the Lewis acidity of Na(Cs)Y zeolites when increasing the Cs loading.

4. Conclusions

The activity and selectivity of Na(Cs)Y zeolites for the alkylation of toluene with methanol greatly depend on the exchange degree. Zeolites of exchange degrees lower than about 40% exhibit poor activity and form essentially ring alkylation products, namely xylenes. Increasing the exchange degree further dramatically changes the zeolite selectivity, forming almost exclusively styrene and ethylbenzene. On these Cs-rich samples the conversion of toluene to styrene/ethylbenzene increases proportionally to the Cs loading. In addition to the surface basicity strength, bimolecular side-chain alkylation reaction would require a specific $O^{\delta-}$-Cs^+ pair configuration to promote the adjacent adsorption of C_1 species and bulkier toluene-derived species. In terms of catalytic activity this surface geometric configuration becomes significant only when the exchange degree is higher than about 40%. In contrast, decomposition of methanol to carbon monoxide increases monotonically with the exchange degree and parallels the change in the Sanderson intermediate electronegativity of the zeolite. Formation of carbon monoxide increases with the basicity of the oxygen lattice because strong basic sites catalyze rupture of CH bonds in the formaldehyde alkylating agent.

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