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Poisoning of aldol condensation reaction with H_2O on acid catalysts

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The effect of chemisorbing water on three catalysts previously evaluated in the acetone condensation reaction has been studied. The active sites in that reaction are Lewis acid sites present either on the surface of alumina or of nonframework alumina in zeolites. These sites are poisoned by water and the reaction rate decreases at the pace of the loss of Lewis sites. The stoichiometry of the poisoning reactions is one water molecule per site on alumina and two water molecules per site on nonframework alumina.

Keywords: acetone condensation, activity, acid sites, poisoning by water, *in situ* IR

1. Introduction

Condensation of acetone over solid acid catalysts has been studied extensively as a test reaction by several research groups [1–4]. NMR [3,4] and IR [1,2] spectroscopies were used and the reaction pathway is well established. This reaction provides an unique possibility for monitoring the evolution of the reactant's and the product's concentrations on the catalyst by IR spectroscopy [5].

Under identical conditions, the reaction rate is faster on alumina than on zeolites, and the condensation goes beyond the formation of mesityl oxide. Zeolites without nonframework aluminum are poor catalysts. On HZSM-5 the reaction is about two orders of magnitude slower than on USY at 105 °C. From these data it appears that Lewis sites, even if they bind acetone less energetically than Brønsted sites, are responsible for the activation of the molecule. On alumina the reaction would take place between gas-phase acetone and acetone adsorbed on Lewis sites. On zeolites with nonframework aluminum and, thus, with Lewis sites, the reaction would involve acetone molecules adsorbed on Brønsted and Lewis sites, the activation occurring on the Lewis site.

Poisoning of a reaction is a classical tool for checking the nature of the active sites. For instance, in the case of zeolite catalysts, the poisoning of Brønsted acid sites with amines or Na^+ has been often applied [6,7]. In order to poison the acetone condensation, a molecule that is able to selectively poison Lewis acid sites should be used. Water seems to be adequate in that respect.

Water adsorption on the Brønsted acid sites of zeolites is well documented [8–13]. Detailed analysis of IR spectra of the water–zeolite system has been published [8,10,12]. It has been found that water is preferably adsorbed by Lewis acid sites [11,12] in dealuminated zeolites.

In addition, water is a by-product of the acetone condensation reaction. The water formed during the formation of mesityl oxide may poison the catalyst and affect the reaction rate. Fortunately, as reported by Xu et al., water does not effect the product distribution of the acetone condensation reaction catalyzed by zeolites [3]. The reaction does not change upon poisoning.

Water can poison Lewis acid sites in two ways:

(1) Lewis acid sites are formed on the surface of nonframework alumina particles (NFAl) and of alumina [14] during the pretreatment of the catalyst at high temperature. Surface hydroxyls are removed and coordinately unsaturated aluminum atoms are formed. These coordinatively unsaturated aluminum sites are Lewis acid sites. The process of the formation of the Lewis acid sites can be reversed by rehydration.

(2) Adsorption of molecular water on a Lewis acid site can block the site and make it inaccessible to acetone.

In the following set of experiments we investigated the effect of water on the activity of acidic catalysts in acetone condensation. Catalysts chosen for this study possessed either Brønsted acid sites (HY), Lewis sites (alumina) or both Brønsted and Lewis acidity (USY).

The possibility of conducting the experiments *in situ* in an IR cell allows us to combine catalysts' poisoning experiments with the probing of the active sites.

2. Experimental

2.1. Catalysts

All catalysts used for the study were described earlier. The nanosized amorphous alumina, rich in coordination defects, was prepared by a sol–gel process [15] and calcined at 600 °C. Its Lewis acidity was carefully characterized

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[16–18]. The total number of Lewis sites is 0.4 meq/g and the surface area is between 300 and 350 m^2/g. USY is a commercial (PQ) catalyst counting an equal amount of Brønsted and Lewis acid sites, e.g., 1.43 mmol/g.

Table 1 shows the Si/Al ratios obtained from ^{29}Si NMR and the numbers of Lewis and Brønsted acid sites obtained by FTIR of chemisorbed NH_3. In order to minimize the dealumination process and, therefore, the number of Lewis sites, NH_4Y was deammoniated at 400 °C under vacuum in the IR cell before use. USY and alumina were dried in the IR cell by outgassing at 500 and 600 °C, respectively, for 5 h under a 10^{-5} Torr residual pressure and pretreated by 20 Torr oxygen at the same temperature to eliminate any organic contaminant.

2.2. Reagents

Acetone (99.9%) was an Aldrich product. Before use it was dried over a 4A molecular sieve and purified by repeating freezing and thawing.

2.3. Instrument

The FTIR spectra were obtained with a Perkin–Elmer 1800 FTIR spectrometer. The spectral resolution was 8 cm^{-1}. Five scans per spectrum were accumulated for the experiments with alumina, while 30 scans for the experiments with zeolites. The weight of the pellets was about 14 mg/cm^2. All spectra were recorded at the reaction temperature. A quadrupole mass spectrograph (UTI100C), linked to the infrared cell by a leak valve, permitted the gas phase to be monitored.

