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Insight into the active sites for the Beckmann rearrangement on porous solids by in situ infrared spectroscopy

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Abstract

The nature and location of the active sites for the Beckmann rearrangement present in microporous and mesoporous solids have been investigated by comparing the results obtained for oximes of different molecular size, using in situ infrared spectroscopy. The rearrangement of acetophenone and cyclododecanone oximes into acetanilide and laurolactam, respectively, was studied using siliceous and Al-containing zeolites Beta and MFI and mesoporous MCM-41 as catalysts. The results indicate that Brønsted acid sites as well as strongly hydrogen bonded silanol groups and silanol nests, located in the pores of zeolites and MCM-41, are active in the reaction. When the external surface or the outer shell of MFI type crystals is considered, the bridging hydroxyl groups appear to be active, whereas no activity in the Beckmann rearrangement of cyclododecanone is observed over silanol groups.

Keywords: Beckmann rearrangement; Acetophenone oxime; Cyclododecanone oxime; IR spectroscopy; MFI; Zeolite Beta; MCM-41

1. Introduction

The Beckmann rearrangement of ketoximes into amides presents a great industrial interest in the production of intermediates for the fabrication of fibers. The most important applications are the transformation of cyclohexanone and cyclododecanone oximes into the corresponding lactams, which are the raw materials for manufacturing nylon-6 and nylon-12, respectively [1]. Much effort is being expended in the field of zeolites and molecular sieves to develop selective catalysts that will generate environmentally friendly technologies [2]. More specifically, in the case of Beckmann rearrangement, continuous research is being carried out to substitute sulfuric acid or oleum used as catalysts in the conventional homogeneous process [3–8]. As a result of the research activity, Sumitomo has recently industrialized the production of ε-caprolactam, using a high-silica MFI-type zeolite as catalyst for the vapor-phase rearrangement [6,7].

Brønsted hydroxyl groups in zeolites are active sites in the Beckmann rearrangement when the reaction occurs in the liquid phase at moderate temperatures [8–11], but the yield to lactam in the vapor-phase reaction increases when zeolites with neutral or very weak acidic silanol groups are used [12–16]. Very recently, Brønsted acid sites present in zeolites have been shown to be able to protonate the nitrogen atom of the oxime, whereas silanol groups form hydrogen bonds with the N or O atoms [17,18]. Therefore, although bridging hydroxyl groups appear to be more favorable for the Beckmann rearrangement, other factors play an important role in the lactam selectivity and the nature of the active sites is not yet clearly established. Moreover, the location of the zeolite hydroxyl groups catalytically active in the Beckmann rearrangement is a matter of debate [7,8,12,14–16,19–21]. Some authors claim that the active sites are very weak acid or neutral hydroxyl groups located at the zeolite surface or inside the pore aperture [7,12,14–16,19,20], whereas others conclude that silanol groups must be located within the zeolite pores [8,21].

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Most of the research on the Beckmann rearrangement, including the nature and location of the active sites in zeolites, involves the transformation of cyclohexanone oxime into ε-caprolactam over MFI-type zeolites in the vapor phase. The conclusion that the selective reaction must proceed at or close to the external surface of the crystals is based on adsorption measurements and molecular modeling indicating that ε-caprolactam, with a seven-member ring, cannot penetrate the micropores of MFI [7,12,14–16,20]. This is supported by an increase in the selectivity to ε-caprolactam when the external surface of the crystal increases [12,15], or when zeolites with pore sizes smaller than cyclohexanone oxime are used as catalysts [14,16,20]. In agreement with this conclusion, geometrical and diffusion constraints of the lactam within the zeolite pores favor the formation of byproducts, thus decreasing the selectivity to ε-caprolactam [14,16,20] and increasing the catalyst deactivation by pore blocking [22] or by formation of residuals on the catalyst surface [16].

The idea that the selective Beckmann rearrangement would proceed exclusively on an outer shell or the external surface of the MFI-type crystals owing to strong diffusion limitations through the zeolite pores has been challenged from adsorption–diffusion studies of cyclohexanone oxime and ε-caprolactam [21]. Kath et al. concluded that both the oxime and the lactam are able to diffuse into the micropores of MFI at temperatures typical for the Beckmann rearrangement and that the reaction occurs, at least in part, inside the pores [21]. They linked the dependence of activity and selectivity on the crystal size to the shorter diffusion pathways in smaller crystallites [21]. These findings support previous results suggesting that internal hydroxyl groups within the zeolite pores, and not those placed at the external surface of the zeolite crystals, are the active and selective sites for performing the Beckmann rearrangement in the liquid phase [8].

