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# Spectroscopic and catalytic characterization of basic zeolites and related porous materials

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The catalytic activity of alkali ion-exchanged zeolites X, Y and Beta as well as of non-zeolitic porous solids impregnated with cesium hydroxide or cesium acetate has been studied in the Knoevenagel condensation of benzaldehyde and malononitrile. Additional information concerning the basic surface sites of the catalysts was obtained by FTIR spectroscopic investigations of adsorbed deuterochloroform. Comparison of the results revealed a good agreement of the spectroscopic and catalytic characterization for the ion-exchanged zeolites. In the case of more strongly basic cesium-impregnated catalysts, the application of deutero-chloroform as a suitable probe molecule may be limited.

## 1. INTRODUCTION

In heterogeneous catalysis, growing attention has recently been payed to basic solids [1]. Several studies were directed towards a reliable characterization of their surface properties, in particular to the strength and density of base sites. Two principal techniques have been applied, viz. the observation of probe molecules adsorbed on the catalyst surface by means of XPS, NMR or FTIR spectroscopy [1-3] as well as catalytic testing of the basic solids via suitably selected reactions, such as the isomerization of butene-1, the side chain alkylation of toluene, the dehydrogenation of isopropanol or similar secondary alcohols or Knoevenagel condensations [1]. However, only few studies have so far been reported in which these two techniques have been combined and a correlation of the respective results has been aimed at. In this work, the catalytic and surface properties of various types of basic catalysts have been investigated in order to examine the suitability of chloroform as a probe molecule for the FTIR spectroscopic characterization and to establish correlations between the spectroscopic and catalytic data. As a test reaction, the Knoevenagel condensation of malononitrile and benzaldehyde was chosen which is unequivocally catalyzed by bases and proceeds at mild reaction conditions [4].

## 2. EXPERIMENTAL SECTION

*Catalysts.* For the synthesis of zeolite HNa-Beta, 1.15 g of sodium aluminate (Riedel-de Haën) were dissolved in 24.6 g of water. 43.2 g of tetraethylammonium hydroxide (Fluka) and 43.2 g of silica sol (30 %, Bayer) were subsequently added to the solution. The resulting gel was crystallized under static conditions in a stainless steel autoclave with a PTFE-insert at

160 °C for 7 days. Calcination was carried out at 450°C. The mesoporous molecular sieves MCM-41 (MCM-41A with $n_{Si}/n_{Al}$ = 337 and MCM-41B with $n_{Si}/n_{Al}$ =14) were prepared as described in [5] using sodium aluminate (Riedel-de Haën), sodium silicate solution (Merck) and tetradecyltrimetylammonium bromide (Aldrich). HNa-Beta, Na-Y and Na-X (Union Carbide) and MCM-41B were ion-exchanged several times with aqueous solutions of akali metal chlorides at 80 °C. Cesium exchanged Na-Y (denoted CsNa-Y) and the MCM-41 samples were further impregnated with cesium hydroxide and cesium acetate, respectively. CsNa-Y was immersed in an aqueous solution of cesium hydroxide. After stirring the suspension for 3 h at 80 °C, the water was evaporated. Impregnation of MCM-41 was carried out by stirring the samples in a methanolic solution of cesium acetate for 3 h at 60 °C and quickly removing the solvent under vacuum in a rotary evaporator [6]. The impregnated materials were subsequently calcined at 500°C for 5 h in air. For comparison, commercial $\gamma$-$Al_2O_3$ (Merck) and silica gel (Fluka) were impregnated with cesium hydroxide following the procedure described for CsNa-Y. All samples were loaded to a degree of 10 wt.-% CsOH.

*IR measurements.* The base sites of the catalysts were characterized spectroscopically using a Perkin Elmer FTIR - Spectrometer (Spectrum 2000) and deuterochloroform as a probe molecule. Self-supporting wafers of the catalyst samples were prepared and activated overnight in vacuum ($p < 10^{-6}$ mbar) at 500 °C. The adsorption of $CDCl_3$ was studied at room temperature with a 4 $cm^{-1}$ resolution and accumulating 20 scans.