Table 1
Physicochemical characteristics[a] of materials used in the study.

Sample	Surface area (m^2/g)	Si/Al chemical analysis	Si/Al NMR	Brønsted sites (mmol/g)	Lewis sites (mmol/g)
Alumina	300	n/a	n/a	0	0.4
HY	900	2.6	2.6	>0.6	n/a
USY	800	2.6	4.9	1.4	1.4

[a] More detailed data can be found in [16,25].

2.4. Reaction

The amount of water introduced in the reaction system and the reaction conditions are shown in table 2. The water was allowed to react for 15 min at the reaction temperature and then the samples were outgassed for 15 min to a residual pressure of 10^{-6} Torr. On zeolites the acetone condensation reaction was run at 105 °C. For all the experiments with zeolites (HY, USY) the initial dose of acetone was 3 mmol/g catalyst, thus, it was always higher then one acetone per acid site. Because of the high reactivity of the alumina toward the condensation of acetone, a lower temperature with a smaller reaction dose was necessary to obtain valid measurements of the reaction rate. In the case of alumina the acetone condensation reactions were run at 105 and 60 °C with an acetone dose of 0.5 mmol/g, which was slightly higher than the number of Lewis acid sites.

The formation of mesityl oxide (MO) was monitored by deconvoluting the spectra in order to record the integrated intensity of the C=C stretch observed at about 1560 cm^{-1} for mesityl oxide adsorbed on Brønsted sites and at 1600 cm^{-1} for mesityl oxide adsorbed on Lewis sites [19]. The surface acetone concentration was followed by the decrease of C=O stretching bands. The band assignment and the values of specific absorbances were published earlier [19].

3. Results

3.1. Water adsorption

The results of water adsorption experiments are summarized in table 2. The samples USYII and USYIII are USY zeolites pretreated in the IR cell as described above, then treated with 0.48 and 0.96 mmol/g of water, respectively; HYII is HY zeolite treated with 0.96 mmol/g of water; and Al60II and Al105II are the alumina treated with 0.3 and 0.2 mmol/g H_2O, respectively. USYI, HYI, Al60I, and Al105I are the original catalysts. No significant residual pressure of water was detected after the adsorption.

The difference spectra of HY and USY zeolites after adsorption of 0.96 mmol/g of *water and the initial state* are shown in figure 1. Four new bands are observed in

Table 2
First-order estimate of the amount of water adsorbed on Brønsted and Lewis acid sites. The integrated intensities are in arbitrary units.

Sample	Amount of water introduced in the cell (mmol/g-cat)	Integrated area before outgassing		Intergrated area after outgassing		Intensity ratio before outgassing ($2450/1650 = r$)	Estimated amount of water adsorbed afer outgassing (mmol/g)	
		1650	2450	1650	2450		Brønsted	Lewis
HYII	0.98	8.0	15.1	1.9	1.4	1.9	0.10	0.14
USYIII	0.98	6.6	3.7	4.8	2.1	0.6	0.15	0.48
USYII	0.46	1.8	3.1	1.6		0.5	0.11	0.30
Al105II	0.2	0.6	–	n.m.	–	–	–	0.1[a]
Al60II	0.3	1.0	–	n.m.	–	–	–	0.2[a]

[a] Amount of dissociatively adsorbed water.

