

Activity in the Knoevenagel condensation of encapsulated basic cesium species in faujasite CsNaX or CsNaY

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Received 24 July 1997; accepted 26 September 1997

Abstract

The activity of basic species generated in zeolite CsNaX or CsNaY by cesium acetate impregnation and calcination under a synthetic air flow has been investigated. The Knoevenagel condensation of benzaldehyde and ethylcyanoacetate was used as a model reaction. The evaluation of the number of basic sites was carried out by CO₂ TPD. Correlations between initial rates and number of basic sites allowed the determination of the TOF for the modified zeolites. It depends mainly on the host zeolite composition. Moreover, activity varies strongly with crystallinity especially for zeolites Y at high loadings. © 1998 Elsevier Science B.V.

Keywords: Basic zeolite; Encapsulation; CO₂ TPD; Knoevenagel

1. Introduction

In the growing field of heterogeneous base catalysis in fine chemicals, our interest has focussed on solids which are able to catalyze C–C bond formation. Up to now, various catalysts have been described [1]. They include resins [2], alkaline earth oxides [3,4], exchanged zeolites [5–9], sepiolites [10,11], layered double hydroxides or mixed metal oxides obtained by thermal decomposition of the latter [12–15] and, more recently, cesium-exchanged MCM-41 silicas [16] or aluminophosphates oxynitrides [17]. Our results [18] showed that basic CsNaX zeolite modified by cesium oxide encapsulation are

well-adapted catalysts to perform such reactions. Up to now, the effect of the support on the activity of these promising catalysts has not been clearly established.

The encapsulation of oxide species inside CsNaX or CsNaY cages may provide an interesting way to improve the CsNaX or CsNaY basicity. We showed [19] that, in the same range of loading (< 26 cesium atoms per unit cell), the stability of the host framework differs, CsNaX being more stable than CsNaY in the same conditions of activation. From CO₂ thermodesorption (TPD) results, a Cs₂O oxide was suggested to be formed in CsNaX α -cages (1 Cs₂O/ α -cage) [20] while in CsNaY, oxides, cesium silicates or cesium aluminates can be obtained, the CO₂ adsorption depending on the crystallinity [19].

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In order to check the role of the support on the basicity of the encapsulated species, the Knoevenagel condensation between benzaldehyde (BA) and ethylcyanoacetate (ECA) in liquid phase was chosen as a model reaction [21]. Taking the acidic character ($pK_a = 9$) of methylenic protons of ECA into account, its activation is easily performed even in a low temperature range. Consequently, all the basic sites of the catalyst can be considered to be effective in this reaction which requires low basicities. Corma et al. [5,6] showed that convenient conversions can be obtained, when reaction takes place without solvent, even using exchanged zeolites which present lower basic strengths than modified zeolites. Previous studies have established the kinetic mechanism of the Knoevenagel condensation using the latter catalysts. Moreover, experimental conditions, well-adapted to the catalytic evaluation of these modified zeolites, were determined. The choice of the solvent (DMSO) [21] was particularly justified.

The aim of this work is to show that the enhancement of basicity which is obtained by cesium acetate impregnation on zeolite CsNaX or CsNaY and subsequent activation depends mainly on the zeolite host. Correlations between activity and basicity are established, the number of basic sites being determined by CO₂ TPD.

2. Experimental

2.1. Catalysts

NaX (13X, Aldrich-Chemie) and NaY (Linde molecular sieve SK-40, Alfa) were twice exchanged in water with cesium acetate at room temperature [20] giving zeolites CsNaX ($\text{Na}_{50}\text{Cs}_{36}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}$) and CsNaY ($\text{H}_5\text{Na}_{17}\text{Cs}_{33}\text{Al}_{55}\text{Si}_{137}\text{O}_{384}$). Modified zeolites CsNaX (CsNaX · *n*Cs) and CsNaY (CsNaY · *n*Cs) were prepared by impregnation of exchanged zeolites with cesium acetate in water solution. Loadings of 4.5 (CsNaX · 4Cs), 9.1

(CsNaX · 9Cs), 11.4 (CsNaX · 11Cs), 15.9 (CsNaX · 16Cs) and 26.4 (CsNaX · 26Cs) added Cs atoms per unit cell were obtained for modified zeolites CsNaX [20]. Loadings of 3.6 (CsNaY · 4Cs), 7.3 (CsNaY · 7Cs), 9.1 (CsNaY · 9Cs), 12.9 (CsNaY · 13Cs), 18 (CsNaY · 18Cs) and 24.4 (CsNaY · 24Cs) added Cs atoms per unit cell were performed from zeolite CsNaY [19].

