

Study on thermal stabilities and symmetries of chemisorbed species formed on K-zeolites upon CO₂ adsorption by TPD and in situ IR spectroscopy

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Abstract In the current study, K-zeolites with different structure, Si/Al ratio and morphology have been prepared and then characterized by different techniques including in situ IR spectroscopy upon CO₂ sorption and CO₂-TPD with the aim of understanding the nature of basic sites present on their surface acting as catalytic sites in aldol condensation reaction. Results showed that depending on the zeolite structure, pore size and Si/Al ratio, two categories of basic sites could be present in potassium modified zeolites. Symmetries of chemisorbed CO₂ on these sites are different and comparing the results of TPD and in situ IR spectroscopy; it can be concluded that highly symmetric species (e.g., monodentate carbonates) have higher thermal stability than low symmetric adsorbed species (e.g., bidentate carbonates). It was found that in the zeolite with relatively smaller pore size or less accessible pores (e.g., MFI), second type of adsorbed species is more popular, while highly symmetric species tend to form on large pore zeolites and on materials with some mesoporosity (e.g., BEA or dealuminated FAU zeolites). It is observed that

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almost all the bidentate species are desorbed at 80 $^{\circ}$ C, while monodentate species are thermally stable at least up to 130 $^{\circ}$ C. Based on combination of experimental data obtained from TPD with IR spectroscopy results, origin and assignment of the TPD peaks were discussed.

Keywords TPD \cdot Zeolite \cdot CO₂ adsorption \cdot Basic sites \cdot Potassium \cdot IR spectroscopy

Introduction

Strength and distribution of acidic or basic sites on the surface of the zeolite catalysts are the most important characteristic of them for catalytic application, and numerous characterization techniques have been developed for identification and investigation of these sites. In the case of acidic catalyst, extensive researches have been performed due to their importance in petroleum chemistry; however, the research about basic catalyst is limited [1, 2]. Basic sites in the oxides and especially zeolites could have different origin and they may be observed directly in the zeolite framework [3] or more possibly as the extraframework species (e.g., oxides of alkali metals) [4]. It was reported that the negatively charged framework oxygen could act as basic site in the zeolites [2] and it is observed in FAU zeolites [5, 6]. As mentioned, the extra-framework species like clusters of the alkali metal oxides inside the zeolite pores could also act as strong basic sites [7]. Strong basic sites in the oxide materials have recently reported as catalyst for different chemical reactions (e.g., transesterification of glycerol [8], soot oxidation and NO_x reduction [9], methylation of phenol with methanol [10], biomass valorisation and aldol condensation [7, 11-17]). Usually, the basic solution like NaOH was implemented as

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homogenous catalyst for these reactions (e.g., aldol condensation [18]); however, heterogeneous catalyst as recyclable material offers green and economical pathways for this purpose. Potassium modified zeolites as heterogeneous recyclable basic catalysts have been recently implemented to facilitate different chemical reactions (e.g., biomass valorisation and aldol condensation [7], transesterification of glycerol [8]) and promising results have been obtained due to their numerous advantages like superior basic activity and shape selectivity [7]. To optimize these materials as basic catalyst, different active sites of them should be well characterized. In previous studies by our group [7, 19], it was reported that extra-framework K₂O clusters could be formed upon thermal activation of potassium modified zeolites prepared by wet impregnation procedure and these clusters are responsible for strong basic behavior of the obtained materials. Proton-accepting or electron pair donating sites (basic sites) in solid catalyst could be identified by suitable acidic molecule and the adsorption of acidic molecule or its reaction outcome could be implemented for characterization and quantification of basic sites. Many methods, e.g., vibrational spectroscopy [1, 20], microcalorimetry [2, 21], temperature programed desorption (TPD) [22] could be utilized for characterization of basic site upon sorption of the acidic probe molecules. Carbon dioxide is well-known acidic probe molecule for studying different basic sites in heterogeneous catalyst due to its abundance and less toxic properties. CO₂ chemisorbed in basic sites, while its interaction with acidic sites is very weak and physi-sorption of CO₂ occurred on acidic sites [20, 23]. Current study is devoted to characterize different basic sites formed in the potassium modified zeolites using CO_2 as probe molecule. For this aim, potassium modified zeolites have been prepared by wet impregnation procedure and temperature programmed desorption (TPD) of CO₂ and in situ IR spectroscopy upon CO₂ desorption were implemented to characterize active sites of prepared materials. Complementary textural and microstructural analyses like N2 sorption and field emission scanning electron microscopy (FE-SEM) techniques have been performed on prepared samples and obtained results implemented to describe the features of the prepared K-zeolites and to relate microstructures and texture of zeolites with distribution of different basic sites. The catalytic activities of investigated materials are also included to find the relation between distribution of different basic sites with catalytic yield and selectivity to aldol condensation of furfural and acetone.