*Catalytic test reaction.* The Knoevenagel condensation of benzaldehyde and malononitrile was chosen as a catalytic test reaction. These catalytic experiments were conducted in a batch reactor in the liquid phase at 50 - 60 °C using 15 mmol of each reactant and 0.05 g of catalyst. When the impregnated samples were applied as catalysts, toluene was used as solvent. The reaction was monitored on a Hewlett Packard gas chromatograph 5890 equipped with a HP-5, 15 m capillary column.

## 3. RESULTS AND DISCUSSION

### 3.1. Catalyst characterization

After ion exchange and impregnation of the zeolites, it was proven that no destruction of the zeolitic lattice had occurred. Even though the X-ray diffractograms seemed to indicate some loss of crystallinity, no extra-framework aluminum could be detected by means of solid state $^{27}$Al MAS NMR. Moreover, a sample which was back-exchanged with sodium displayed the original intensity in the X-ray diffraction pattern, leading to the conclusion that the variation in peak intensities was caused by the high electron densities of the bigger alkali cations, as already reported in the literature [3]. The peak intensities in the X-ray diffraction patterns of cesium-impregnated MCM-41 are likewise reduced. The adsorption-desorption isotherms of nitrogen on these materials are similar in shape for the parent and the impregnated samples and typical of mesoporous systems. However, the inflection point becomes less sharp and shifts towards lower relative pressures after the impregnation, indicating a narrowing of the mesopores. The sorption isotherms and the pore diameter distribution of MCM-41A and Cs/MCM-41A are shown in Figure 1. It can be seen that the average pore diameter of the MCM-41 material has been markedly reduced by impregnation. This indicates that the decrease in BET surface area (830 $m^2/g$ for MCM-41A and 660 $m^2/g$ for Cs/MCM-41A) is caused by a reduction of pore diameters through deposition of the guest component inside the pores and a partial pore filling, rather than by a destruction of the

mesoporous structure. Similar results have been described by Kloetstra et al. for the preparation of MCM-41 impregnated with CsLa mixed oxides [6].

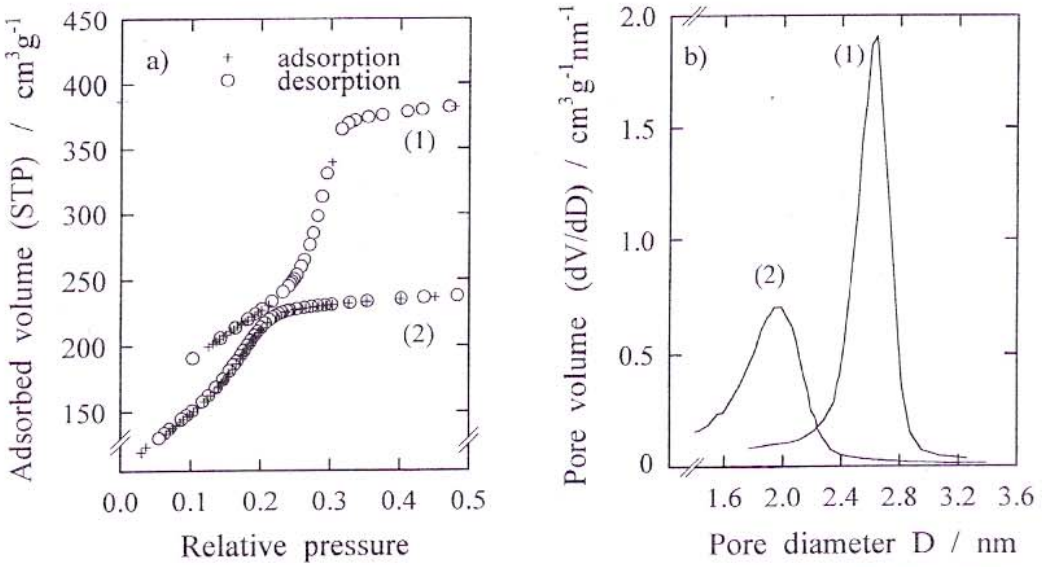



Figure 1. a) Sorption isotherms of nitrogen at -196°C on (1) MCM-41A and (2) Cs/MCM-41A.
b) Resulting pore size distribution.