Basic species were generated by the calcination of crude zeolites CsNaX · *n*Cs or CsNaY · *n*Cs under a flow of synthetic air (80% N₂, 20% O₂) at 550 or 400°C for 6 h with a heating rate of 1°C/min, just before characterization or reaction.

2.2. Characterization of the catalysts

The catalysts were characterized by differential thermal analysis, X-ray diffraction, N₂ volumetry, ²⁷Al and ²⁹Si MAS NMR and CO₂ TPD [19,20].

2.3. Catalytical experiments

ECA, BA and DMSO 99% were purchased from Aldrich Chemicals. BA was kept on basic alumina in order to remove traces of benzoic acid and DMSO was dried on molecular sieves (4 Å). All experiments were carried out under a nitrogen atmosphere in a pyrex reactor equipped with a magnetic stirrer, a controlled heating, a sample tube with a frit and a rubber septum for introduction of reagents by syringe. After calcination of the catalyst in situ at 550 or 400°C and temperature equilibration at 80°C, 50 ml of a solution of ECA (0.3 M) in dried DMSO was introduced through the septum. Then, 5 ml of a solution of BA (0.3 M) was added. The progress of the reaction was monitored by periodically withdrawing samples. Analyses were performed by GC (Delsi serie 30 with a flame ionization detector) using a 25 m OV-1 capillary column, dodecane as external standard and subsequent temperature programming: 80°C (3 min), 15°C/min, 220°C.

The products were identified by GC-MS chromatography or were analyzed by ^1H and ^{13}C NMR after Et_2O extraction. The spectra were recorded on a Bruker 200 MHz spectrometer, with CDCl_3 as solvent and TMS as internal standard.

3. Results and discussion

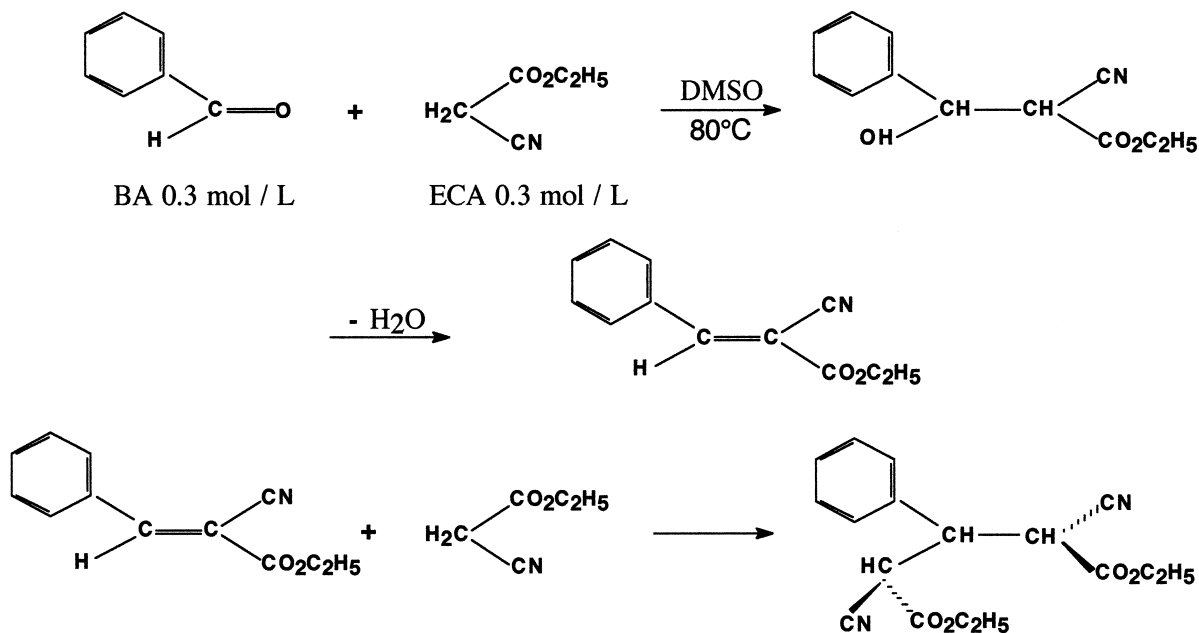
A few studies deal with the effect of the support on the activity of encapsulated species in zeolite cages. However, in the case of cesium oxide encapsulation, crossed interactions between oxygen or cesium of the generated oxide on the one hand and extraframework cations or oxygen framework on the other hand, may lead logically to various basicities of the added species.