Experimental

Material synthesis

Commercial H-FAU, H-BEA and H-MFI zeolites with different Si/Al ratio obtained from Zeolyst International and were implemented as parent zeolite for further modification by potassium. Parent zeolites (list of them is reported in Table 1) have been impregnated with potassium nitrate with similar procedure to the earlier report of our group [7]. Briefly, the as-received protonated zeolites were impregnated using aqueous KNO₃ solutions with concentration of 0.7 M of salt (Fig. S1). The suspension was stirred at 80 °C with the speed of 200 RPM for 2 h. Then, the solids were filtrated using a Buchner funnel without any washing. Resultant samples were then dried in ambient environment overnight and heat treated at T = 530 °C for 3 h. These samples were labeled as K-zeolite type(xx) where xx stands for Si/Al ratio of parent zeolite. Table 1 lists the descriptions of all prepared samples for the study.

Material characterization

The morphology of prepared materials was evaluated by scanning electron microscopy images using a JEOL JSM-7500F instrument with a cold cathode-field emission (parameters of measurements: 1 kV, GB high mode). BET surface area, micropore volumes and external surface were determined from nitrogen adsorption/desorption experiments performed at - 196 °C after sample activation in vacuum at 300 °C for 12 h using a Micromeritics ASAP 2020 unit and applying BET model and t-plot calculated by using of Harkins-Jura thickness curve equation. IR spectra of the prepared samples were recorded on Nicolet 6700 FTIR spectrometer equipped with a MCT detector. Before CO₂ adsorption coupled with IR experiments, the selfsupporting sample wafers were placed into a home-made IR cell for transmission spectra measurement. Samples were heat treated in a dynamic vacuum (residual pressure $< 10^{-4}$ mbar) overnight (12 h) at 450 °C. CO₂ adsorption was performed at room temperature, and initial pressure was 2 mbar (the heat treatment time was 24 h for in situ IR study) after dosing CO2, the system was equilibrated for 20 min (30 min in the case of studying equilibration time effect) before evacuation. IR spectra recording proceeded (accumulating 8 scans with the resolution of 2 cm^{-1}) during adsorption equilibrium and gradual evacuation procedure. To perform in situ IR study, after adsorption of CO₂, the cell was first evacuated to the pressure of 0.01 mbar and then the samples gradually

Zeolite framework type	Sample	Si/Al	$S_{\rm BET}/{\rm m}^2~{\rm g}^{-1}$	$V_{\mu}/\mathrm{cm}^3~\mathrm{g}^{-1}$	$S_{\rm ext}/{\rm m}^2~{\rm g}^{-1}$	K/mass%
BEA (beta)	H-BEA(11.5) ^a	11.5	653	0.181	203	_
	K-BEA(11.5) ^a	11.5	257	0.059	114	5.52
	H-BEA(19)	19	714	0.226	138	-
	K-BEA(19)	19	542	0.165	134	3.0
MFI (ZSM-5)	H-MFI(21)	21	545	0.172	30	-
	K-MFI(21)	21	387	0.150	29	3.88
FAU ^b (Y)	H-FAU(15)	15	847	0.320	84	-
	K-FAU(15)	15	349	0.144	82	4.56
	H-FAU(40)	40	761	0.286	81	-
	K-FAU(40)	40	319	0.137	64	4.03

Table 1 List of the prepared samples and their descriptions

^aData adopted from the our recent work [7]

^bData adopted from the our recent work [19]

heated up to 200 °C and IR spectra recorded at different temperatures.