### 3.2. Base sites on alkali ion exchanged zeolites

The results of the IR spectroscopic characterization of alkali exchanged zeolites X, Y and Beta, assumed to possess base sites of low or medium strength, are summarized in Figure 2. On these catalysts, the base sites are thought to be framework oxygen. Their strength is measured by the shift of the C-D stretching mode of adsorbed deuterochloroform towards lower wavenumbers. The shift is explained by a weakening of the C-D bond when deuterochloroform undergoes D-bonding interactions with the basic surface sites [2]:

$$O_s^{2-} + D - CCl_3 \rightarrow O_s^{2-} \cdots D - CCl_3$$

As reported by Xie et al. [7] for the adsorption of $CHCl_3$ on alkali ion-exchanged faujasites, the C-D stretching band of adsorbed deuterochloroform is equally shifted towards lower wavenumbers with increasing size of the exchanged cation. For alkali ion-exchanged zeolite X, two different stretching bands can be observed, one at a constant wavenumber of ca. 2232 $cm^{-1}$, while the second one shifts to lower wavenumbers after the introduction of potassium, rubidium and cesium ions. In the literature, this finding has been explained either by two different adsorption modes of $CDCl_3$ as displayed in Figure 3 A and B [2] or by the existence of different kinds of adsorption sites with different base strength [7]. The zeolites examined in this study contain 10 % (KNa-X), 27 % (RbNa-X) and 40 % (CsNa-X) residual sodium ions, respectively, which during the calcination possibly migrate from the sodalite cages into the supercages. We conclude that the C-D stretching band at 2232 $cm^{-1}$ results from the interaction of deuterochloroform with base sites adjacent to sodium cations and is, therefore, the same in all exchanged samples. The second band, the position of which depends on the kind of exchanged cation, reflects the adsorption of $CDCl_3$ on base sites in the neighborhood of K, Rb and Cs cations, respectively. From the wavenumber shift it can be inferred that, by the introduction of Rb and Cs cations into the zeolite, base sites of similar strength are created. In alkali ion-exchanged zeolite Y only one band can be observed in the

C-D stretching frequency region. If this material contains base sites of different strengths, the difference may be too small for a detection by chloroform adsorption [7].

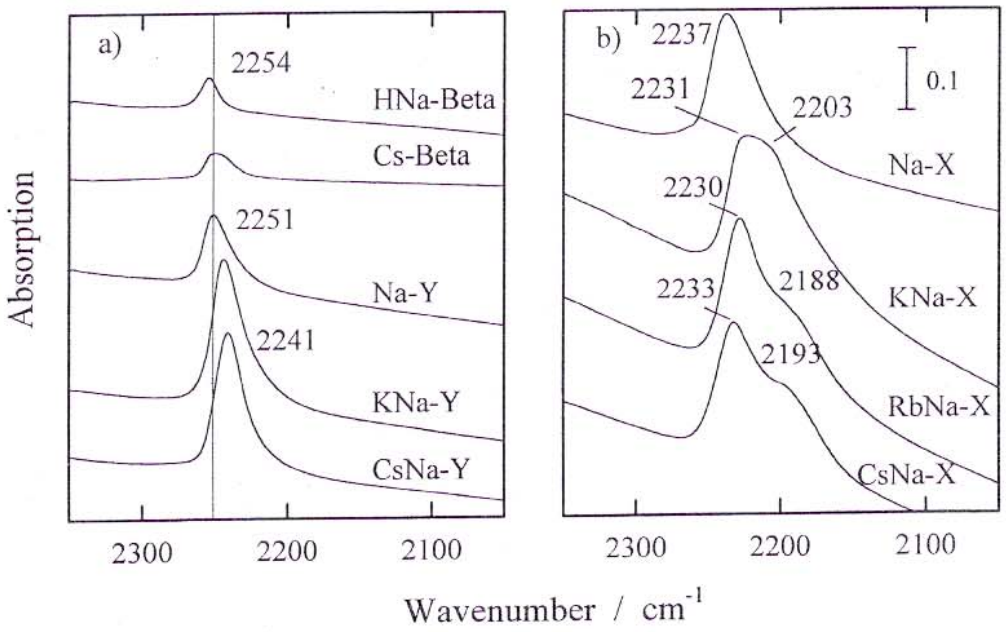



Figure 2. IR spectra in the C-D stretching region for $CDCl_3$ adsorbed on various zeolites at 303 K.