The Knoevenagel condensation of ECA and BA (Scheme 1) is a good model reaction used by various authors [5,6,10–14,16–18]. It can be

performed in liquid phase and in moderate conditions [17,18]. ^1H and ^{13}C RMN studies showed that using stoichiometric concentrations of reactants, excellent selectivities in *trans*- α -ethyl-2-cyanocinnamate (mono-adduct) were obtained. The consecutive Michael reaction does not proceed in these conditions. Our previous results [21] showed that the uncatalyzed reaction does not take place in DMSO unlike in protic solvents such as EtOH. Hence, DMSO was chosen in order to correlate activities, measured by initial rates, with basicities of modified zeolites CsNaX or CsNaY. The reaction is first order in each reactant, the determining step being the condensation between the adsorbed reactants, in a concerted mechanism [21].

3.1. Determination of the number of basic sites by CO_2 TPD

Previous results demonstrated the efficiency of a gas-phase carbon dioxide molecule as a probe for the basicity of oxides. CO_2 adsorption on exchanged and modified zeolites was per-



Scheme 1. Model Knoevenagel condensation between BA and ECA.

Table 1
CO₂ desorption from zeolites CsNaX · nCs and CsNaY · nCs after activation under a synthetic air flow, at 550 or 400°C (6 h)

CsNaX · nCs	CsNaX · 4Cs	CsNaX · 9Cs	CsNaX · 11Cs	CsNaX · 16Cs	CsNaX · 26Cs	
Added Cs (wt%)	3.5	7.0	8.8	12.3	20.4	
Added Cs (atoms/u.c.)	4.5	9.1	11.4	15.9	26.4	
Activation at 550°C						
CO ₂ ^a (molecules/u.c.)	3.0	5.5	7.1	10.7	13.3	
CO ₂ ^b (mol/g) × 10 ⁵	6.1	19.8	27.0	43.2	57.3	
CsNaY · nCs	CsNaY · 4Cs	CsNaY · 7Cs	CsNaY · 9Cs	CsNaY · 13Cs	CsNaY · 18Cs	CsNaY · 24Cs
Added Cs (wt%)	3.0	6.0	7.4	10.5	14.7	19.9
Added Cs (atoms/u.c.)	3.6	7.3	9.1	12.9	18.0	24.4
Activation at 550°C						
CO ₂ ^a (molecules/u.c.)	1.6	2.8	2.7	2.7	2.9	1.7
CO ₂ ^b (mol/g) × 10 ⁵	4.5	11.5	10.6	10.2	11.2	4.3
Activation at 400°C						
CO ₂ ^a (molecules/u.c.)	3.1	4.9	4.9	6.5	8.9	8.0
CO ₂ ^b (mol/g) × 10 ⁵	11.2	21.6	21.0	28.9	40.5	33.6

^aCO₂ total up to and including 750°C.

^bCO₂ total up to and including 750°C for the modified zeolite–CO₂ total up to and including 750°C for the corresponding exchanged zeolite, per g of activated solid.

formed at 100°C. The amount of desorbed CO₂ is expressed in molecules per unit cell (Table 1). However, in order to correlate with initial rates, the average value from various experiments was calculated per g of activated catalyst by subtracting values obtained for Cs-exchanged zeolites X or Y from values measured for the corresponding modified zeolites (Table 1). The amount of CO₂, desorbed up to 750°C included, from exchanged zeolites depended only on the sodium content, whatever the cesium exchange level [19]. Therefore, for modified zeolites, this increasing amount was related with adsorption on the basic sites of added species. From CO₂ TPD profiles, it was concluded that partial deposit of cesium oxide on the external surface of zeolites CsNaX · nCs could be significant for loadings higher than 16 cesium atoms per unit cell. In this case desorptions took place above 550°C.

The amount of CO₂ desorbed from zeolites CsNaY · nCs depends on the activation temperature and thus, on the crystallinity (Table 1). When crystallinity is retained by activation at

lower temperatures (400°C), the amount of desorbed CO₂ increases and becomes of the same order of magnitude than the one for zeolites CsNaX · nCs with corresponding loadings. Desorptions above 550°C are lower for modified zeolites Y than for modified zeolites X, in all cases.