The CO₂–TPD has been measured by Micromeritics AutoChem II 2920 instrument. The desorbed products were assessed by TCD calibrated for CO₂. Prior to TPD experiments, the samples were heated to 530 °C in He flow and treated in O₂ flow at the same temperature for 2 h for activation. After cooling to the RT, the samples were saturated with CO₂ (10% CO₂/He; 25 mL min⁻¹) for 25 min. The physisorbed CO₂ was desorbed during He flow (25 mL min⁻¹) for 60 min. The end of both saturation and flushing was checked by mass signal stabilization. The CO₂–TPD proceeded with temperature ramp of 10 °C min⁻¹ from 0 to 530 °C in He flow of 25 mL min⁻¹.

Catalytic activity of the K-MFI(21) and K-BEA(19) samples was investigated in aldol condensation of furfural (Sigma-Aldrich) and acetone (Lach-Ner, s.r.o., Czech Republic, pre-dried before the experiments with a molecular sieve) implementing the same procedure of earlier report [7]. Briefly, the catalytic tests were performed in a 300 mL autoclave at 100 °C. In a catalytic run, 1 g of freshly heat-treated (at 530 °C for 3 h) catalyst was mixed together with a stirred mixture of 39.5 g acetone and 6.5 g of furfural (acetone/furfural molar ratio 10/1). The desired temperature was achieved in ~ 60 min after starting of the heating, and the autoclave was then kept at T = 100 °C for additional 2 h. Analysis of the reaction products was performed after 2 h at the reaction temperature using an Agilent 7890A GC equipped with a flame ionization detector and an HP-5 capillary column (30 m/0.32 ID/ 0.25 µm). The products were identified based on the standard reference compounds as well as additional GC-MS analyses. Finally, the selectivity to product and conversion of furfural could be calculated by obtained data. In case of Y zeolites, the catalytic data for comparison and discussion were adopted from our recent work [19] and for K-BEA(11.5) sample data obtained in earlier report [7].

Results and discussion

Textural and microstructural properties of prepared K-zeolite

SEM images of the main prepared samples are illustrated in Fig. 1. K-MFI(21) sample (Fig. 1a) has submicron size crystallite (ca 300-600 nm), while the K-BEA(11.5) sample shows nanoparticle character with particle size in the range of 20-30 nm. In case of the dealuminated Y zeolites, SEM images in Fig. 1c, d show that samples have micron size crystals (ca. 900-1100 nm). A pores and surface roughness can be observed on the surface of the Y zeolites crystals with sizes around 30 nm which are formed during the dealumination by partial dissolution of the zeolite framework. The textural properties of the samples provided in Table 1 evidence good microporosity of all parent zeolites (high values of micropore volume (V_{μ}) typical for such type of zeolites). External surface area of parent zeolites differs significantly. The highest external surface area exhibits BEA zeolites [203 and $138 \text{ m}^2 \text{ g}^{-1}$ for BEA(11.5) and BEA(19), respectively] as a consequence of the nanosize of zeolite crystallites. FAU zeolites exhibit mediocre external surface area (slightly above 80 m² g⁻¹) despite large crystallites (see Fig. 1c, d). This is caused by secondary mesoporosity formed during dealumination of the original zeolite (usually synthesized with Si/Al ratio around 2.5). MFI zeolite exhibits the lowest surface area because of large crystallites with only internal microporosity. Presence of potassium in the zeolites leads to drop in total surface area and volume of micropores by about 30-55 rel.% compare to parent zeolite. It is caused by partial pore blocking by the K₂O clusters.



Fig. 1 SEM images of the a K-MFI(21), b K-BEA(11.5), c K-FAU(15), d K-FAU(40) samples

IR spectroscopy and TPD upon CO₂ adsorption

IR spectroscopy before and after thermal activation

IR spectra of samples before and after thermal activation at 450 °C over a night (12 h) are provided in Fig. S2 of supplementary information (SI). IR spectra shows that before calcination the bands related to trapped KNO₃ in the pores of sample could be detected (bands at 1370 and 1405 cm⁻¹ for BEA structure related to splitted $v_3(e')$ vibration bands arise from the effect of the cation field on the nitrate ion removing the threefold axis of symmetry and producing a common symmetry between nitrate and cation field of C_{2v} [24], small shift observed in other structures due to different dispersion interaction and same result observed in [25]); however, after thermal activation at 450 °C over a night, this band disappeared which indicated that nitrates are decomposed and K₂O clusters formed or the potassium is exchanged with the zeolitic Brønsted protons by means of solid state reaction [26–28]. Results of the previous research [7, 19] indicate that exchanged K^+ cations do not form strong basic sites in BEA or FAU zeolites; however, in potassium impregnated zeolites with excess of potassium, the stable clusters of K₂O as strong basic site could be formed.