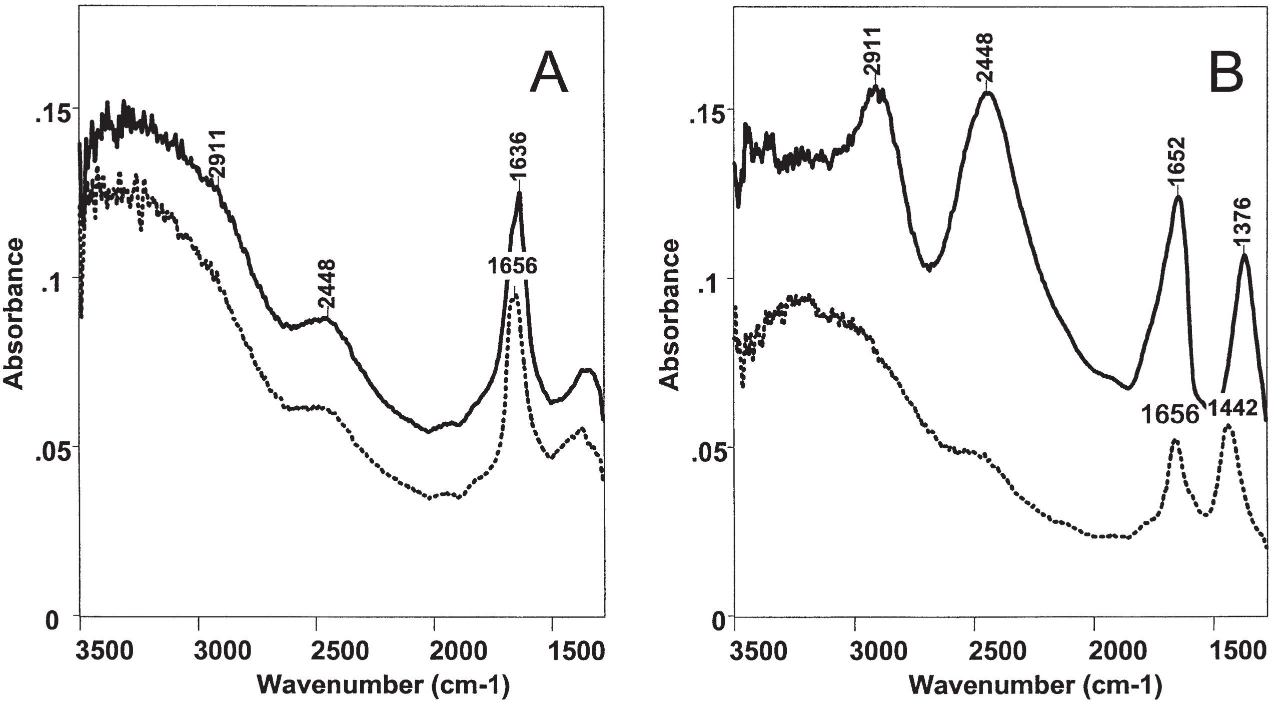

Figure 1. Difference spectra of USY (A) and HY (B) treated with 0.96 mmol/g of water. Spectra recorded: (—) after adsorption or (- - -) after outgassing to 10^{-5} Torr.

the spectra of USY zeolite after water adsorption: 2900, 2450, 1636, and 1450 cm^{-1}. The bands at ~2900 and ~2450 cm^{-1} and the weak line at ~1400 cm^{-1} indicate that some water molecules are hydrogen-bound to the bridging OH, that is, to the Brønsted acid sites. The bands at 2900 and 2450 cm^{-1} were assigned to the so-called “A and B bands of the A, B, C trio arising from the resonant interactions between the $<(\mathrm{OH}) \pm <(\mathrm{OH}\cdots\mathrm{O})$ combination modes and the δ(OH) and γ(OH) overtones of perturbed bridging OH group” [8]. The band at 1640 cm^{-1} is due to the δ(H–O–H) vibration of chemisorbed water. The band at ~1400 is due to the δ(OH) vibration of perturbed bridging OH [9,10]. Outgassing of the sample causes a slight decrease in the intensity of the band at 1650–1635 cm^{-1}. The sharp peak at 1635 cm^{-1} disappears. Presence of residual weak bands due to hydrogen-bound OH after outgassing indicates that a small amount of water remains adsorbed on the Brønsted acid sites.

For the purpose of this study an estimate of the number of water molecules affecting the acid sites is necessary. The estimate is based on the comparison of the intensities of the bands at 2450 and 1650 cm^{-1}. Since the band at 2450 cm^{-1} is due to the acidic bridging OH interacting with chemisorbed water, its integrated intensity is proportional to the number of water molecules interacting with Brønsted acid sites. The band at 1650 cm^{-1} is due to deformation vibration of H_2O chemisorbed on both Brønsted and Lewis acid sites. The correlation between the integrated area of the band at 1650 cm^{-1} and the amount of water introduced on USY and HY suggests that the extinction coefficients of δ(H–O–H) and H_2O adsorbed on Brønsted and Lewis acid sites are similar. In addition, the water *is not* dissociatively adsorbed on the Lewis acid sites of USY. Therefore, the integrated intensity of this band can be used as a measure of the total amount of water adsorbed on the acid sites.

In the case of HY zeolites we can assume that before outgassing most of the water is adsorbed by Brønsted acid sites (since the Lewis sites content is very small). In this case the ratio between the integrated absorbances at 2450 and 1650 cm^{-1} will give the ratio (r) between specific absorbances of perturbed acidic OH (2450 cm^{-1}) and water (1650 cm^{-1}) in the $H_2O\cdots H\text{–}OZ$ system. Measuring the intensity of the band at 2450 cm^{-1} for the samples with a much higher degree of dealumination and using r we can calculate the contribution of the water adsorbed on Brønsted acid sites to the band at 1650 cm^{-1}. From the specific absorbance of the band at 1650 cm^{-1} we can recalculate the contributions as the amount of water adsorbed on Brønsted or on Lewis acid sites of NFAl (table 2).