The aim of this work is to gain further insight into the nature and location of the sites active in the Beckmann rearrangement by performing in situ reactions within the infrared cell. In this work, we have reacted molecules of different molecular size over catalysts with various pore sizes and catalytic active sites. More specifically, the rearrangement of acetophenone and cyclododecanone oximes to acetanilide and laurolactam, respectively, has been investigated over pure silica zeolite Beta and silicalite-1 and mesoporous MCM-41, as well as on the corresponding aluminosilicates. The choice of reactants and catalysts allows us to differentiate whether the reaction occurs on the external surface or in the pores, and on silanol groups or on bridging hydroxyl groups.

2. Experimental

The H-ZSM-5 (Si/Al = 15) and H-Beta (Si/Al = 12.5) zeolites used were commercial samples produced by P.Q. Industries (CBV3020) and Zeolyst (CP811), respectively. Siceous zeolite Beta-D containing connectivity defects (silanol groups) and Beta-ND (without defects) were synthesized hydrothermally at 413 K using tetraethyl ammonium as a structure-directing agent, and OH^- and F^- as mineralizing agents, respectively, as described elsewhere [8]. Silicalite-N was prepared following the method described previously for silicalite-1 [19,23] and was treated in a basic medium as done previously [19] to generate silanol nests. Then, 5 g of zeolite calcinated at 823 K for 12 h was impregnated with 20 g of an aqueous solution of ammonia (25 wt%) and ammonium nitrate (7.5 wt%) and heated in an stainless steel autoclave at 373 K overnight. The final silicalite-N catalyst was recovered after washing with deionized water, filtering, and drying at 383 K for 4 h. Al-containing H-MCM-41 (Si/Al = 12) and pure silica Si-MCM-41 were obtained as described previously [24]. Acetophenone oxime was synthesized by reaction of acetophenone (4.29 mmol) with hydroxylamine hydrochloride (14.42 mmol) in a mixture of water (5 ml) and sodium acetate (24.39 mmol) at 368 K for 1 h. Cyclododecanone oxime was synthesized by mixing the corresponding ketone (0.27 mmol) and hydroxylamine hydrochloride (0.73 mmol) with ethanol (0.5 ml) and pyridine (0.05 ml) and heating at 360 K for 1 h. Before use, the acetophenone and cyclododecanone oximes were recrystallized from ethanol and ether, respectively, and identified by NMR.

Fourier transform infrared spectra (FTIR) were recorded in a Nicolet 710 FT spectrophotometer at 293 K. Samples were pressed into self-supported wafers and introduced into a quartz IR cell sealed with CaF_2 windows and connected to a vacuum line to perform thermal treatment and in situ reactions. The presence of hydroxyl groups in the zeolite was established using 10 mg/cm^2 of catalysts compressed into a wafer, after outgassing at 673 K under 10^{-2} Pa for 16 h. To follow the Beckmann rearrangement, approximately 0.20, 0.13, and 0.16 mmol of oximes were mixed with 300 mg of zeolites Beta, MFI type, and mesoporous MCM-41, respectively, previously outgassed at 673 K. The solids were mixed and homogenized under an inert atmosphere in a glove box. Approximately 10 mg was used to prepare the pellets, which were introduced into the IR cell and outgassed to a final pressure of 10^{-2} Pa before recording the spectrum. The mixture was then heated at increasing temperatures between 373 and 673 K for 1 h at the vacuum line; after cooling, the IR spectra were recorded at 293 K after each treatment. To verify formation of the products, the pellets were submitted to continuous solid–liquid extraction with dichloromethane in a micro-Soxhlet equipment. The extract was then concentrated under reduced pressure and analyzed by GC-MS.

3. Results and discussion

3.1. The catalysts

Fig. 1 shows the IR spectra of the hydroxyl groups existing in the zeolites and the MCM-41 type materials used here as catalysts. The spectra of the siliceous zeolites (Beta-ND, Beta-D, silicalite-N) and mesoporous Si-MCM-41 show bands in the range 3725–3745 cm^{-1}, attributed to isolated silanol groups [19,25–28]. The position of the maxima suggests that in Beta-ND and silicalite-N, these hydroxyl groups are more abundant inside the zeolite pores (3725–3735 cm^{-1}), whereas in zeolite

Beta-D, they are located mainly at the external surface of the crystals (3740–3745 cm^{-1}) [19,25–28]. A band at 3690 cm^{-1} in the IR spectrum of zeolite Beta-ND indicates the presence of hydrogen-bonded or vicinal silanol groups [19,25–28]. The appearance of broad bands in the range 3700–3300 cm^{-1} for zeolites Beta-D and silicalite-*N* and mesoporous MCM-41 are explained by the presence of hydrogen-bonded SiOH groups [19, 25–28]. The band at 3500 cm^{-1}, usually attributed to hydrogen-bonded silanol groups forming nests, dominates the spectrum of zeolite silicalite-*N*. Comparing the FTIR spectra of Beta-ND and Beta-D shows that the overall intensity is much lower for the former, in agreement with the lower number of structural defective sites present in the zeolites synthesized using fluoride instead of hydroxyl groups as a mineralizing agent [29].