Zeolite Beta has been studied in its HNa-form (HNa-Beta) as well as after cesium ion exchange (Cs-Beta). The C-D stretching band of $CDCl_3$ adsorbed on HNa-Beta appears at 2254 $cm^{-1}$. After chloroform adsorption on zeolite Cs-Beta a rather broad band is observed that may be composed of two poorly resolved bands. This would indicate the existence of two different adsorption sites. As in this material no residual sodium could be detected, the different adsorption sites might be bridging oxygen atoms and SiOH groups.

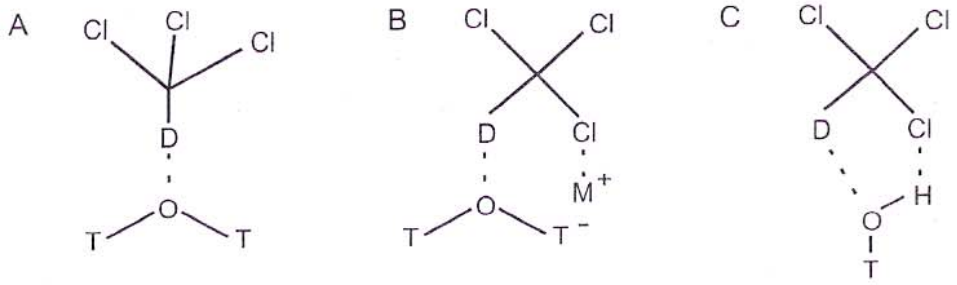



Figure 3. Possible adsorption modes of $CDCl_3$ on zeolites and oxides [2,7].

The results of the Knoevenagel condensation of malononitrile and benzaldehyde on the alkali ion-exchanged zeolites are depicted in Figure 4. The yield of benzylidenemalononitrile as a function of reaction time is shown. When HNa-Beta is used as catalyst, no reaction takes place, confirming that this reaction does not proceed on acidic materials, hence its attractiveness as a test reaction for basic catalysts. With zeolite Cs-Beta, traces of the reaction product are observed after a reaction time of 80 minutes. Although by chloroform adsorption, sites of similar basic strength are detected on zeolites Cs-Beta and Na-Y, zeolite Na-Y shows a far higher activity in the Knoevenagel condensation. This observation may be explained by a different number of (accessible) active sites. In the series of alkali ion-exchanged X and Y

zeolites, the results of the Knoevenagel condensation are consistent with the IR spectroscopic observations; the catalytic activity increases with increasing bathochromic shift of the C-D stretching wavenumber. Both characterization techniques lead to the conclusion that CsNa-X and RbNa-X possess base sites of similar strength.