For alumina the situation is completely different, the deformation band nearly disappears after outgassing. The integrated area of the deformation band and its disappearance after outgassing suggest a dissociative adsorption of water. This process is exactly the reverse of the process by which the Lewis sites are created. Assuming that in the case of alumina, a Lewis site disappears for each water molecule dissociatively chemisorbed, the number of poisoned Lewis sites should be about 0.2 mmol/g or 50% of the initial content of Lewis acid sites (table 1). Similar observations have been reported for the rehydration of η- and γ-aluminas [20,21]. It is interesting to mention that the heat of NH_3 chemisorption on alumina is very close to the heat of water chemisorption [22].

3.2. Reaction

USY: The IR spectra obtained during the reaction of acetone over USY are shown in figure 2. The treatment with water had little effect on the shape of the spectra of acetone adsorbed on the zeolites at 105 °C. Only a slight shift of the line due to CO of chemisorbed acetone toward higher frequencies is observed, when the water was introduced on the zeolite. Acetone was more energetically bound to acidic OH than water. According to data reported by Fărcaşiu, the proton gas phase affinities of H_2O, acetone and NH_3 were 166.5, 196.7 and 204 kJ/mol, respectively [23].

Because the adsorption of acetone on Lewis acid sites is less energetic than the adsorption on Brønsted acid sites, most of the acetone adsorbed on the zeolite at 105 °C is the acetone adsorbed on Brønsted acid sites. Intensities and the positions of the peaks due to acetone interacting with the bridging acidic OH of zeolite were not affected. Therefore, the overall IR spectra in all three experiments with USY are quantitatively similar.

At reaction conditions (time, temperature, the dose of the reagent) the only reaction was the condensation of acetone in MO. The spectral characteristics of MO adsorbed on the Brønsted acid sites (1620, 1560, 1450 cm^{-1}) grew more intense with the increasing reaction time. Accordingly, the intensity of the C=O band of acetone (1700–1650 cm^{-1}) decreased (figure 2).

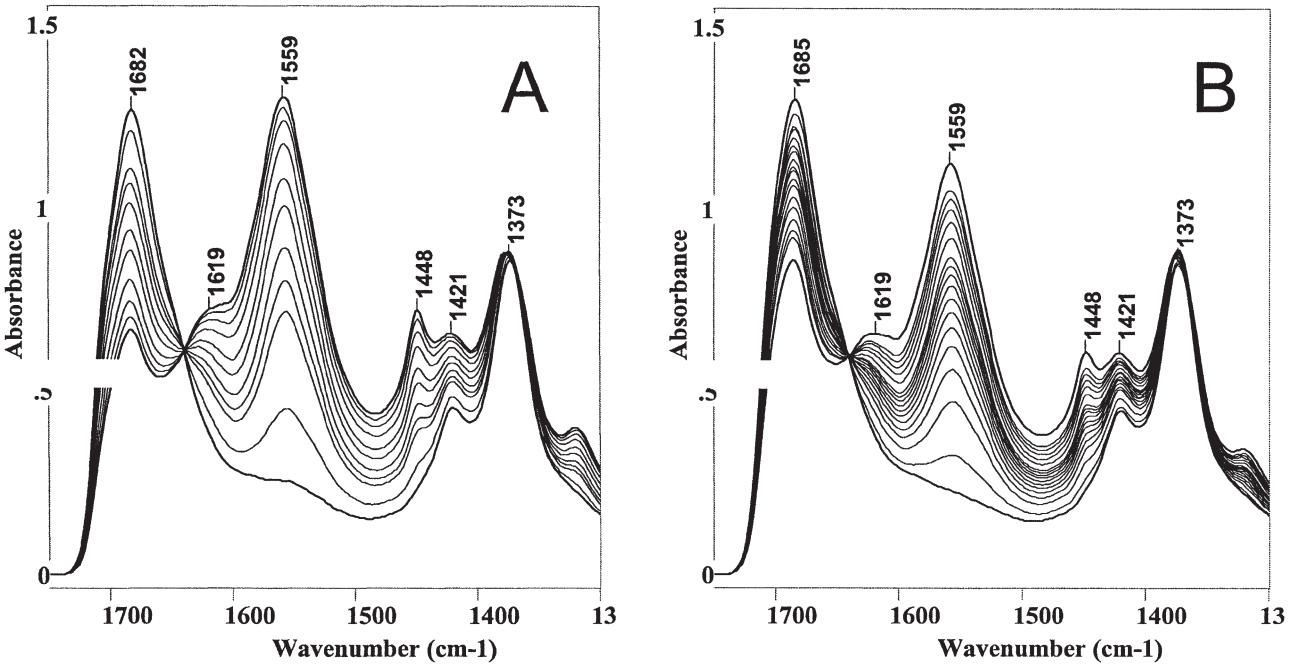

Figure 2. Evolution of the infrared spectra of USY zeolite treated with 3 mmol/g at 105 °C. (A) Original USY zeolite. (B) USY zeolite treated with 0.96 mmol/g of water. At the beginning of the reaction the spectra are taken every 2 min.

