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EFFECT OF ALKALI METAL IONS ON DIFFERENT ZEOLITES FOR ALKYLATION OF CUMENE

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Abstract

The effects of alkali metal treatment on different zeolite catalysts are investigated to better understand the nature of alkali metal species for the selective catalytic alkylation of cumene by ethylene.

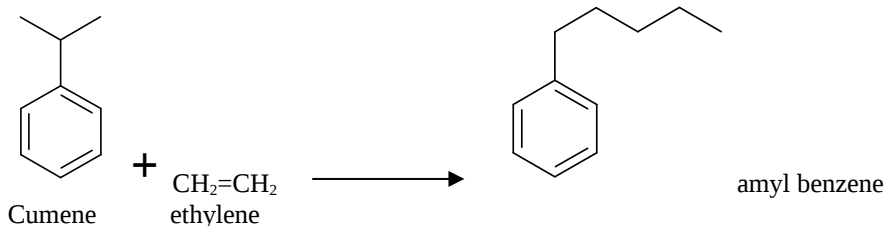
H-ZSM5, Y and BEA zeolite catalysts with various molar ratios of K, Rb, and Cs are prepared by ion exchange method and calcined at 550 °C in air atmosphere for 2 h. The study was carried out at 300, 350, 400 and 450 °C for reaction times of 2 hours. Cumene conversion was found to increase with all different alkali metal additions and the reaction temperatures. The catalysts are characterized by temperature-programmed desorption of NH₃/ or CO₂ (TPD), Fourier transform infrared (FT-IR) after pyridine adsorption and inductively-coupled plasma emission spectrometry (i.c.p.e.s.). The FTIR results are compared to Lewis and Brønsted acid sites. Furthermore, the relation between atomic size of alkali metal ion exchanged and the basicity of the catalyst is discussed. Among them the 0.025 M Cs exchanged is found as very active catalyst for alkylation of cumene with ethylene resulted in amyl benzene, styrene and ethyl benzene.

Keywords: ZSM-5, Y, BEA zeolite, alkylation, TPD, ICPEs, FTIR.

Introduction

Crystalline microporous materials such as zeolites are used as catalysts for acid-base catalyzed reactions [1]. They can be prepared with well-defined and isolated acid/base sites [2] in combination with a wide range of pore dimensions [3] matching the size of the organic reactants. This allows the chemical reactions to take place in a specifically chosen and well-defined environment (i.e., in the cages or channels of the molecular sieves, which act as nano scale reactors). To improve reaction yields and selectivities, knowledge of the chemical and structural properties of the active sites and their relation to the sorbent-sorbate structure is essential for a rational catalyst design.

For the alkylation of cumene with ethylene, it was found that zeolites with predominantly basic properties catalyze side chain alkylation i.e., the formation of amyl benzene, on addition of toluene, each of styrene and ethyl benzene are side products resulted in decomposition of cumene.



This study is designed to explore the relation between addition of alkali metal ions (K^+ , Rb^+ , Cs^+) into Y, BEA and ZSM-5 zeolites catalysts and their acidity. Acidity of these catalysts was investigated by Fourier transform infrared (FTIR) after pyridine adsorption, temperature programmed reduction (TPD) with CO_2 or NH_3 adsorption and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The physicochemical properties of three commercial zeolites – namely BEA, X, Y and ZSM-5 – for the alkylation of cumene with ethyl benzene were investigated. BEA, Y and ZSM-5 are widely known for their regular pore structures and high surface areas. While BEA and Y have large pores sizes, ZSM-5 has medium pore sizes [4-9].

Clearly, the basic character of the catalysts affects the side-chain alkylation of toluene. However, the porosity of the catalysts may also play a critical role in the reaction since nearly all of the active catalysts studied to date are microporous.

The aim of this work is to determine the variation of the acidity of ZSM-5, Y and BEA zeolites catalysts by the addition of alkali metal cations.

2. Experimental

2.1. Materials

HZSM-5 (Modul $SiO_2/Al_2O_3 = 25.5$) supplied by PQ Zeolites (CBV 2050E). X and Y zeolites in the sodium form are also provided by Zeolyst International Company (CBV100). BEA zeolite in the sodium form was obtained from Chemie Uetikon AG (ZEOCAT® PB). Cs, Rb, and K alkali cations exchanged HZSM-5, NaY and BEA zeolites were prepared using cesium chloride, potassium chloride, and rubidium chloride (99.9%). The suspension was stirred at $100^\circ C$ for 22 h, cooled to room temperature, washed, dried, and subsequently calcined in a muffle furnace in air atmosphere at $550^\circ C$ for 2 h.

2.2. Apparatus and techniques

ICP-AES

Bulk elemental analysis is measured with Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES) on a spectroflame D (Spectro Analytic

Instrument). The samples are dried at 120°C for 24 h. Then they are solved in the mixture of 2 ml 98 % H₂SO₄, 44 ml distilled water and 4 ml HF (40 %). In few cases ultrasound bath is used to dissolve samples.