The IR spectra of the Al-containing zeolites H-Beta and H-ZSM-5 in the hydroxyl region, shown in Fig. 1, are characterized by a signal of silanol groups at the external surface of the crystals and another one attributed to bridging hydroxyl groups associated with Al appearing at ca. 3605 cm^{-1} [25]. Zeolite H-Beta gives an additional band at 3780 cm^{-1} attributed to hydroxyl groups bonded to aluminum species [25]. Finally, only a band of isolated silanols is distinguished in the spectrum of the Al-containing mesoporous H-MCM-41.

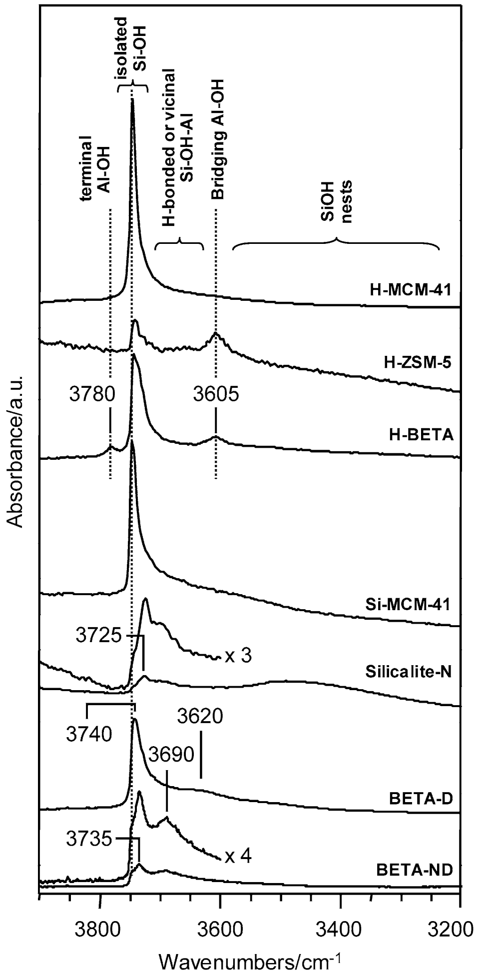


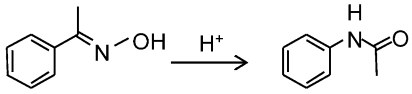
Fig. 1. FT-IR spectra of the solids tested as catalysts in the present study, after dehydration at 673 K.

3.2. Beckmann rearrangement of acetophenone oxime to acetanilide

To investigate the nature of the active sites, we studied the Beckmann rearrangement of acetophenone oxime to acetanilide (Scheme 1) over zeolite Beta (0.7 nm pore diameter) and mesoporous MCM-41 (3.0 nm pore diameter). Aluminosilicate and pure silica materials, containing bridging hydroxyls or silanol groups as main active sites, respectively, have been used as catalysts. Because both the oxime and amide are able to enter the pores of zeolite Beta and MCM-41 [30], comparing the results will allow us to ascertain the possible effect of pore dimension on catalyst performance.

3.2.1. Pure silica solids

The FTIR spectra in the 1775–1325 cm^{-1} range of acetophenone oxime and acetanilide adsorbed on zeolite Beta-D are compared in Fig. 2. The spectrum of acetophenone oxime (Fig. 2a) gives bands at 1450 cm^{-1} from the asymmetric [$\delta_{asym}(CH_3)$] and 1375 cm^{-1} from the symmetric [$\delta_{sym}(CH_3)$] bending frequencies of the methyl CH_3 group, at 1500 cm^{-1} from the υ(C=C) of the aromatic ring, and at ca. 1635 cm^{-1}, broad and of moderate intensity, characteristic of the υ(C=N) stretching [31]. The IR spectrum of acetanilide on Beta-D (Fig. 2b) presents the two bands from methyl groups, along with two additional ones at 1600 and 1500 cm^{-1} from the aromatic ring. Besides these, the characteristic band amide I υ(C=O) of acetanilide is broad and complex, with a maximum at 1645 cm^{-1}, and the band amide II, involving δ(NH), appears at 1540 cm^{-1} [31]. Similar IR spectra are obtained when the amide (not shown) or the oxime is adsorbed on siliceous Beta-



Scheme 1.