3.2. Activity in the model Knoevenagel condensation

3.2.1. Modified zeolites X

Fig. 1 shows variations of the initial rate and of the amount of desorbed CO₂ versus the cesium loading for zeolites CsNaX · nCs. An increase in cesium loading leads to simultaneous increases in both parameter values. Total CO₂ desorption was considered for temperatures up to 750°C. Such an approach does not take into account the nature of the basic species which can change with cesium loading as previously pointed out [19,22,23] for high loadings. However, we have shown [19] that the amount of CO₂ which desorbs per added cesium atom

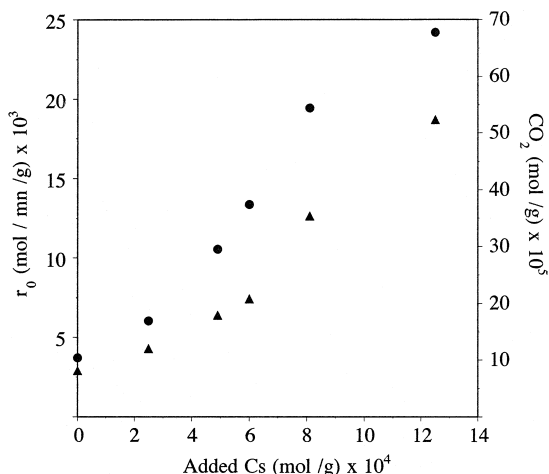


Fig. 1. Initial rate (▲) and total CO₂ desorption (●) versus added cesium content for zeolites CsNaX · *n*Cs.

(0.5 mol) for modified zeolites X is essentially the same whatever the considered range of temperatures (up to 550 or 750°C) for loadings up to 16 cesium atoms per unit cell (2 cesium atoms per supercage, 12.3 wt%). In the same way, Yagi et al. [24] assumed that the excess cesium species are located in the supercages for samples containing an excess of 1.1 and 2.9 cesium atoms per supercage. Hence, whatever the loading up to 16 cesium atoms per unit cell, our results (Fig. 1) are consistent with the conservation of crystallinity of modified CsNaX after activation at 550°C (6 h). On the other hand, they suggest that an homogeneous loading is achieved in such conditions. These results corroborate the ones previously reported taking into account XRD data and the regular decrease of microporous volume with loading [19].

3.2.2. Modified zeolites Y

Two kinds of results are described depending on the activation temperature.

First when CsNaY · *n*Cs were calcined at 550°C (Fig. 2), curves going through a maximum are obtained either for the initial rate or for the amount of desorbed CO₂ versus theoretical cesium loading. At low loadings, an increase in loading results in increases of both initial rate and CO₂ desorption. For loadings higher than

approximately 9 Cs atoms per u. c ($\cong 5.2 \cdot 10^{-4}$ mol/g), a decline in CO₂ desorption accounts for a decrease in initial rate. These results agree with losses of crystallinity which have been noticed (XRD, N₂ adsorption–desorption isotherms, ²⁹Si, ²⁷Al MAS NMR) [19], specially for loadings higher than 9 Cs atoms per u.c. Activity and number of basic sites go through a maximum with cesium loading. Thus, it can be considered that sites become no more accessible to reactants or carbon dioxide molecules.

Secondly when zeolites CsNaY · *n*Cs were activated at 400°C, same profiles (Fig. 3) than the ones described for zeolites CsNaX · *n*Cs are obtained. Linear relationships between either initial rate or amount of desorbed CO₂ with cesium loading are observed. Hence, activity can be related with crystallinity of modified zeolites Y. Fig. 4 shows that the initial rate linearly increases with CO₂ desorption whatever the activation temperature. A possible loss of crystallinity, even after activation at 400°C, may be responsible for the variation observed for the most loaded zeolite Y [19].