Temperature programmed techniques (TPD)

The TPD analysis is conducted on a Carlo Erba TPDRO 1100 Series Thermo Finnigan. The samples are degassed at 500 °C in a helium atmosphere. NH₃ or CO₂ are physisorbed at room temperature. Then the samples are heated up to 600 °C at 1 °/min and the amounts of desorbed gas are recorded by the TCD.

Infrared spectroscopy

FT-IR spectra of samples are taken in the range of 4000-400 cm⁻¹ on a (Nicolet Protégé 460), equipped with an evacuable furnace cell with KBr windows, containing sample wafer. Initially, catalyst powder is pressed into a 5 mm wafer, which is loaded into the IR chamber and heated up 400 °C over night under reduced pressure of 10⁻³ mbar. After the cell was cooled down to 50 °C the background spectra is recorded. The spectra are always collected as an average of 200 runs with 0.5 cm⁻¹ definition.

The pyridine adsorption is carried out slowly where the catalyst is equilibrated with pyridine vapours at 50 °C. The spectrum is recorded and heated stepwise scanning with IR spectroscopy after 60 minutes evacuation.

2.3. Catalytic activity measurements

The catalytic alkylation of cumene with ethylene is studied at different temperatures starting from 300 to 450 °C under atmospheric pressure. Prior to the reaction test; the catalyst is pretreated at 500 °C using 3 L / hour ethylene as carrier gas.

Catalyst powders are pressed at 10 tons to tablets, which are crushed and sieved (0.63- 1mm) [10]. The catalyst grains are loaded into the single pass stainless steel fixed bed reactor. All the experiments are carried out over 3.5 grams catalyst.

3. Results and discussion

3.1. Catalyst characteristics

3.1.1. Acidity and Basicity

The acidity of the pure HZSM-5 catalyst calcined at 550 °C is determined by NH₃-TPD. Figure (1) shows two well resolved desorption peaks: the low temperature peak (LTP) at 140-275 °C and the high temperature peak (HTP) at 420-580 °C. Generally, LTP and HTP correspond to weak and strong acid sites [9, 10],

respectively. On the other hand, TPD-CO₂ analyses give almost a straight line. This means that, there are only a few basic sites in HZSM-5 catalyst. Recently Ordonsky and co-works [9] found the same result when they analyzed HZSM-5 by NH₃-TPD, since they attributed these two peaks observed at the same temperatures to weak and strong acid sites.

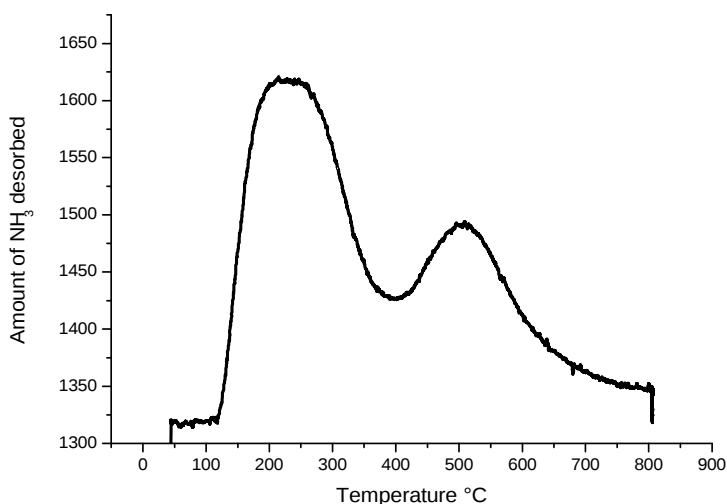


Fig. (1) NH₃-TPD curve of HZSM-5.

FT-IR spectra of pyridine adsorbed on HZSM-5 and the ZSM-5 catalyst ion exchanged with 0.025 M Na, K, Rb and Cs and calcined at 550 °C are shown in Fig. (2).

In all the spectra, there are well-resolved bands at about 1440, 1545, 1575, 1640 and 1490 cm⁻¹. The bands located at 1440 and 1575 cm⁻¹ are assigned to pyridine adsorbed on Lewis acid-bound, whereas the bands assigned at 1545 and 1640 cm⁻¹ corresponding to Broensted acid-bound. The bond assigned at 1490 cm⁻¹ is corresponding to both Lewis and Broensted acid-bound [10, 11]. On the other hand, a noticeable decrease in the amplitude of the bands is shown with increasing of atomic size of alkali metals. So, it is clear from Figure (2) that KZSM-5 exhibits more acidic nature than that the other alkali metals.

Figure (3) represents the NH₃-TPD analysis of 0.025 M K and 0.025 M Cs exchanged HZSM-5.