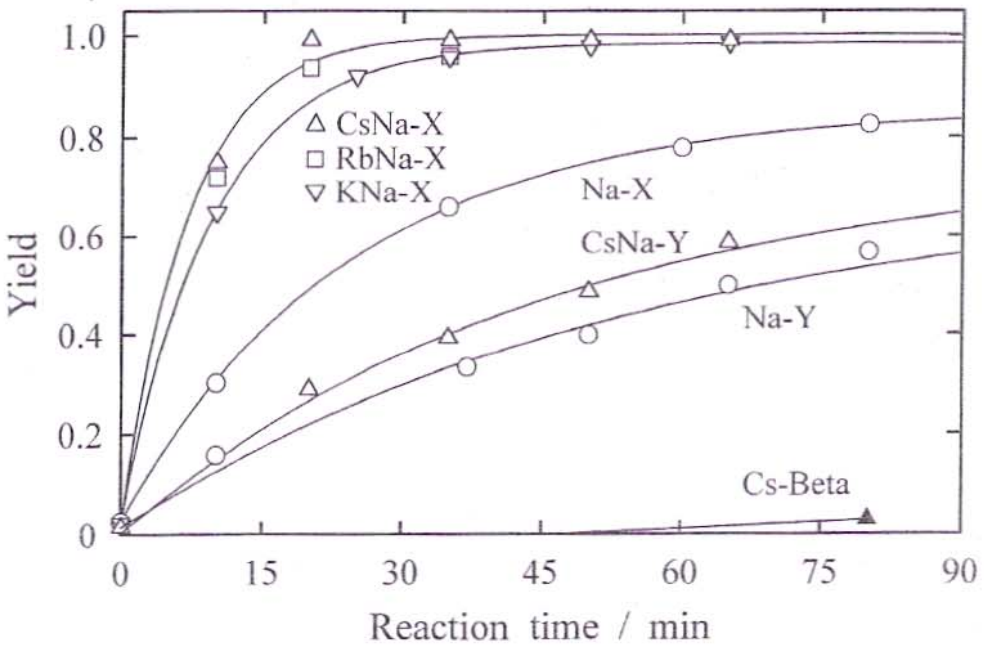



Figure 4. Knoevenagel condensation of benzaldehyde and malononitrile carried out with 15 mmol of each reactant, 0.05 g of catalyst and at a reaction temperature of 90 °C.

### 3.3. Base sites on impregnated catalysts

In the IR spectrum of $CDCl_3$ adsorbed on zeolite CsNa-Y impregnated with CsOH, a new band is observed at 2212 $cm^{-1}$ (Fig. 5a). This band hints at the presence of a guest component with stronger base sites than those of the host framework. In the literature, this guest component has been identified as cesium oxide clusters inside the zeolitic pores [8]. In addition, the guest oxide seems to influence the basicity of the zeolite framework: This is expressed by a shift in the C-D stretching wavenumber of adsorbed deuterochloroform from 2241 $cm^{-1}$ to 2239 $cm^{-1}$.

The spectra recorded after adsorption of $CDCl_3$ on different materials impregnated with cesium hydroxide, including $\gamma$-$Al_2O_3$ (1), silica gel (2) and MCM-41 (3 and 4), are displayed in Figure 5b. In the C-D stretching frequency region, at least three different bands can be seen. The band at 2254 $cm^{-1}$ can only be observed after the adsorption of high amounts of deuterochloroform. In the literature, this band has been explained by the interaction of $CDCl_3$ with surface sites such as OH groups [9]. This explanation seems to be justified, since simultaneously with the appearance of this band the O-H stretching bands of the supporting oxides are shifted towards lower wavenumbers and become significantly broader. The interaction of $CDCl_3$ with OH groups, possibly as shown in Figure 3 C, takes place particularly after the preferred strong basic adsorption sites have been saturated. For non-impregnated $\gamma$-$Al_2O_3$, silica gel and MCM-41 ($n_{Si}/n_{Al}$ = 337), the band at 2254 $cm^{-1}$ is the only one observed. However, as on the pure supports a slight shift of this band with increasing amounts of adsorbed $CDCl_3$ is observed, an influence of physisorbed deuterochloroform

cannot be excluded. For Cs/CsNa-Y, even at high amounts of adsorbed $CDCl_3$, the band at 2254 $cm^{-1}$ does not appear, possibly because of the high internal surface area of this material, leading to a higher number of base sites.