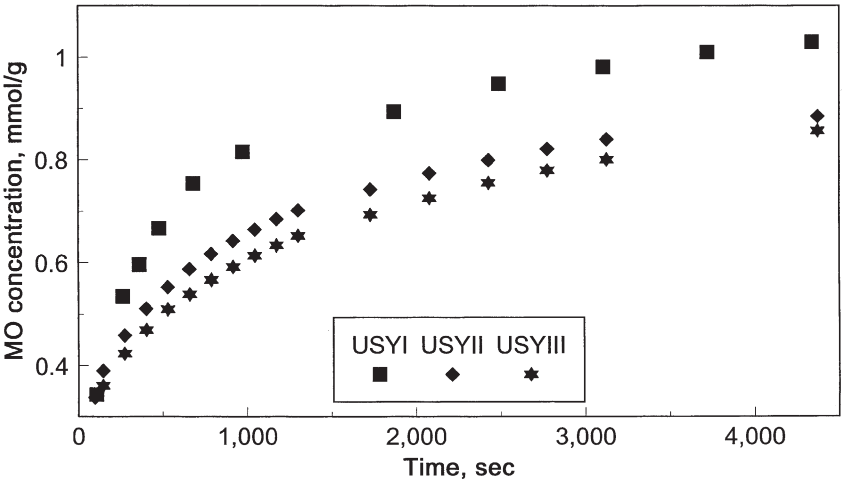

Figure 3. Kinetic curves for MO formation over USY zeolite (USYI) and USY zeolite treated with 0.5 and 1 mmol/g of water (USYII and USYIII, respectively) at 105 °C. Initial dose of acetone 3 mmol/g.

At 105 °C no significant amount of MO or water appeared in the gas phase. MO remained adsorbed by Brønsted acid sites (band at 1560 cm^{-1}) and the water remained chemisorbed on the surface of zeolite. The bending band of the chemisorbed water was masked by more intense bands of C=O of acetone and/or MO.

The sets of FTIR spectra for each sample (like that shown in figure 2) were deconvoluted and the surface concentrations of acetone and MO were calculated as described in [5]. The specific absorbances [19] used for the calculation of the surface concentrations were 10.0 ± 0.5 cm/μmol (γ(C=C) of MO) and 6.0 ± 0.5 cm/μmol (γ(C=O) of AC), respectively. For the USY catalysts the kinetic curves are shown in figure 3. The negative effect of chemisorbed water is obvious. From the data these initial rates of MO formation were calculated, see table 3.

Figure 4 is shown to support the validity of the specific absorbances and of the calibration parameter used here. The amount of the acetone in the gas phase and of acetone on the surface are plotted versus the amount of MO formed at increasing time. It takes one acetone molecule from the gas phase and one molecule of acetone strongly adsorbed by Brønsted sites to form one molecule of MO. The dependence does not give information about the reaction mechanism but it does show that the material balance is obeyed.

Table 3
Summary of the reaction conditions and reaction rate.

Experiment	T (°C)	H_2O added (mmol/g)	R_0 (μmol/(g s))	ACS (mmol/g)
USYI	105	0.00	1.70	1.08
USYII	105	0.48	0.71	1.08
USYIII	105	0.96	0.50	1.10
Al60I	60	0	3.35	0.13
Al60II	60	0.3	1.67	0.12
Al105I	105	0	6.04	0.076
Al105II	105	0.2	6.85	0.076
HYI	105	0	0.07	2.0
HYII	105	0.96	0.02	2.0

HY: Under the indicated conditions (see section 2) the rate of MO formation on HY zeolite is much less than that on USY. Two bands due to C=C stretch of MO were observed at 1580 and 1560 cm^{-1}. The first was assigned to MO adsorbed on weakly acidic hydroxyls of zeolite, while the latter one is due to acetone adsorbed on Brønsted sites [19]. The kinetic curves are shown in figure 5 and the reaction data are summarized in table 2. The Y zeolite lattice is thermally unstable and even at 400 °C [16], that is, at the temperature at which deammoniation is over, NFAl is formed in small amounts even if the outgassing time is small (2 h). In an earlier paper [5], the outgassing was carried out for 12 h and judging from the reported data, the amount of Lewis acid sites may have been several times larger than here. The treatment with water does not change the initial surface concentration of acetone but it decreases the reaction rate (table 3).