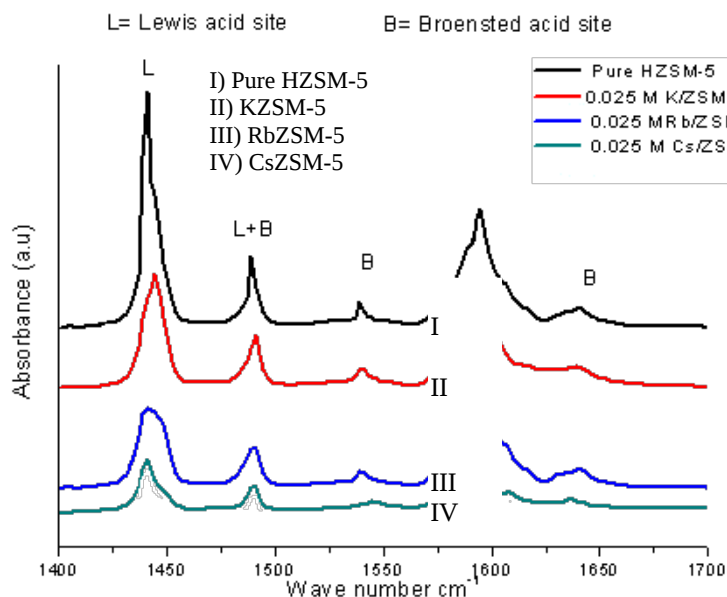


Fig. (2) FT-IR spectra of pyridine adsorbed on HZSM-5 and the different ion exchanged catalysts at 100 °C in the region 1400 – 1700 cm^{-1} .

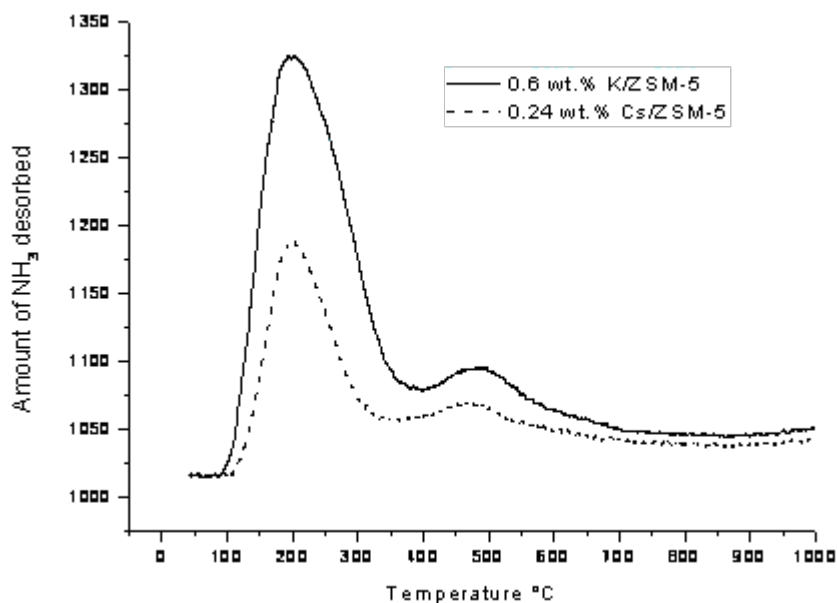


Fig. (3) NH_3 -TPD curves of HZSM-5 ion exchanged with 0.025 M of KCl and CsCl.

Two desorption peaks maximized at 200 and 460 °C are observed for both samples. These two peaks may correspond to weak and strong acid sites, respectively [12]. It can be also observed that, 0.025 M KZSM-5 has a higher amount of NH_3 adsorbed than that of 0.025 M Cs/ZSM-5.

Investigation of the basicity of pure Y zeolite catalyst is detected and plotted in figure (4).

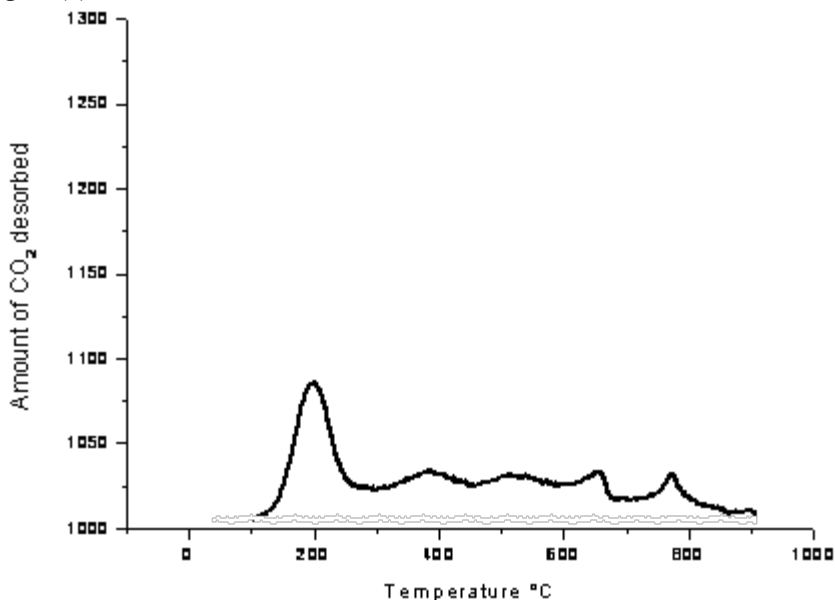


Fig. (4) CO_2 -TPD desorption curves of pure Y zeolite.