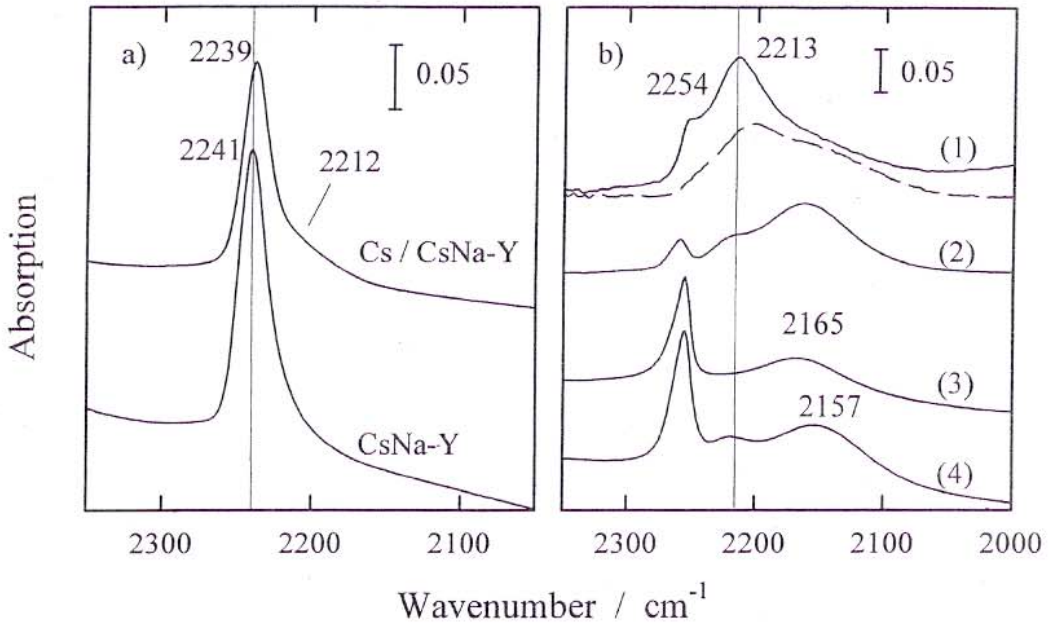



Figure 5. C-D stetching range of deuterochloroform adsorbed on a) CsNa-Y and Cs/CsNa-Y and on b) Cs/$\gamma$-$Al_2O_3$ (1), dotted line: lower amount of $CDCl_3$; Cs/$SiO_2$ (2); Cs/MCM-41A (3) and Cs/MCM-41B (4).

A second common band can be observed for all impregnated catalysts at 2213 $cm^{-1}$ which indicates the presence of base sites. The position of this band depends on the nature of the guest component: When different alkali metal hydroxides or acetates are used in the impregnation step, it is shifted towards lower wavenumbers with increasing size of the alkali metal cation. Therefore, it can be concluded that this band results from the interaction of deuterochloroform with the supported guest component. For all impregnated catalysts, except Cs/CsNa-Y, a third band is present at significantly lower wavenumbers of 2166 $cm^{-1}$ (Cs/$\gamma$-$Al_2O_3$, Cs/$SiO_2$ and Cs/MCM-41A) and 2157 $cm^{-1}$ (Cs/MCM-41B), respectively. This hints at the existence of even stronger base sites than those responsible for the band at 2213 $cm^{-1}$. The position of this third band is equally shifted towards lower wavenumbers with increasing size of the alkali metal cation introduced by impregnation. It varies slightly with different supports, while the band at 2213 $cm^{-1}$ is the same for all catalysts. Interestingly, the intensity ratio of the two bands depends on the nature of the support: For Cs/$\gamma$-$Al_2O_3$, the band at 2213 $cm^{-1}$ is dominating the spectrum, whereas for Cs/$SiO_2$ and Cs/MCM-41 the band beyond 2200 $cm^{-1}$ is the stronger one. From the spectroscopic characterization of the impregnated catalysts it can be concluded that at least two different kinds of base sites exist on the catalyst surface. They are equally strong when the same alkali metal component is present as guest species, but their relative number depends on the nature of the supporting material. Recently [10], NMR studies of alkali metal oxides revealed that commercial cesium oxide is composed of $Cs_2O_2$ and $CsO_2$. From this, it might be concluded that on cesium-impregnated catalysts, different types of oxides are present as well, leading to base sites of different strength. Furthermore, the structural environment (e.g., edges or corners) could also influence