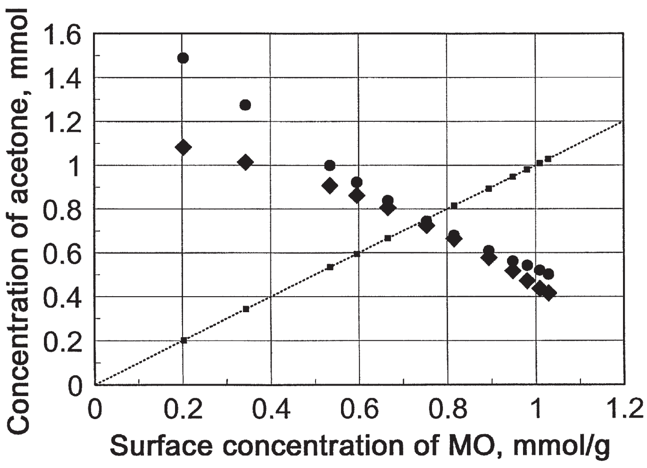

Figure 4. Concentrations of acetone in the gas phase (●), on the surface (◆) and the surface concentration of MO (■). The catalyst was a USY zeolite treated with 3 mmol/g of acetone at 105 °C.

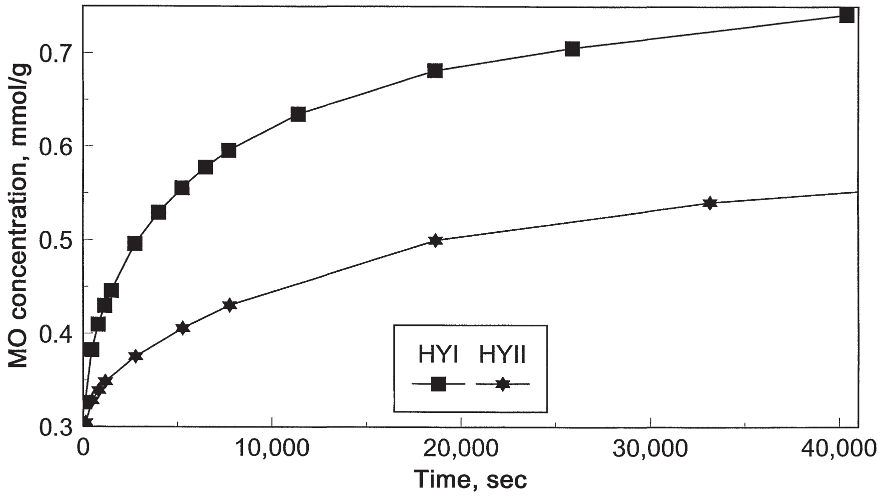

Figure 5. Kinetic curves for MO formation over HY zeolite (HYI) and HY zeolite treated with 1 mmol/g of water (HYII).

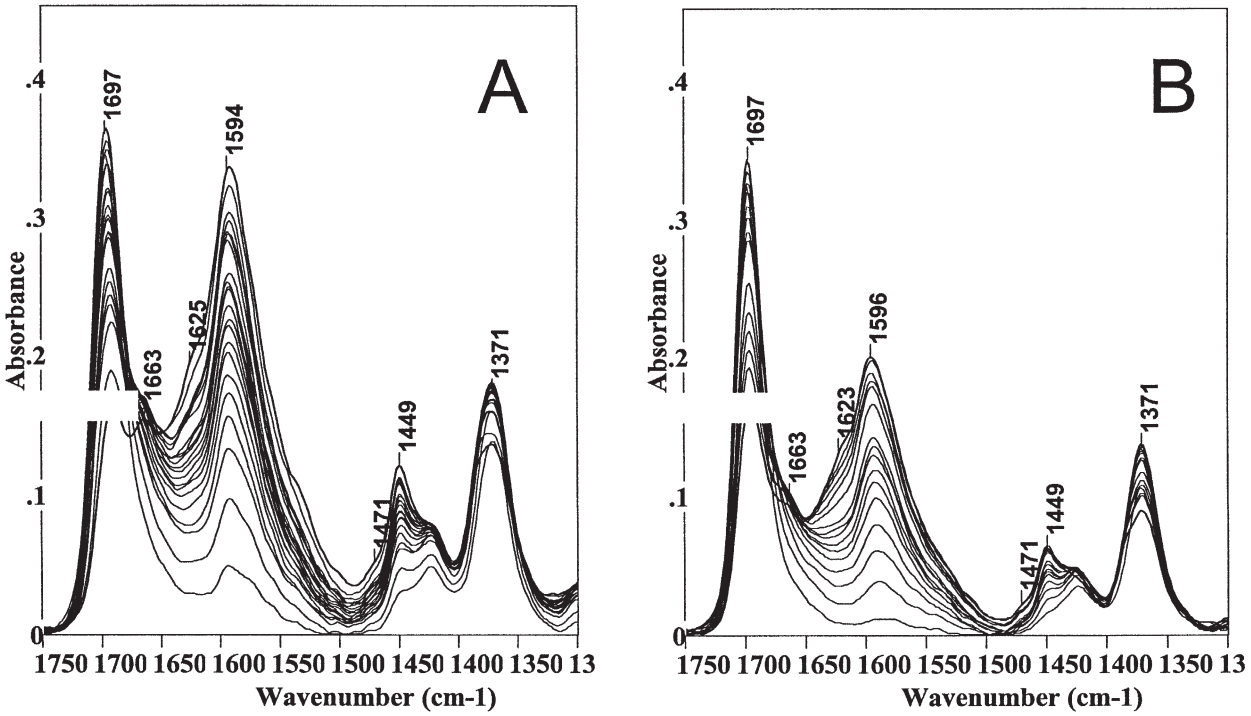

Figure 6. Evolution of infrared spectra of alumina having adsorbed acetone at 60 °C. (A) Original alumina. (B) Alumina treated with 0.3 mmol/g of water. At the beginning of the reaction the spectra are taken every 20 s.