Figure 4 shows CO_2 -TPD desorption curves of pure Y zeolite, where three small peaks have been detected at 200, 680 and 780°C respectively. These peaks corresponded to weak, medium and strong acid sites [12, 13]. That means a view basic sites are found on pure Y zeolite catalyst.

Figure 5 shows the NH_3 -TPD curves of the different metal ion exchanged Y zeolite. Since pure Y zeolite has one desorption peak starting at around 150 °C. This peak is shifted to 250 °C for the other alkali metal ions exchanged Y zeolites, corresponding to mild acid site [12, 13]. It can be observed, that the amount of NH_3 adsorbed decreased by increasing atomic size of alkali metal ion exchanged. Therefore NaY zeolite has highest amount of NH_3 desorbed than other alkali metal ion containing material. This means pure Y zeolite has more acidic sites than the others alkali metal ion exchanged materials. In contrast, 0.025 M Cs/Y zeolite has

lowest amount of NH₃ desorption than others alkali metal ions; therefore 0.025 M Cs/Y zeolite has lowest acidic sites, but most probably the highest basic sites.

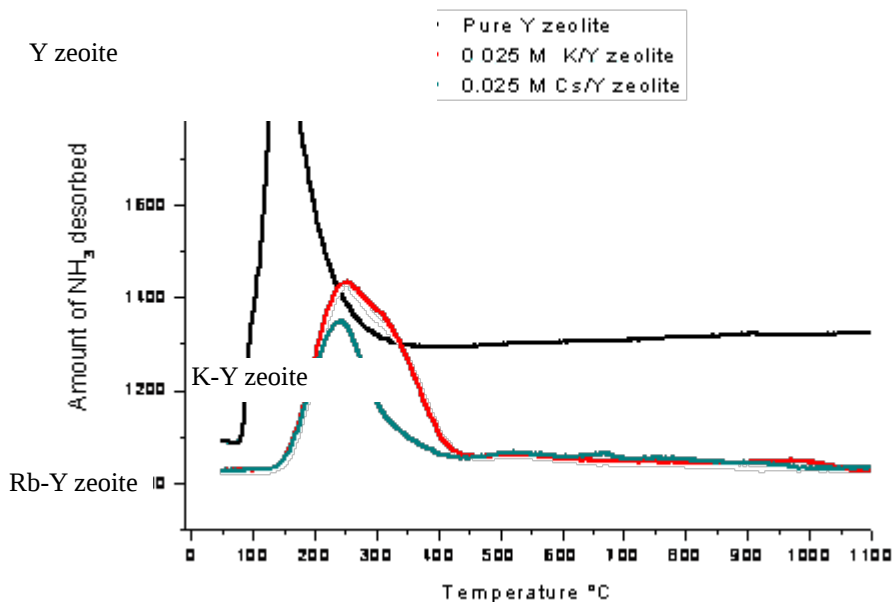


Fig. (5) NH₃-TPD curves of pure Y zeolite, 0.025 M K and 0.025 Cs /Y zeolite.

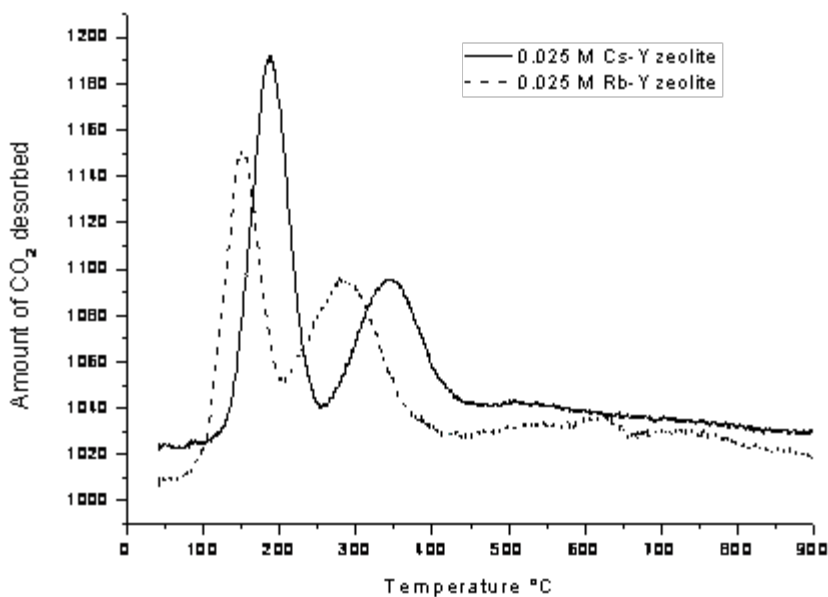


Fig. (6) CO₂-TPD desorption curves of 0.025 M Rb and Cs / Y-zeolite.