To quantify the density of formed basic sites as well as characterization of their strength, CO₂ as probe molecule has been utilized. Interaction of the CO2 with acidic sites is weak which results in molecularly physisorbed CO₂ characterized by stretching (v_3) vibration band at about 2350 cm^{-1} [29, 30], while it has strong interaction with basic sites and consequently, it is good probe molecule for characterization of basic sites [1, 20]. IR spectra of prepared samples after CO₂ adsorption are provided in Fig. S3 of SI. It could be seen that the bands related to physisorbed CO_2 (main band at 2350 cm⁻¹) are disappeared upon short evacuation at room temperature, while the bands with lower wavenumbers ($< 1800 \text{ cm}^{-1}$) falling in the ranges related to carbonates and chemisorbed species are persist even after dynamic evacuation. These bands could be utilized for characterization of basic sites in the samples. Basically, free carbonate ion has a simple stretching band (v_3) at 1415 cm⁻¹. However, upon adsorption of carbonate ion on the surface, its symmetry lowered from D_{3h} to C_{2v} [31] due to covalent bonding through one or two oxygen and this band (v_3) is splitted into two other bands in either sides of 1415 cm⁻¹ with lower and higher wavenumbers. The splitting wavenumber, Δv_3 , can be implemented to measure the strength of the base sites: the lower splitting is

IR spectroscopy during CO₂ sorption

associated with the stronger the basic site [1]. Δv_3 values of about 100, 300, and 400 cm^{-1} are generally ascribed to monodentate, chelating bidentate, and bridging bidentate structures, respectively [23]. Figure 2 shows the observed bands in IR spectra of samples after CO₂ adsorption and subsequent evacuation. Interestingly, the formed bands are changing with the change of the zeolite type; however, in case of the samples with same structure and different Si/Al ratio, just the intensities of the bands are different (Fig. 2b, c). The chemisorbed CO₂ in impregnated K-BEA(11.5) and K-BEA(19) could be detected by bands at 1688 cm^{-1} (moved to 1680 cm^{-1} at low coverage), 1354 and 1325 cm^{-1} (Fig. 2b, c). The species related to the bands at 1354 and 1680 cm^{-1} are very stable even after dynamic vacuum. Δv_3 is about 363 cm⁻¹ (1688–1325 cm⁻¹) and decreased to 326 cm⁻¹ (1680–1354 cm⁻¹) at low coverage for BEA structure. Considering the extent of splitting, it can be concluded that two sets of bidentate species may be present in K-BEA zeolite and upon evacuation the one with higher stability and lower splitting persists. Bands of chemisorbed carbonate-like species in K-MFI(21) at room temperature are very stable and they are observed at 1675 cm^{-1} (1672 cm⁻¹ in lower coverage) and 1368 cm⁻¹ $(1365 \text{ cm}^{-1} \text{ in lower coverage})$ (Fig. 2a). In this sample, splitting Δv_3 is about 307 cm⁻¹ at room temperature (lower Δv_3 in comparison with BEA zeolite result in higher stability at room temperature). It should also considered that CO₂ adsorption on alkali modified MFI zeolite result in the formation of sole bridged CO₂ adsorption considering the microcalorimetry and volumetry analysis [32] which is somehow in agreement with current result.

In FAU (Y zeolites) samples with Si/Al ratios of 15 and 40 (see Fig. 2d, e), the bands related to chemisorbed species could be detected and their splitting is about 362 cm⁻¹ (340 cm⁻¹ at lower coverage). A very weak band at 1447 cm⁻¹ could also be detected in IR spectra of these samples which exhibits the lowest Δv_3 (100–200 cm⁻¹) which is close characteristics of highly symmetric monodentate species. Summarizing this part, it could be concluded that the main type of adsorbed species on the

K-zeolites at room temperature considering the splitting wavenumber is bidentate species (these species itself can also be divided into two subgroups in some cases like BEA zeolite considering the Δv_3 and they can be attributed to different chelating and bridging bidentate species [1].). Moreover, in some samples (for instance K-FAU(15) and K-FAU(40)), additional bands (e.g., band at 1447 cm^{-1}) with lower splitting wavenumber (100–200 cm^{-1} , Fig. S3 in SI, the counter part of the band at 1447 cm^{-1} is in right shoulder of the band at 1690 cm⁻¹ considering Fig. S4 in SI) more possibly related to monodentate species are also observed [23, 33]. Additional experiment with longer time of thermal activation (24 h) and longer time of CO₂ adsorption (30 min) equilibration (see Fig. S5 in SI) revealed that formation of chemisorbed species has slow kinetic and the density of species with higher symmetry (lower Δv_3) increased with longer activation or equilibration time.