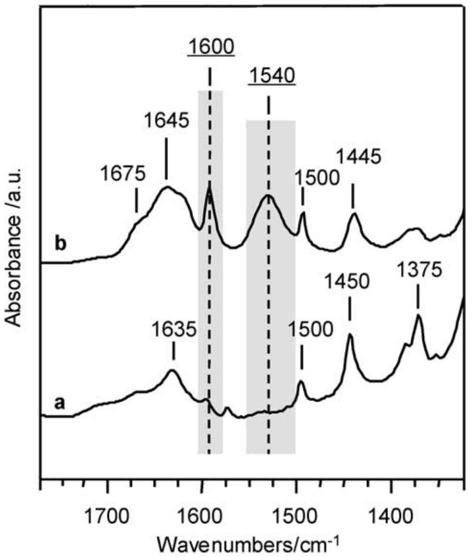


Fig. 2. FT-IR spectra of (a) acetophenone oxime and (b) acetanilide, adsorbed on zeolite Beta-D at 293 K. Shaded regions indicate the bands of interest.

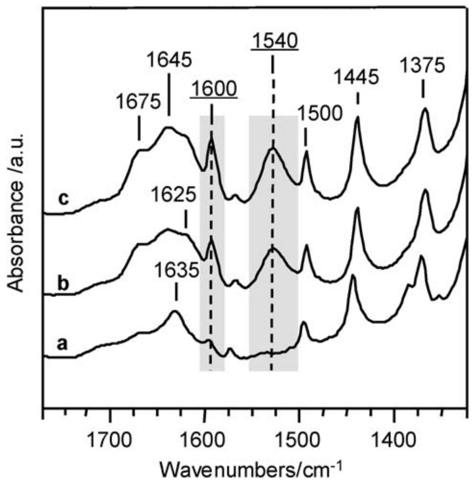


Fig. 3. FT-IR spectra of acetophenone oxime adsorbed on zeolite Beta-D at (a) 293 K, and after heating at (b) 373 K and (c) 523 K. Shaded regions indicate the bands of interest.

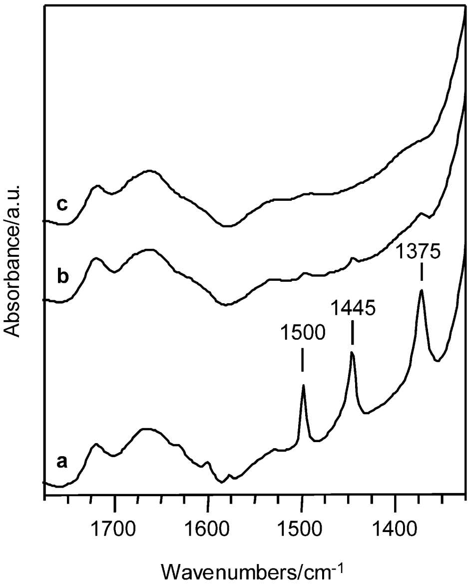


Fig. 4. FTIR spectra of acetophenone oxime adsorbed on zeolite Beta-ND at (a) 293 K, and after heating at (b) 373 K and (c) 523 K.

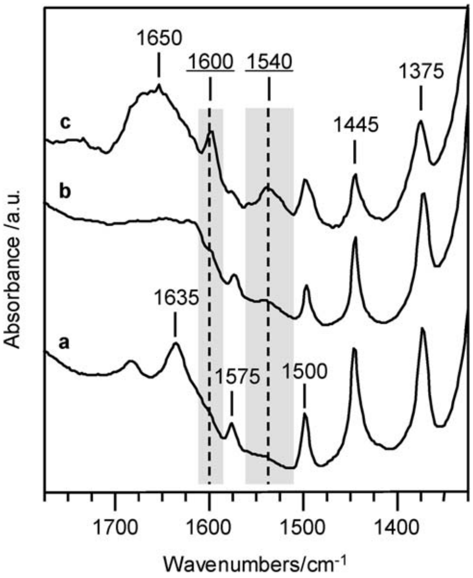


Fig. 5. FTIR spectra of acetophenone oxime adsorbed on mesoporous Si-MCM-41 at (a) 293 K, and after heating at (b) 373 K and (c) 523 K. Shaded regions indicate the bands of interest.

ND (Fig. 4a) and on mesoporous MCM-41 (Fig. 5a). The most distinctive spectral features of acetanilide compared with acetophenone oxime are the band at 1600 cm^{-1} from the aromatic ring and the amide II band at 1540 cm^{-1} (see the shaded areas in Fig. 2). Therefore, these two bands will indicate the formation of acetanilide, and their evolution will allow us to follow the Beckmann reaction.