Figure (6) shows the CO₂-TPD curves of the Rb and Cs metal ions exchanged Y zeolite. For 0.025 M Cs/Y zeolite the desorption peaks are at 150 and 300 °C and for 0.025 M RbY about 200 and 350°C, respectively [13]. That means both zeolites have weak and medium strong basic sites. The Cs containing sample contains higher basic strength than the Rb containing material. The amount of the CO₂ desorbed increases slightly by increasing the atomic size of alkali metals.

In the CO₂-TPD NaBEA zeolite gives only a little desorption of CO₂ in contrast to the Rb and Cs BEA zeolites (see Figure 7).

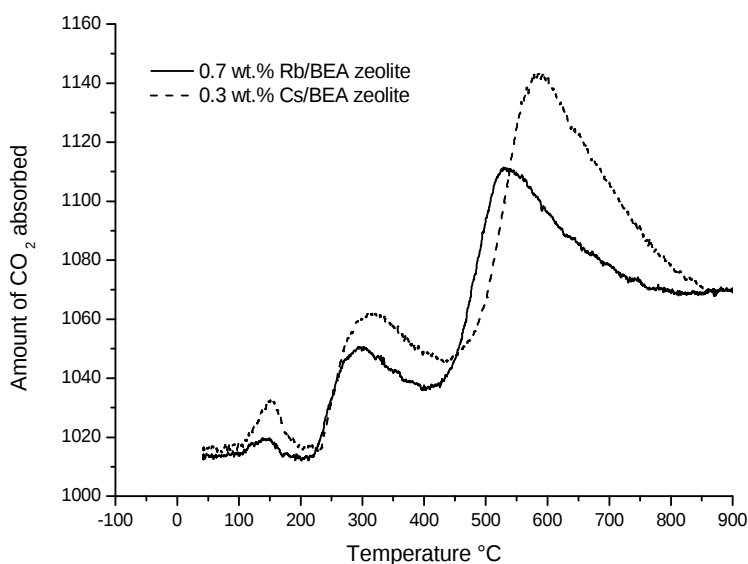


Fig. (7) CO₂-TPD adsorption curves of Rb and Cs / BEA zeolite.

Three adsorption peaks at 150, 300 and 530 °C for Rb-BEA zeolite, and at 150, 300 and 590 °C for Cs-BEA corresponding to weak, medium and strong basic sites, respectively, were indicated [13]. The basic property of Cs exchanged BEA-zeolite is somewhat stronger than the Rb-BEA zeolite.

Figure (8) illustrates the NH₃-TPD curves of the different metal ions exchanged BEA zeolites.

Pure BEA zeolite

K-BEA zeolite

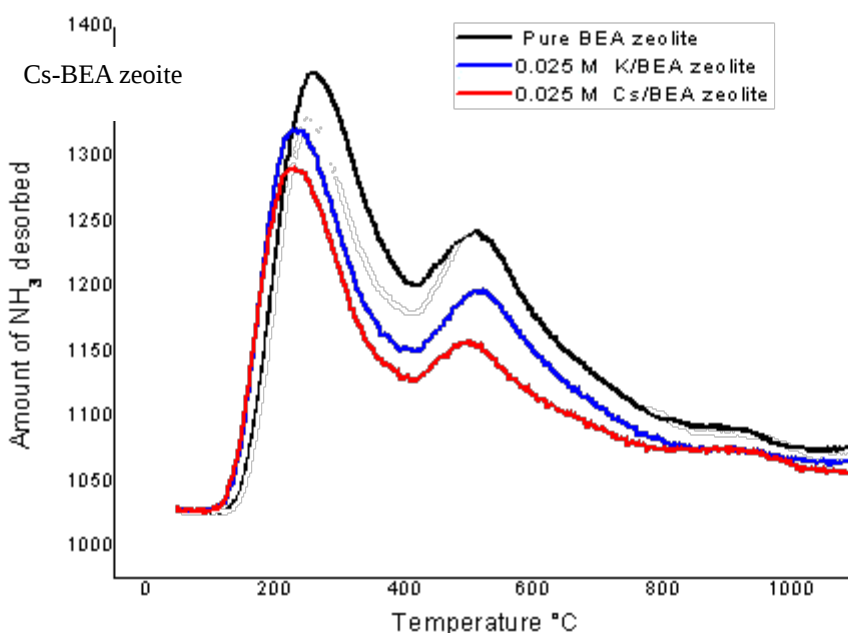


Fig. (8) NH_3 -TPD curves of BEA zeolite treated with 0.025 M KCl and CsCl solutions.

All curves have two desorption peaks starting at about 250 and 500 °C, corresponding to weak and strong acid sites, respectively.