In these conditions, it can be concluded that activity of modified zeolites in the Knoevenagel condensation is related with the number of accessible added basic species. Taking similarities

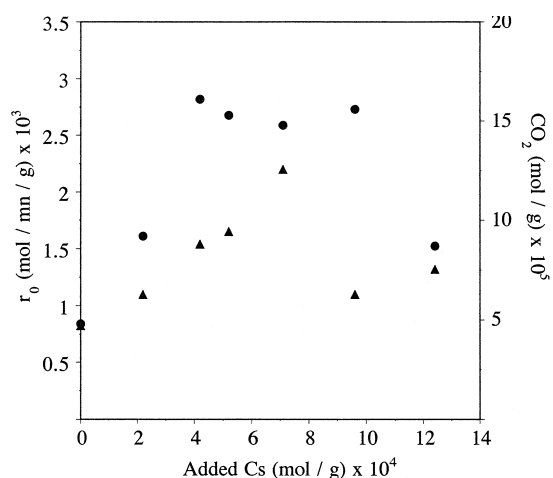


Fig. 2. Initial rate (▲) and total CO₂ desorption (●) versus added cesium content for zeolites CsNaY · *n*Cs after activation at 550°C, 6 h.

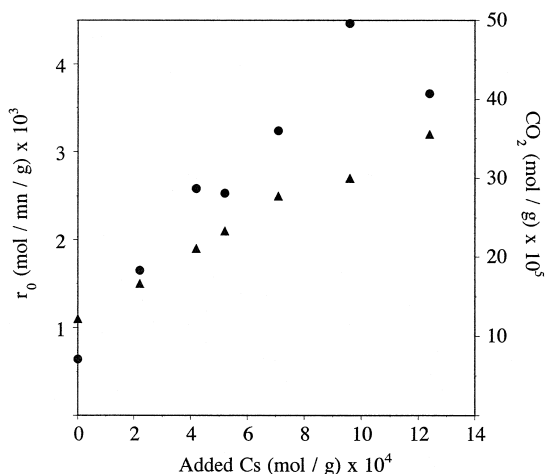


Fig. 3. Initial rate (▲) and total CO₂ desorption (●) versus added cesium content for zeolites CsNaY · nCs after activation at 400°C, 6 h.

of profiles obtained either for r_0 or for the amount of desorbed CO₂ with cesium loading into account, the number of moles of desorbed CO₂ can be used as a measurement of the number of basic sites.

3.3. Correlations activity / basicity

Considering basic exchanged zeolites as acid–base pairs [25], carbon dioxide adsorption on such solids may be related with the Lewis

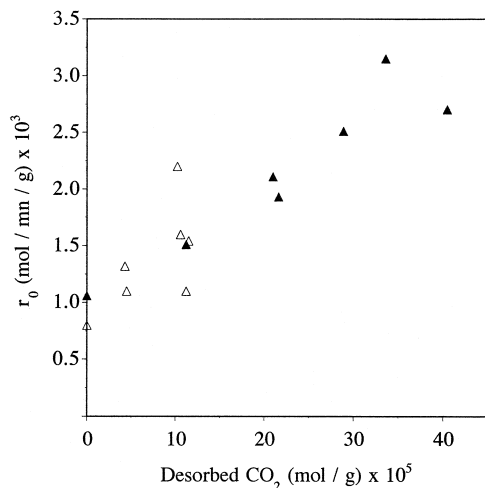


Fig. 4. Initial rate versus total amount of desorbed CO₂ for zeolites CsNaY · nCs. (▲) Activation at 400°C (6 h); (△) activation at 550°C (6 h).

acid character of the cation [19]. We have shown that adsorption on extraframework cesium cations can be neglected, adsorption on exchanged zeolite CsNaX or CsNaY being related with the sodium content. Hence, subtracting the amount of desorbed CO₂ for exchanged zeolites from the amount for modified zeolites leads to the amount adsorbed on added species (Table 1) which reflects the number of basic sites which are accessible to reactants. Correlations between initial rates and desorbed CO₂ (Fig. 5) are obtained for CsNaX · nCs and CsNaY · nCs activated at 400°C, respectively. Linear relationships lead to the determination of the turn over frequency (TOF), 21 and 5 min⁻¹, respectively whereas TOF = 1.7 min⁻¹ for cesium carbonate (Fig. 6).

Hence, catalytic activity is higher for modified zeolite X than for modified zeolite Y. It appears that contribution of external species if any, should be low for modified zeolites X by comparison with cesium carbonate activity. However, one must be careful because it can be considered that cesium species dispersed on the outer surface of the zeolite are not exactly in the bulk form [26]. Only low amounts of CO₂ desorb at temperatures higher than 550°C for modified Y zeolites indicating that more basic species can enter CsNaY rather than CsNaX cages [19].