Temperature programmed desorption of CO₂

CO₂-TPD curves of the prepared K-zeolites are depicted in Fig. 3. Two different desorption peaks could be detected in the most of the cases; however, in case of K-MFI(21), the high temperature desorption peak is negligible. It should be considered that the observed peaks in CO₂-TPD patterns are different than what observed for basic mixed oxide [34] and the peaks are well differentiated in this case. The lowtemperature desorption peak is observed at ≈ 50 °C, while the high temperature peak observed at ≈ 130 °C for different samples. Considering this results, it can be concluded that two categories of the basic sites may present in the samples which agrees with IR results. It seems that the smaller pore size of MFI zeolite (10 membered rings, ~ 5.5 Å) in comparison with BEA (12 membered rings, ~ 6.68 Å) and super-cage of Y zeolite (12 membered entrance window ~ 7.4 Å with cavity of 11 Å in diameter) is the main reason that K₂O clusters would not form inside the MFI pores. The lattice parameter of the crystalline K₂O with cubic structure is 6.436 Å [35] which

Fig. 2 IR spectra of (a) K-MFI(21), (b) K-BEA(11.5), (c) K-BEA(19), (d) K-FAU(15), (e) K-FAU(40) sample after CO_2 adsorption at room temperature (P = 1 mbar, equilibration time = 20 min) (blue curve labeled by legend 1) and then evacuation in dynamic vacuum (red curves labeled by legend 2). (Color figure online)





Fig. 3 TPD of CO₂ recorded on (a) K-MFI(21), (b) K-BEA(11.5), (c) K-BEA(19), (d) K-FAU(15), (e) K-FAU(40) samples after thermal activation at 530 $^{\circ}$ C

is bigger than the channel size of MFI zeolite (two channels exist in MFI structure, both of them consist of 10 tetrahedra with the sizes 5.5×5.1 Å and 5.3×5.6 Å) [36]. It should also be considered that based on molecular dynamics simulations [35] with decreasing the size of the K₂O clusters its stability decreasing (free energy increased). Therefore, it can tentatively be claimed that the formed K₂O clusters in MFI channels are thermodynamically unstable due to high surface area. Another explanation would be diffusion constrain which caused the inaccessibility of possibly formed K₂O clusters in MFI channels. In any case, it can be assumed that accessible basic species (K₂O clusters) in MFI structure are mainly formed on the surface of the zeolite crystals (SEM image in Fig. 1), while in samples with larger micropores the accessible basic sites could probably be present inside the zeolite channels as evidenced by TPD and CO₂-IR data.

To further proof the harmony of the TPD data and results of IR study of CO₂ sorption on samples, the correlation between the area under the TPD curves and the area of IR bands related to chemisorbed species (bands observed in the range of $1300-1800 \text{ cm}^{-1}$) after normalization of IR spectra by weight of prepared self-supporting pellets is displayed in Fig. 4. TPD and CO₂-IR data are well correlated and show linear behavior. Outcome of this observation is that in situ IR spectroscopy upon desorption of CO₂ could be implemented for unraveling the peaks observed in CO₂-TPD curves. Considering literatures, there are controversial reports about thermal stability of different types of chemisorbed CO₂ on basic sites due to complexity of basic sites in investigated materials. For instance in [23], it was reported that bidentate species are desorbed upon heating up to 50 °C, while monodentate carbonate are thermally stable and they may persist upon heating even up to 400 °C on the surface of hydrotalcite-



Fig. 4 Correlation of area under TPD curves and area of bands related to chemisorbed species in the range of $1300-1800 \text{ cm}^{-1}$

derived mixed oxides using calorimetry and FTIR spectroscopy upon CO_2 adsorption, while in some old literatures [1, 37] opposite trend is presented and authors believed that monodentate complex is less stable. Comparing with many other basic solids (e.g., hydrotalcite like materials [23]), K-zeolite shows quite unique behavior of CO_2 adsorption and the obtained IR spectra and TPD results are simpler than other basic solid. Consequently, thermal stabilities of different chemisorbed species could be easily determined in this case.