This indicates that the acidic properties of different metal ion exchanged on BEA-zeolite are still present and roughly the same. But it is observed that the desorbed amount of NH_3 somewhat increases by decreasing atomic size of alkali metal ion exchange. Pure BEA zeolite has higher desorption of NH_3 . That means it has more acidic sites than the others alkali metal ion exchanged catalysts. NH_3 -TPD analyses of different alkali metals on BEA zeolite should be in agreement with alkylation results on the aromatic ring.

Recently, Delgado and Arean [8] studied the adsorption of Carbon monoxide, dinitrogen and carbon dioxide on Beta-zeolite, and they concluded that, all of these gases investigated form adsorption complexes with the Brønsted acid OH groups of the Beta-zeolite as testified by both, corresponding changes in the O-H stretching band and simultaneous appearance of the characteristic IR absorption bands of the adsorbed molecules.

3.1.2. ICP analyses

Si/Al ratios of alkali ZSM-5 are decreased with increasing the size of the alkali metal used for the exchange (Table 1) due to increase of the number of basic sites on ZSM-5 [14]. It can be observed that the weight of silicon decline with increase of the size of alkali metal. However, the concomitant decrease in Si/Al ratio affects the strengths of the acidic sites, hence catalytic activity and selectivity [15].

Table 1: Summary of ICP AES analyses ion exchanged of HZSM-5 with different metals.

Sample	Aluminium (mg/g)	Silicon (mg/g)	Si/Al (weight/weight)	Alkali metal (mg/g)
Pure ZSM-5	14.8	421	28.5	1.63
0.025 M KCl/ZSM-5	13	412	31.7	6
0.025 M RbCl/ZSM-5	12.9	400	31	4
0.025 M CsCl/ZSM-5	12.5	370	29.6	2.4

Pure ZSM5 has lower weight of Si and higher weight of Al than the other ion exchanged materials; as a result this catalyst has a higher share of acidity than the other alkali exchanged catalysts [16].

Different concentrations of alkali metals on BEA zeolite as provided from Chemie Uetikon AG (ZEOCAT® PB) are presented in Table (2).

Table 2: Summary of ICP AES analyses ion exchanged of BEA zeolite with different Metals.

Sample	Aluminium (mg/g)	Silicon (mg/g)	Si/Al (weight/weight)	Alkali metal (mg/g)
Pure NaBEA	39.3	388	9.87	2.5
0.025 M KCl/ BEA	38.5	390.7	10.10	9.2
0.025 M RbCl/ BEA	38.8	393.6	10.14	7
0.025 M CsCl/ BEA	37.9	389.3	10.27	3

Si/Al ratios of alkali BEA were increased with increasing the size of the alkali metal used for the exchange. This results in an increase of the number of basic sites on BEA zeolite [17]. Pure BEA has lower weight of Si and higher weight of Al than the other ion exchanged materials; as a result pure BEA zeolite catalyst has a higher share of acidity than the other alkali exchanged catalysts [16].

3.2. Cumene alkylation with ethylene over pure zeolite catalysts

Alkylation of cumene with ethylene over pure HZSM-5 catalyst is presented in Table (3), at different temperatures in the range from 300 up to 450 °C under atmospheric pressure.

Table 3: Alkylation of cumene with ethylene over HZSM-5 catalyst at different reaction temperatures.

Reaction temperatures	Conversion cumene (mol. %)	Sele. styrene (mol.%)	Sele. ethyl benzene (mol.%)	Sele. benzene (mol.%)	Sele. Toluene (mol.%)	Sele. amyl benzene (mol.%)
300 °C	60	0	1.4	45	54	0
350 °C	88	0.2	5	47	48	0
400 °C	93	0.3	5.2	51	42.3	0
450 °C	93	0.3	5.1	55	40	0

Conversion of cumene slightly increases with increasing temperatures and reaches up to 93 mol. % at 400 °C to form mainly benzene and toluene. The selectivity to benzene and toluene increased, too, due the decomposition of cumene. No amyl benzene detected at all reaction temperature. This means no basic sites on HZSM-5 catalyst fund. The side chain alkylation occurs on basic sites [16-18] of the catalysts. The major undesirable side reaction thereby is the decomposition of cumene to benzene and toluene.

Table (4) represents concerning cumene alkylation over Y-zeolite catalyst at different reaction temperatures.

Table 4: Alkylation of cumene with ethylene over Y-zeolite catalyst at different reaction temperatures.

Reaction temperatures	Conversion cumene (mol.%)	Sele. styrene (mol.%)	Sele. ethyl benzene (mol.%)	Sele. benzene (mol.%)	Sele. Toluene (mol.%)	Sele. amyl benzene (mol.%)
300 °C	40	0	0.9	40	58	0.1
350 °C	49	0	3	46	51	0.2
400 °C	69	0.1	5	50	44	0.2
450 °C	70	0.11	5.1	51	43	0.3

Conversion of cumene increases with increasing temperatures and reaches up to 70 mol. % at 450 °C. The high selectivity to benzene and toluene observed due to

the decomposition of cumene. Only a small amount of amyl benzene is detected at different reaction temperature. This may linked with the basic sites present on Y zeolite catalyst. That is in agreement with the acidity and basicity CO₂-TPD analyses (Figure 4).