Fig. 3 shows the results obtained after heating the acetophenone oxime adsorbed on zeolite Beta-D at increasing temperatures up to 523 K. The two bands at 1600 and 1540 cm^{-1} characteristic of acetanilide on siliceous zeolites are evident in the spectrum of Fig. 3b, indicating that the Beckmann rearrangement already starts at 373 K. Note, however, that it is not possible to determine the extent of the reaction because of the superimposition of the different bands. When the reaction temperature increases to 523 K, the resulting spectrum is very similar to that of acetanilide adsorbed on Beta-D (see Fig. 2b), suggesting complete transformation of the oxime.

The IR spectra obtained for the reaction of acetophenone oxime on zeolite Beta-ND are displayed in Fig. 4. The three bands from the methyl group and the aromatic ring in the spectrum recorded before any heating (see Fig. 4a) indicates the presence of acetophenone oxime. When the sample is heated under vacuum at 373 K, the bands of the oxime sharply decrease and completely disappear at 523 K, whereas the bands at 1600 cm^{-1} and the amide II, indicative of the formation of acetanilide, are not observed. The results illustrated in Fig. 4 suggest that the interaction of the oxime with zeolite Beta-ND is weak and that the Beckmann rearrangement does not proceed.

The spectra describing the rearrangement of acetophenone oxime over purely siliceous mesoporous MCM-41 as catalyst are displayed in Fig. 5. After heating at 373 K, very weak bands appear at 1600 and 1540 cm^{-1}, suggesting that if present, the concentration of acetanilide is very low. These two bands become more evident after heating the sample at 523 K, indicating that the oxime is rearranged to acetanilide over Si-MCM-41.

These results and the infrared spectra in the hydroxyl region of pure silica samples Beta-D, Beta-ND, and Si-MCM-41, suggest that isolated (internal and external) and weakly hydrogen-bonded or vicinal (band at 3690 cm^{-1}) silanol groups present in zeolite Beta-ND are not active to promote the Beckmann rearrangement. The presence of a larger number of silanol groups with stronger hydrogen bonds in the 3300–3600 cm^{-1} region in zeolite Beta-D makes the reaction possible. Hydrogen-bonded hydroxyls present in mesoporous MCM-41 (a very broad band around 3550 cm^{-1}) are also active in the Beckmann reaction; however, the required temperature for the reaction is higher than that on siliceous zeolite Beta. This difference in activity can tentatively be explained by confinement effects of the reactant within the smaller pores of zeolite beta and/or the slightly different acidity of the active centers. Therefore, our results suggest that isolated silanols are not active and that medium–strong hydrogen-bonded silanols are required for the Beckmann rearrangement to proceed.

3.2.2. Aluminosilicate solids

The results obtained on the rearrangement of acetophenone oxime over acid zeolite H-Beta and mesoporous H-MCM-41 are depicted in Figs. 6 and 7, respectively. At first glance, the IR spectra appear quite different from those recorded for siliceous materials (Figs. 2–5); the main spectral features of acetophenone oxime and acetanilide change depending on their adsorption over aluminosilicate acid or siliceous solids (compare Figs. 2a and 6a, and Figs. 2b and 6d). The main difference in the spectra of the oxime resides on the $\upsilon(\mathrm{C{=}C})$ bands from the aromatic ring at 1495–1500 cm^{-1} and 1590–1600 cm^{-1}; only the former is evident on siliceous Beta-D, Beta-ND, and Si-MCM-41 (Figs. 3a, 4a, and 5a), whereas only the latter appears on Al-containing zeolite H-Beta and on H-MCM-41 (Figs. 6a and 7a). The spectrum of acetanilide adsorbed on the solids containing Brønsted acid sites (Fig. 6d) is characterized by absence of the amide II band (appearing at 1540 cm^{-1} on the siliceous samples), and the sharp intensity of the amide I band at 1620–1630 cm^{-1} (weaker, broader, and more complex on siliceous solids). Therefore, the formation of acetanilide on the acid catalysts can be recognized by the appearance of two bands, an intense one at 1620–1630 cm^{-1} (amide I) and another one at 1495 cm^{-1} from the aromatic ring, absent in the spectrum of acetophenone oxime.

Fig. 6 shows the spectra recorded for the Beckmann rearrangement of acetophenone oxime over zeolite H-Beta. The changes observed after heating the system at 373 K (i.e., the appearance of a band at 1495 cm^{-1} and the increased intensity of the broad band at 1620 cm^{-1}) clearly indicate the formation of acetanilide. When the reaction temperature is increased up to 523 K, the spectrum suggests that the amount of acetanilide has increased. Similar results are obtained when the reaction is carried out over acid H-MCM-41, depicted in Fig. 7, and no important differences between the catalysts are observed.