In situ IR study during the CO₂ desorption

Figure 5a shows the in situ IR spectra recorded on K-FAU(15) upon desorption of CO_2 . It could be seen that the bands with higher splitting disappear first and the bands with lower splitting are stable (even slightly grows in the intensity) up to 80 °C and then they start to diminish mainly at 130-150 °C. This means that species with lower symmetry (higher splitting, $\Delta v_3 > 300 \text{ cm}^{-1}$) are less stable and therefore these species (mainly bidentates considering the splitting wavenumbers, $\Delta v_3 > 300 \text{ cm}^{-1}$) are removed/transformed to species with higher symmetry, most probably monodentate type, considering the splitting wavenumber ($\Delta v_3 \sim 100-200 \text{ cm}^{-1}$). The bands with lower splitting ($\Delta v_3 < 200 \text{ cm}^{-1}$) grow up in intensity/ stable upon heating up to 80 °C (e.g., observed bands at 1635, 1590, 1431 and 1441 cm⁻¹, Fig. 5a) which indicate that bidentate species are desorbed by heating and some of them adsorbed as monodentate species with higher symmetry). In case of K-BEA(11.5) sample (Fig. 5b) upon heating, the bands with lower splitting are formed (bands at 1629, 1580, 1472, 1436 and 1404 cm⁻¹) which can be explained by same concept. In case of K-MFI(21), negligible amount of monodentate species are present as



Fig. 5 In situ IR spectra upon thermal desorption of CO_2 (the results could be implemented to describe the observed desorption peak in the TPD curves). **a** K-FAU(15), **b** K-BEA(11.5), **c** K-MFI(21) after

evidenced by the absence of the bands with low splitting in IR spectra (Fig. 5c) and as it could be observed, almost all the bands are removed upon heating up to 80 °C, which agree with the presence only low-temperature peak in CO_2 -TPD.

All in all, CO_2 -TPD and IR results indicate that two different types of the basic sites may be present in K-zeolites and upon CO_2 adsorption, they form chemisorbed carbonate-like species with different symmetries. Depending on the zeolite pore size and morphology, the distribution of these two types is also different. It is also observed that the highly symmetric species have higher thermal stability in comparison with lower symmetric species.

Catalytic test

The aldol condensation of furfural and acetone as important reaction for biomass valorization [11, 15, 16] was performed on K-BEA(19) and K-ZSM(21) samples in according to the instruction given in earlier report of our

thermal activation at 450 °C (24 h) and CO₂ adsorption (1 mbar, 20 min). (Color figure online)

group [7]. The main possible products of the reaction with their IUPAC names are listed in Table 2. For sake of brevity, the abbreviations will be used in the following text. For K-BEA(11.5) and K-FAU samples, the data were adopted from [7, 19], respectively. The results are summarized in Fig. 6a, b and Table 3. Considering Table 3, K-BEA(11.5) and K-FAU(15) samples show high furfural conversion and selectivity to long chain product (F₂Ac) is higher on these samples in comparison with other samples. BEA(19) and K-FAU(40) samples with same structure and higher Si/Al ratio show lower activity most probably due to less basic sites and potassium content (Table 1). K-MFI(21) also shows less activity and selectivity to F_2Ac . To correlate these results with characterization data, CO₂-TPD data were compared with catalytic activity. Conversion of furfural increases with the increasing CO2-TPD area (Fig. 6a) and even have better correlation with area of HT desorption peak in TPD curves (inset of Fig. 6a) which indicates that basic sites detected by TPD (mainly those form HT peak in TPD) are the active species catalyzing the reaction. What is more, considering Table 3, selectivity of

 Table 2
 Main possible products obtained after aldol condensation of furfural and acetone on heterogeneous catalyst

Other names/naming	
etone	
e	



Fig. 6 a Correlation of observed furfural conversion on different samples with calculated TPD area, \mathbf{b} plot the selectivity to different products upon the aldol condensation of furfural and acetone on the samples versus the area of high temperature desorption peak in TPD