Alkylation of cumene over pure BEA zeolite catalyst at different reaction temperature was presented in Table (5).

At 450 °C maximum conversion of cumene is detected to form mainly benzene. A little higher amount of amyl benzene than in case of pure Y zeolite detected. Selectivity of ethyl benzene is increased with increasing reaction temperature reaching to 11.8 mol. % at 450 °C.

Table 5: Alkylation of cumene with ethylene over BEA zeolite catalyst at different reaction temperatures.

Reaction temperatures	Conversion cumene (mol.%)	Sele. styrene (mol.%)	Sele. ethyl benzene (mol.%)	Sele. benzene (mol.%)	Selec. Toluene (mol.%)	Sele. amyl benzene (mol.%)
300 °C	19	0	1.5	96	1.2	0.3
350 °C	38	0.5	9	87	2.9	0.5
400 °C	65	0.5	11	86	2	0.2
450 °C	71	0.4	11.8	84	3.5	0.3

In general 400 °C is suitable reaction temperature for alkylation of cumene because it has higher conversion of cumene and higher selective to styrene and ethyl benzene but a little bit more amyl benzene was found.

3.3. Effect of different alkali metals over HZSM-5 catalyst for alkylation of cumene

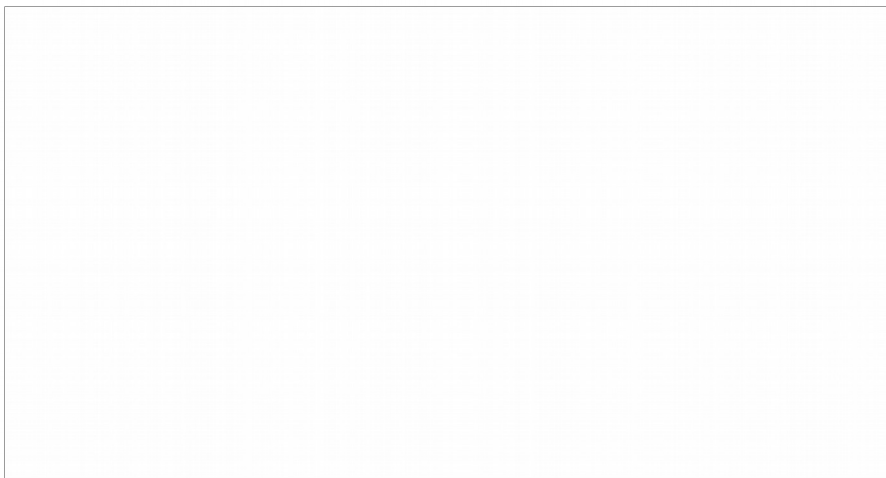
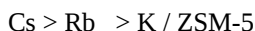


Fig. (9) Comparison between different alkali metal ions exchanged on ZSM5 at 400 °C for alkylation of cumene

The study of the comparison between different alkali metal ions exchanged HZSM-5 zeolite at 400 °C as suitable temperature is illustrated in Figure 9.

In the presence of Rb and Cs/ZSM-5, highest conversion of cumene at around 99 mol.% and lowest selectivities of styrene of about 4 mol.% are observed. The selectivity to amyl benzene increases with increasing the content of alkali metal addition on zeolite catalyst. Therefore it can be observed that Cs/ZSM-5 has highest selectivity to amyl benzene than other alkali metal ion addition. On the other hand, selectivity to benzene start decline by addition of alkali metal on ZSM-5 catalyst and decreases by increasing the size of alkali metal ion addition.

Order of decreasing activity and selectivity to amyl benzene was as follow:



Which is in great of agreement with the catalytic performance in the alkylation of cumene obtained before in the FT-IR spectra of pyridine adsorbed on the different alkali metal ions exchanged HZSM-5 (Figure 2)? Also these results are in good agreement with ICP analysis of different alkali metal exchanged on HZSM-5, since

the size of the alkali metal led to wt.% increase of the metals on HZSM-5 as well as to an increase in the Si/Al ratio. Such behavior is already found by Barthomeuf [19]. This means that side chain alkylation of cumene depends on the size of alkali metal ion exchanged on HZSM-5.

3.5. Effect of different alkali metals over Y-zeolite catalyst for alkylation of cumene

Figure 10 represents the effect of different alkali metal ion exchanged on Y zeolite catalyst for alkylation of cumene at 400 °C as suitable reaction temperature.