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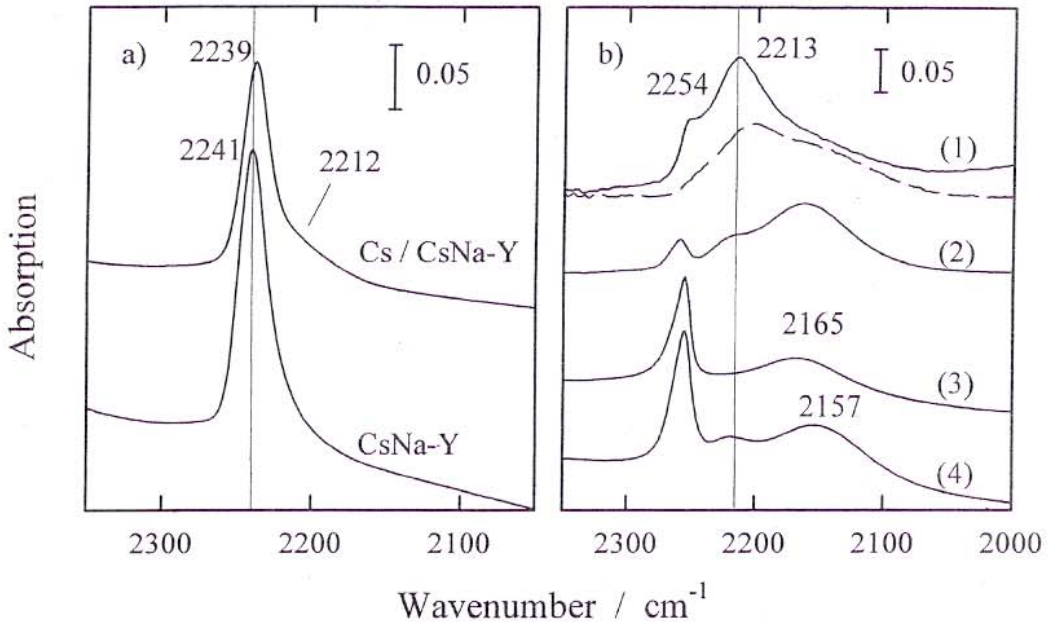



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the base strength of different sites [1]. In the literature [1,8], it is stated that alkali ion-impregnated catalysts possess stronger basic properties than alkali ion-exchanged zeolites. By adsorption of chloroform, base sites stronger than those of CsNa-X can be detected on all impregnated materials except on Cs/CsNa-Y.

In Figure 6, the yield of benzylidenemalononitrile obtained with the impregnated catalysts in the Knoevenagel condensation of benzaldehyde and malononitrile is displayed as a function of reaction time. Zeolite CsNa-X has been used under the same reaction conditions as a reference material.