The results obtained here indicate that Brønsted acid sites on zeolite H-Beta and H-MCM-41 are active in the Beckmann rearrangement of acetophenone oxime to acetanilide even at low temperatures, in agreement with previously reported results in the liquid phase [8]. The Beckmann rearrangement of acetophenone oxime using solid catalysts was also investigated previously [32,33]. In previous work, hydrolysis of the oxime to give acetophenone was considered as a competing reaction, and in reference [33], the authors reported the formation of N-methyl benzamide, the isomer of acetanilide, on acid solid catalysts. Indeed, the GC-MS analyses of the organic products extracted from the acid catalysts after reactions showed the presence of N-methyl benzamide. Nevertheless, no conclusive results on the formation of this byproduct can be obtained from the comparison of the IR spectra shown in Figs. 6 and 7 with those of N-methyl benzamide adsorbed on H-Beta and H-MCM-41.

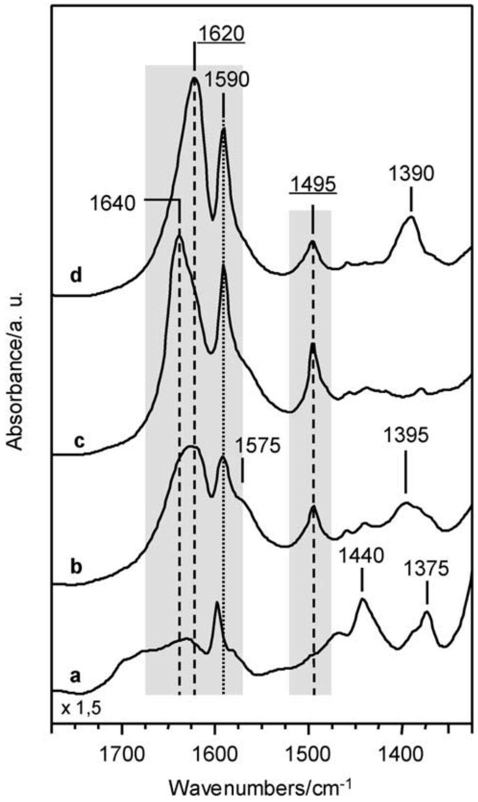


Fig. 6. FTIR spectra of acetophenone oxime adsorbed on zeolite H-Beta at (a) 293 K, and after heating at (b) 373 K and (c) 523 K. (d) FT-IR spectrum of acetanilide adsorbed on zeolite H-Beta. Shaded regions indicate the bands of interest.

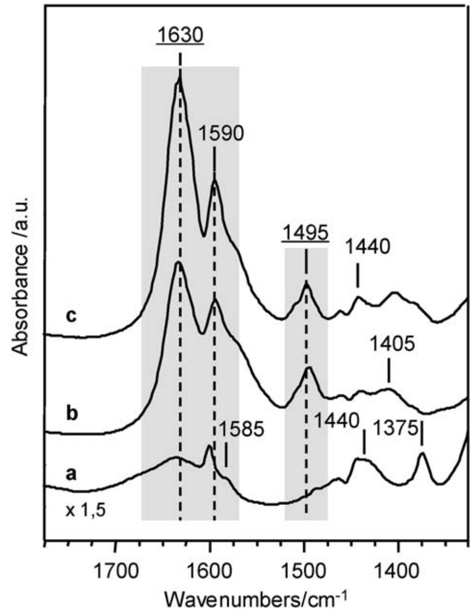


Fig. 7. FT-IR spectra of acetophenone oxime adsorbed on mesoporous H-MCM-41 at (a) 293 K, and after heating at (b) 373 K and (c) 523 K. Shaded regions indicate the bands of interest.

The differences observed in the IR spectra of the organic molecules adsorbed on pure silica and on silica–alumina catalysts indicate that the interaction of the oxime and the amide with the inorganic framework changes depending on the presence of Brønsted acid or silanol groups. Indeed, it has been previously reported that the bridging hydroxyl groups readily protonate the oxime at the N atom at room temperature, whereas silanol groups form only hydrogen bonds [18]. None of the modifications observed in the IR spectra of the oxime adsorbed over Brønsted acid sites can be clearly interpreted as the N-protonation; however, the changes in the absorption modes of both the acetophenone oxime and the acetanilide must reflect differences in the inorganic–organic interaction.