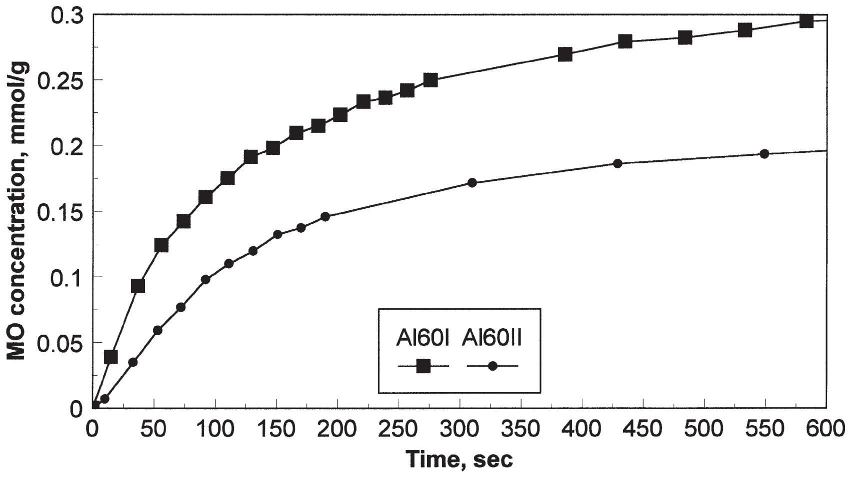

Figure 7. Kinetic curves for MO formation over alumina at 60 °C. Al60I (■) – alumina; Al60II (•) – alumina treated with 0.3 mmol/g of water.

Alumina: Figure 7 shows the spectral evolution after introduction of 0.5 mmol/g of acetone on alumina at 60 °C. The band due to acetone adsorbed on Lewis acid sites (1690 cm^{-1}) decreases in intensity over time. The band due to the MO, C=C stretch vibration (1594 cm^{-1}) increases accordingly. Kinetic curves are shown in figure 5. The experimental data are summarized in table 3. Pretreatment of the catalyst with water decreased the amount of acetone adsorbed on the surface at the beginning of the reaction.

At 60 °C the treatment with water decreased the initial rate by about two times, while at 105 °C the initial rates were about the same.

In all three catalysts, the water was not detected in the gas phase during the reaction; it remained chemisorbed. Also, it does not show up in the IR spectra because the bands are weak and overlapped by the strong bands due to acetone and mesityl oxide.

4. Discussion

We have observed [5] that the reaction rate of acetone condensation on zeolites was a linear function of the ratio

$$(\mathrm{Ac_s})(\mathrm{Ac_w})/\mathrm{MO_s},$$

where $\mathrm{Ac_s}$ stands for acetone strongly adsorbed by contrast to $\mathrm{Ac_w}$, which stands for weakly adsorbed acetone. The carbonyl stretching of $\mathrm{Ac_s}$ is between 1650 and 1690 cm^{-1}, and it is between 1690 and 1705 for Ac_w. MO_s is the mesityl oxide adsorbed on Brønsted acid sites.

The following reaction mechanism was suggested. Let Ac^e be an enol which is the classical reaction intermediate. The Lewis ($*$) and Brønsted ($\Box$) sites are covered with acetone or

$$\mathrm{Ac} + * \rightarrow \mathrm{Ac}* \quad \text{and} \quad \mathrm{Ac} + \Box \rightarrow \mathrm{Ac}\Box \tag{1}$$

Then

$$\mathrm{Ac}* \xrightarrow{k_1} \mathrm{Ac}^e + * \tag{2}$$

$$\mathrm{Ac}^e + \mathrm{Ac}\Box \xrightarrow{k_2} \mathrm{P}\Box \tag{3}$$

$$\mathrm{Ac}^e + \mathrm{P}\Box \xrightarrow{k_3} \mathrm{Ac} + \mathrm{P}\Box \tag{4}$$

$$2\mathrm{Ac} + \Box \rightarrow \mathrm{P}\Box \tag{5}$$

Step (2) corresponds to the activation step of acetone into enol by $*$. $\mathrm{Ac}\Box$ would be Ac_s. Thus, Ac_w could be identified as $\mathrm{Ac}*$. From (3) and (4) and at steady-state condition for Ac^e, it comes that

$$\frac{\mathrm{d}(\mathrm{P}\Box)}{\mathrm{d}t} = k_1k_2(\mathrm{Ac}\Box)(\mathrm{Ac}*)/\left[k_2(\mathrm{Ac}\Box) + k_3(\mathrm{P}\Box)\right],$$

where $\mathrm{P}\Box$ is MO_s. For the experiments with USY (and at constant concentration of acetone in the gas phase), the initial rate R_0 is proportional to the number of Lewis acid sites. Thus, the activation occurs on the Lewis acid site.