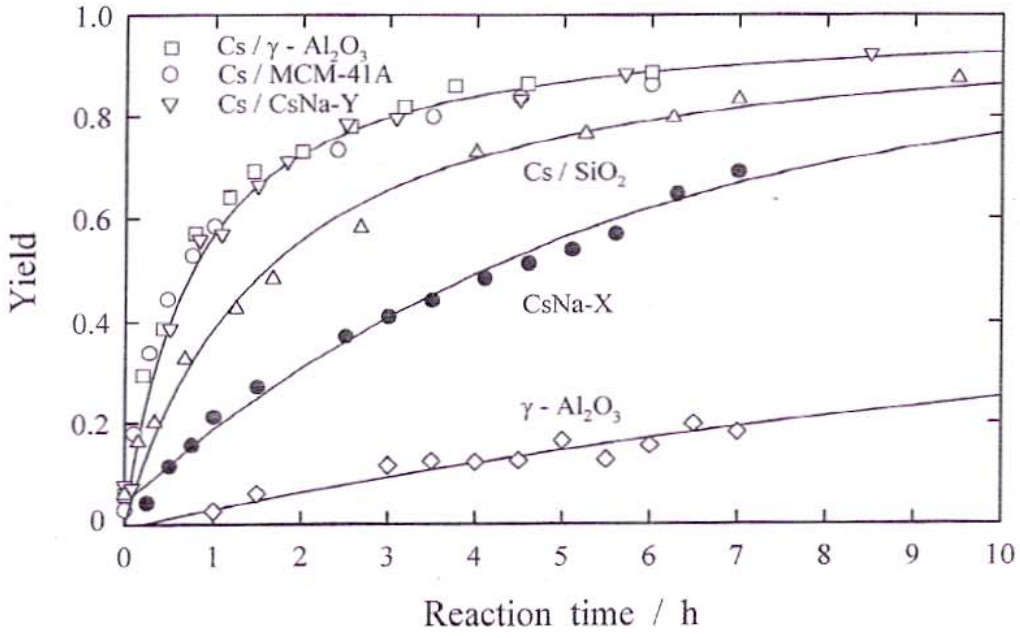



Figure 6. Knoevenagel condensation of benzaldehyde and malononitrile carried out with 15 mmol of each reactant, 0.05 g of catalyst, 2 g of toluene as solvent and at a reaction temperature of 60 °C.

All impregnated catalysts show a significantly higher activity in the condensation reaction than CsNa-X which confirms a stronger „basicity" of these materials as described in the literature [1,8]. Unfortunately, a test reaction does not discriminate between the strength and number of base sites, both an increasing number of sites and an increasing base strength lead to an enhanced catalytic activity. Furthermore, when micro- and macroporous catalysts are compared, transport limitations may also influence the catalytic activity. Some conclusions can nevertheless be drawn from the catalytic experiments: By impregnation of $\gamma$-$Al_2O_3$ with cesium hydroxide and subsequent calcination, base sites are created which increase the catalytic activity of this material significantly. Cs/$\gamma$-$Al_2O_3$ (BET surface = 103 $m^2/g$) is even more active in the Knoevenagel condensation than Cs/$SiO_2$ (BET surface = 178 $m^2/g$), although both materials have been impregnated to the same degree. This is not expected from the spectroscopic results which indicate the presence of a higher number of stronger base sites on Cs/$SiO_2$. Probably, the base strength of the weaker sites is sufficient to catalyze the reaction, so that the total number of base sites determines the catalytic activity of the materials. Furthermore, the strongest base sites on Cs/$SiO_2$ might not be fully effective in the Knoevenagel condensation, because they might be poisoned by water or carbon dioxide [1]. MCM-41 is proposed in the literature [6] as a promising support for basic guest components, possessing a high surface area and pores large enough for bigger molecules. In the

Knoevenagel condensation of benzaldehyde and malononitrile, for materials cesium-impregnated to approximately the same degree, no difference between Cs/MCM-41A and Cs/CsNa-Y is observed concerning the catalytic activity. However, no band at 2160 $cm^{-1}$ can be observed after adsorption of deuterochloroform on Cs/CsNa-Y which would indicate the presence of strong base sites. In this case, the probe molecule seems to be not sensitive enough, because the catalytic activity of Cs/CsNa-Y in comparison to Cs/MCM-41A and CsNa-X indicates the existence of those sites. The condensation reaction does not seem to be hindered by diffusion in the zeolitic pores so that an advantage of MCM-41 as supporting material is probably only effective with molecules larger than those applied in the test reaction. Cs/MCM-41, however, shows a higher catalytic activity than Cs/silica gel, presumably because of its higher surface area.

## 4. CONCLUSIONS

For alkali ion-exchanged zeolites, the catalytic and spectroscopic results are in good agreement. With increasing size of the exchanged cation, the C-D stretching band of deuterochloroform is shifted towards lower wavenumbers, indicating the presence of stronger base sites. In the same order, the catalytic activity of these materials in the Knoevenagel condensation increases. On cesium-impregnated catalysts, at least two different base sites can be detected by adsorption of deuterochloroform. Their strength is almost the same on all catalysts whereas their relative number is influenced by the support. On Cs/CsNa-Y, probably not all sites are detected by the probe molecule. In the catalytic test reaction, all impregnated catalysts turned out to be more active than the alkali ion-exchanged zeolites.

## 5. ACKNOWLEDGMENTS

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