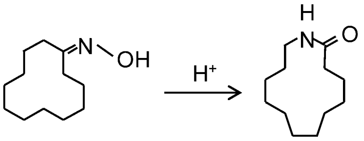
3.3. Beckmann rearrangement of cyclododecanone oxime to laurolactam

As mentioned above, the rearrangement of cyclohexanone oxime over MFI-type zeolites is by far the most studied catalytic system on the Beckmann reaction. Nevertheless, as mentioned earlier, there is no general consensus on the diffusivity of ε-caprolactam, and even cyclohexanone oxime, through the pores of MFI-type zeolite [7,8,12,14–16,19–21]. Consequently, it has not yet been clearly established whether the sites that are operative for the Beckmann rearrangement are those in an outer shell or those at the interior of the zeolite crystals. To investigate this, we chose the rearrangement of cyclododecanone oxime to laurolactam (see Scheme 2) over siliceous and Al-containing MFI-type zeolites. This bulky oxime (0.9 nm) cannot penetrate the pores of MFI (0.5 nm), and the reaction can proceed only if active sites are located near the external surface of the crystals. To aid interpretation of the IR spectra, we also used mesoporous MCM-41, which allows the diffusion of both reactant and product through the pores with no constraints.

Fig. 8 shows the FTIR spectra of cyclododecanone oxime and laurolactam adsorbed on H-MCM-41. In both cases, two bands with the maxima in the region 1440–1470 cm^{-1} quite intense for the oxime, assigned to $\delta(CH_2)$ bending are present. Besides these, the cyclododecanone oxime (Fig. 8a) gives a broad band centered at approximately 1640 cm^{-1}, attributed to $\upsilon(C{=}N)$ stretching. The most characteristic bands of laurolactam (Fig. 8b) are the amide I $\upsilon(C{=}O)$ at 1630 cm^{-1} of high intensity and the amide II at 1565 cm^{-1}. Therefore, for acetophenone oxime and acetanilide, the increased intensity of the band at 1630 cm^{-1} and the appearance of the band at 1565 cm^{-1}, attributed to amides I and II, respectively, will be taken as evidence of amide formation.

The spectra of cyclododecanone oxime on H-MCM-41 heated at increasing temperatures are shown in Fig. 9. When the system is treated at 373 K, the bands amide I and amide II of laurolactam emerge, the former, very intense, at 1630 cm^{-1} and the later at 1565 cm^{-1}, indicating that the Beckmann rearrangement occurs. An increase in the reaction temperature to 473 K (Fig. 9c) produces only some decrease of the overall spectral intensity, which is more important at 573 K (not shown), suggesting that the lactam is being progressively desorbed from H-MCM-41.

Fig. 10 shows the FTIR spectra of cyclododecanone oxime on H-ZSM-5 and silicalite-N at room temperature and after treatment at increasing temperature. The spectra of the bare zeolites, consisting on a combination band of the framework Si–O bonds, are included for comparison. At room temperature, the spectra of the oxime on the two zeolites exhibit weak $\delta(CH_2)$ bands and a broad band at 1650 cm^{-1} from the MFI framework, probably superimposed to $\upsilon(C{=}N)$. These observations suggest that the amount of oxime remaining in the solid after degassing at room temperature is low compared with that on H-MCM-41. This result agrees with the fewer active sites of the MFI structure accessible to the bulky cyclododecanone oxime, which are only those located close to the external surface of the zeolite crystal. The IR bands of the organic material



Scheme 2.

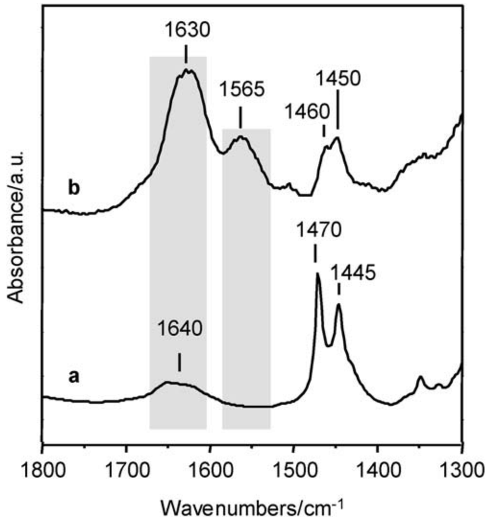


Fig. 8. FTIR spectra of (a) cyclododecanone oxime and (b) laurolactam, adsorbed on H-MCM-41 at 293 K. Shaded regions indicate the bands of interest.