Table 3 Furfural conversion (X%) and selectivity (S) to different products measured on different samples after catalyst testing for aldol condensation of furfural and acetone

Sample	X/%	$S_{\rm FAc}/\%$	$S_{\rm FAcOH}/\%$	$S_{\rm F2Ac}/\%$	$S_{(FAc)2}$ /%
K-MFI(21)	8	32	70	7	0
K-BEA(11.5) ^a	85	29	2	69	0
K-BEA(19)	35	46	14	40	0
K-FAU(15) ^b	42	36	48	16	0
K-FAU(40) ^b	39	41	45	14	0

^aData adopted from the our recent work [7]

^bData adopted from the our recent work [19]

product is also function of the distribution and density of different basic sites as well as pore size of zeolites. The longer chain products F_2Ac (C13), which is favorable product for biodiesel application [17], is formed in samples with strong basic sites and larger pores (those formed monodentate carbonate upon CO₂ adsorption on BEA and FAU samples). More interestingly, no (FAc)₂ products were detected in the reaction mixture. Formation of (FAc)₂ products needs presence of acid site, as documented on acidic form of zeolites MWW [12], BEA [7, 13], MFI [13] and USY [13, 19]. Impregnated samples do not possess any acidic site (due to exchange of proton with potassium during the impregnation, as documented by the absence of



curves (Inset) Correlation of observed furfural conversion on different samples with area of high temperature peak in TPD curves. (Color figure online)

OH group stretching vibrational band at about 3600 cm^{-1} , cf. Fig. S2 in SI) and therefore this product is not formed. The integrated area of high temperature (HT) desorption peak in TPD curves plotted against selectivity of product (Fig. 6b) clearly showed that with increasing of the area (increasing the number of strong basic sites), amount of longer chain product (F_2Ac) increased, while the selectivity to FAcOH decreased. The selectivity to FAc is almost constant indicating that FAc production is not strongly related to basic sites characterized by HT in CO2-TPD curves. From Table 3, it can also be observed that BEA and dealuminated Y zeolites exhibit much higher furfural conversion than MFI zeolite which could be correlated with CO₂-TPD and CO₂-IR results. It is also clearly visible that BEA zeolite exhibits the highest selectivity to F₂Ac product from all investigated zeolites. Considering the selectivity data in Fig. 6b, it can be observed that the correlation is not always straightforward and the trend of change is more complex because not only character of basic sites but also inner void space around these sites influenced products of the reaction.

Schematics of the formed basic sites on different zeolite are shown in Fig. 7. Summarizing all the results one could be noted that morphology and structure of zeolite particles (crystal size, porous microstructure and Si/Al ratio) are the main factors affecting the distribution and types of formed basic sites. The possible inter/intra K_2O clusters are the two Fig. 7 Schematic of formed basic sites on different samples (two major type of basic sites most probably inter or intra K_2O clusters could be formed in K-zeolite and their distribution is function of morphology)



major types of formed basic site and their distribution plays important role on the basicity of the samples. It seems that basic sites formed inside the pore of the zeolite are highly active and responsible for formation of more symmetric monodentate carbonate-like species upon CO_2 adsorption. The higher activity of these small clusters may be related to confined space effect which alters the symmetry of adsorbed species.

Conclusions

Study of the formed basic sites in the K-zeolites with different structure and Si/Al ratio by CO_2 as probe molecule indicates that K-zeolite shows quite unique behavior of CO_2 adsorption and the obtained IR spectra and CO_2 -TPD results are simpler than other basic solid (e.g., mixed oxide of alkaline earth metals). Two major types of adsorbed CO_2 species are present in the K-zeolite. In K-zeolite with relatively smaller pores size and large crystallite size, less symmetric type of adsorbed species (mainly bidentate carbonate-like species) is popular, while highly symmetric adsorbed species also tend to form on basic sites of large pore zeolites and materials with some mesoporosity (e.g., BEA or dealuminated FAU zeolites). Moreover, it is observed that almost all the bidentate species are desorbed at 50–80 °C, while monodentate species are thermally stable at least up to 130 °C. Catalytic tests also showed that sample with stronger basic sites (those formed monodentate carbonates upon CO_2 adsorption) is more active for aldol condensation of furfural and acetone and forms longer chain products.

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