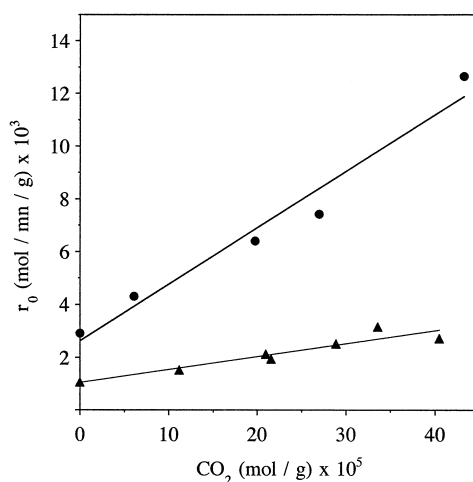


Fig. 5. Activity of basic cesium species added in faujasites CsNaX or CsNaY. (●) CsNaX · nCs; (▲) CsNaY · nCs.

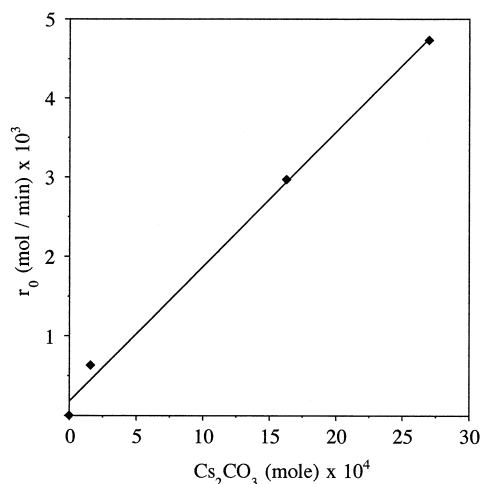


Fig. 6. Activity of cesium carbonate.

Activation conditions are certainly of prime importance. Activation under an helium flow can lead to the partial formation of cesium suboxide (Cs_7O) for activation temperatures higher than 350–400°C [27]. Moreover, Yagi and Hattori assumed that catalytic activity of cesium-added zeolite X for 1-butene isomerization was completely poisoned by oxygen [24]. Our catalytic results show that the basicity of the guest species mainly depends on the composition of the host zeolite when activation under a synthetic air flow is performed at temperatures, for which crystallinity is retained, but sufficiently high to remove carbon dioxide from basic species. They corroborate CO_2 TPD data according to which the maximum of the desorption peak shifts toward higher temperatures ($200 < T$ (°C) < 300) for $\text{CsNaX} \cdot n\text{Cs}$ than for $\text{CsNaY} \cdot n\text{Cs}$ ($100 < T$ (°C) < 200).

Up to now, it is generally assumed that stronger basic sites are generated by cesium acetate impregnation and subsequent activation than by alkali-ion exchange of zeolites. Various authors [19,20,24,27] proposed the formation of cesium oxide species in zeolite X. Cs-added zeolite X is more active than other alkali-added zeolites X [26]. Few results are concerned with zeolite Y as a basic host [27–29]. No effect on the activity of the entrapped species was reported using modified zeolite X or Y respec-

tively, as a host. However, the nature of the basic species was shown to be different from that the ones occluded in microporous carbon and from bulk Cs_2O [27]. Moreover, an effect of the support was suggested concerning the stability of cesium oxide which seems to be stabilized when encapsulated in zeolite X or Y [27].

Therefore, the effect of the composition of the host zeolite on the catalytic activity can be accounted for either by the local formation of defects on $\text{CsNaY} \cdot n\text{Cs}$ without loss of crystallinity or by interactions between the guest oxide and the host zeolite. These interactions may depend on the Si/Al ratio, on the compensating cation location or on the electric field inside the zeolite cages. At the present time, we are unable to distinguish between these possibilities.

4. Conclusion

The activity of Cs-exchanged zeolites X and Y modified by cesium acetate impregnation and activation under a synthetic air flow was accessed using the model Knoevenagel condensation between benzaldehyde and ethylcyanoacetate, in liquid DMSO. Data indicate clearly that the basicity of generated guest species ($\text{TOF} = 21$ and 5 min^{-1} , respectively) depends on the host composition. The activity varies with the crystallinity of the catalysts. When a loss of crystallinity takes place entrapped basic species become no more accessible either to reactants or to the probe CO_2 molecules. Our results suggest that homogeneous loadings are performed whatever the CsNaX or CsNaY host when crystallinity is retained.

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