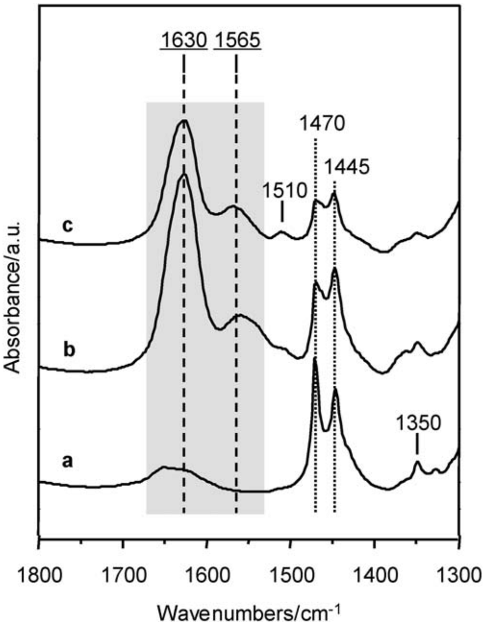


Fig. 9. FT-IR spectra of cyclododecanone oxime adsorbed on H-MCM-41 at (a) 293 K, and after heating at (b) 373 K and (c) 473 K.

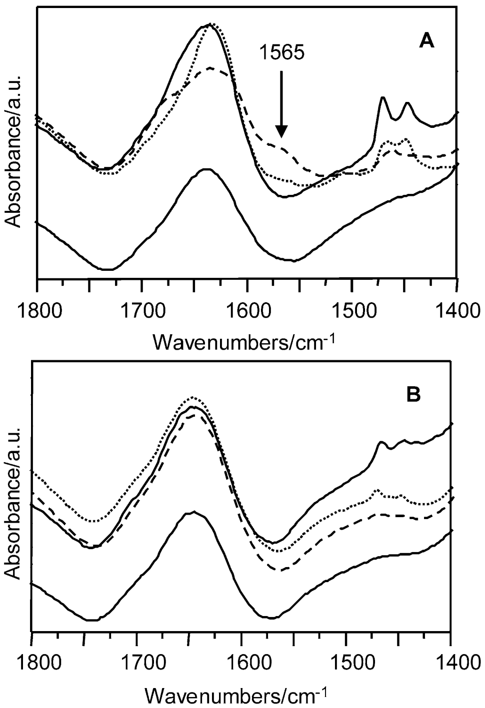


Fig. 10. FT-IR spectra of cyclododecanone oxime adsorbed on zeolites H-ZSM-5 (A) and silicalite-*N* (B) at room temperature (upper solid line), and degassing at 473 K (dotted line) and 573 K (dashed line). The spectra of zeolites H-ZSM-5 (A) and silicalite-*N* (B) dehydrated at 673 K (lower solid lines) are included in the figure for comparison.

adsorbed on H-ZSM-5 become weaker when the reaction temperature is raised to 473 K (see Fig. 10), although it is still possible to distinguish a broad band at 1565 cm^{-1} (the same position as the amide II band), more evident after heating at 573 K, strongly suggesting the formation of laurolactam on H-ZSM-5. However, similar experiments carried out for silicalite-*N* (see Fig. 10B) show further decreases in the intensity of IR bands coming from the organic molecules. No evidence of the formation of laurolactam is found in the spectra, suggesting that the rearrangement does not occur.

Consequently, we can conclude that Brønsted sites present on the external surface of the crystallites of H-ZSM-5 are able to perform the Beckmann rearrangement of cyclododecanone oxime. However, our results suggest that no potential active sites, such as silanol nests, are located at the external surface of silicalite-*N*.

Comparing the results obtained for the reaction of acetophenone and cyclododecanone oximes over mesoporous H-MCM-41 solids reveals some differences. The intensity of the IR bands of the resulting laurolactam sharply decreases after the treatment at 473 K, whereas that of the IR bands of acetanilide increases at 523 K. The lower desorption temperature of laurolactam suggests a weaker interaction with the Brønsted acid sites of the mesoporous solid compared with that of acetanilide.

4. Conclusion

The results obtained by in situ FT-IR measurements on the Beckmann rearrangement of acetophenone and cyclododecanone oximes indicate that Brønsted acid sites located in the micropores and mesopores of the zeolites and MCM-41, respectively, are active in the reaction. Isolated hydroxyl groups or weakly hydrogen-bonded vicinal silanol within the zeolite pores seem to be inactive. Hydrogen-bonded silanol groups giving bands in the IR region 3300–3600 cm^{-1} with slightly stronger acidity are needed for the reaction. When pore size is considered, micropores appear to be more favorable than mesopores, probably because of a certain activation of the oxime molecule by confinement effects.

The results obtained on the rearrangement of cyclododecanone oxime on MFI-type zeolites suggest that Brønsted acid sites located on the external surface of the crystals are active in Beckmann rearrangements, whereas external silanols appear to be nonreactive. When the two substrates are considered, the interaction of the active sites with laurolactam seems to be weaker than that with acetanilide.

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