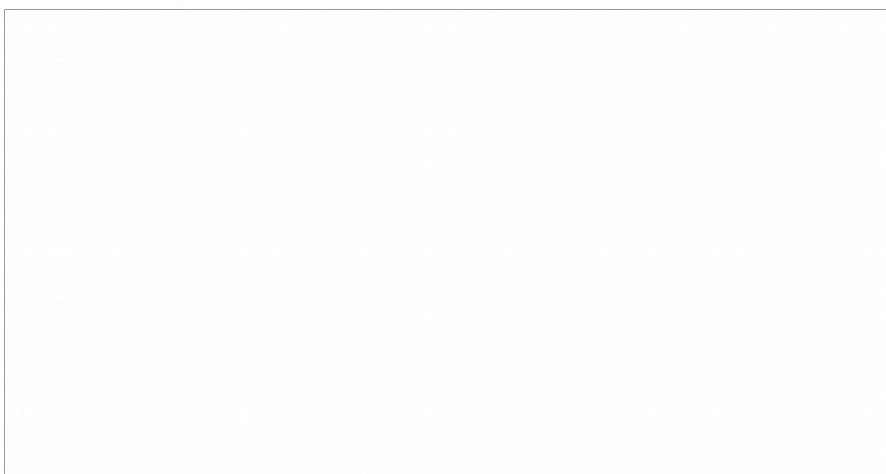


Fig. (10) Comparison between different alkali metal ions exchanged on Y zeolite at 400 °C for alkylation of cumene.

Maximum conversion of cumene (about 99 mol. %) was obtained when Rb and Cs are used for addition on Y zeolite. Selectivity to amyl benzene was increased by increasing the size of alkali metal addition reaching to maximum about 11 mol. % for Cs/Y zeolite. Rb/Y zeolite catalyst has maximum selectivity to styrene and toluene about 4.3 and 32 mol. % respectively. Selectivity to benzene was decreased with increasing of the size of alkali metal ions.

In general, in all reaction tests CsY-zeolite performed the highest selectivities to amyl benzene. This means that the selectivity to side chain alkylation increases with the increase of the cation size. These results are in agreement with the CO₂-TPD analyses (see Figure 6), since pure Y zeolite ion exchanged with 0.025 M CsCl solution has higher CO₂ desorption peak than the other zeolite catalysts.

Also, these results are in agreement with NH_3 -TPD analyses of pure Y-zeolite and different alkali metal ion added on Y-zeolite catalysis. Since, Cs/Y zeolite has lowest amount of NH_3 desorption than others alkali metal ions.

3.6. Effect of different alkali metals over BEA zeolite catalyst for alkylation of cumene

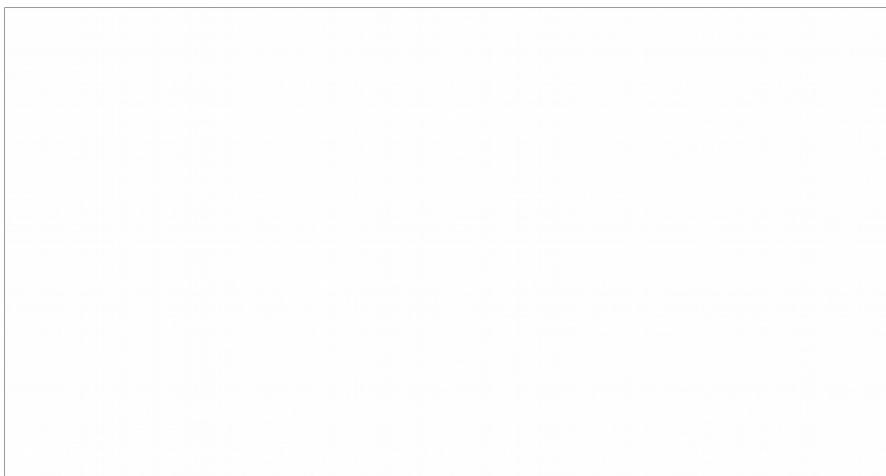


Fig. (11) Comparison between different alkali metal ions exchanged on NaBEA zeolite at 400 °C for alkylation of cumene.

The comparison between different alkali metal ions exchanged BEA zeolite should be studied at 400 °C as most suitable reaction temperature.

Figure (11) represents alkylation of cumene with ethylene over different alkali metal ion exchanged NaBEA zeolite at 400 °C. As found before the alkali metal exchange plays a role in the conversion of cumene and selectivities of amyl benzene and other products, therefore CsBEA zeolite results in highest conversion of cumene with about 86 mol.% and selectivities of amyl benzene, toluene and ethyl benzene reaches 2.2, 1 and 13 mol.% respectively. The CsBEA zeolite also performs the lowest selective for benzene. The selectivity to styrene is almost constant at around 0.4 mol. %.

Conclusion

Additions of alkali metal ions on zeolite raise the activity and selectivity of zeolites for side chain alkylation of cumene. The order of the alkali cation in the



When ZSM-5, Y and BEA zeolite catalysts treated with different concentrations of alkali metal, selectivity of amyl benzene is increased. On the other hand the selectivities to benzene and toluene were decreased.

Acknowledgements

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