The predicted linear relationship between R_0 and the initial number of Lewis sites was well obeyed for all zeolites [5] and the correlation coefficient was $1.19 \times 10^{-3}\ \mathrm{s}^{-1}$.

On alumina, at 105 °C, the situation is very different. MO_s and the intensity of the quadrupole mass signal for mass 58 follows a linear variation with $\ln t$ and reaches a constant value at $t = 2.5$ min, when the system runs out of reagent. A kinetic law in $\ln t$ suggests that the rate obeys the Elovitch [24] relationship. A gas-phase molecule hitting the surface is transformed into MO after colliding with a molecule activated by a Lewis site.

The difference between the aldol condensation initial kinetics on alumina and zeolites is a warning that the poisoning by water could be different, even if the activation occurs on Lewis sites on both kinds of solids. In addition, the mechanism of water chemisorption is different for alumina and zeolites.

Wakabayashi et al. [11] studied the adsorption of water on dealuminated and nondealuminated HZSM-5 zeolites. The authors found that the water is preferably adsorbed by Lewis acid. The same conclusion can be drawn from our data obtained for HY and USY zeolites (figure 1, table 2). After outgassing at 105 °C only a small portion of hydrogen-bound water remains adsorbed.

Dissociative adsorption of water on aluminas has been reported in the literature [20,21]. From our data (table 2), it follows that most of the water introduced on alumina is dissociatively adsorbed. The dissociative adsorption decreases the number of Lewis acid sites and results in the formation of new nonacidic hydroxyls.

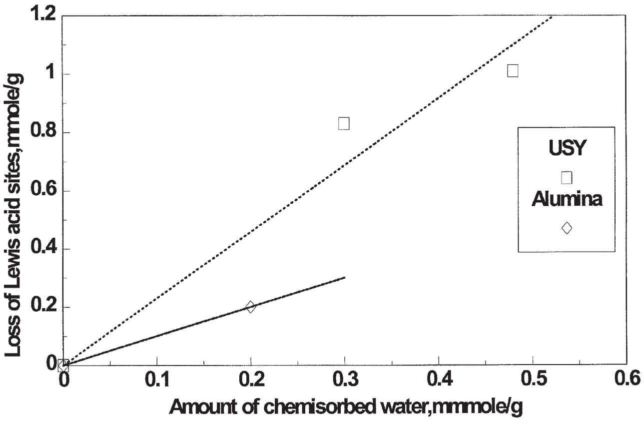

Figure 8. Loss of active Lewis sites from the drop of the initial rates of the acetone condensation reaction versus the amount of water chemisorbed on Lewis sites.

In order to evidence the poisoning effect of water the experimental results will be presented in the following way. From the initial rate the number of active Lewis sites is obtained by using the linear regression shown in [5, figure 9]. Of course, in absence of water the initial concentration in Lewis sites is as shown in table 1. Then, the loss of active Lewis sites is calculated by subtracting the number of active Lewis sites from the initial number of Lewis sites. The results of this calculation are represented in figure 8 by plotting the loss versus the amount of water chemisorbed on the catalysts.

For the three zeolites USYI, USYII and USYIII, there is a reasonable linear relationship ($R^2 = 0.95$) and the slope is equal to 2.2 ± 0.2. The two experiments performed on alumina Al60 I and II are on the line with slope 1.

In the case of HY zeolite, the initial rate is very slow (0.07 mmol/(g s)) and it is reduced by a factor of about 3 upon chemisorption of water. The amount of chemisorbed water is, as expected, also very small. Therefore, the experimental errors in the experimental data obtained for HY are much higher than those for the other catalysts and they should not be considered as an indicator of a behavior different from that of the other zeolites.

The experiments performed at 105 °C on alumina present an interesting case of the shift of the limiting step due to the increase in temperature. An Arrhenius law with a temperature coefficient of 8 kcal/mol was observed from 20 to ~80 °C. On alumina from the Arrhenius plot the initial rate at 105 °C should be about 13 mmol/(g s), but the actual rate was about one-half of the value.

This may suggest that the rate limiting step on alumina at 105 °C is the rate of acetone adsorption and not the aldol condensation. At 105 °C the residence time on the surface of alumina is lowered and, thus, the probability of reacting with a molecule activated by Lewis acid site.

The first striking difference between alumina and nonframework alumina in the USY is the stoichiometry of the reaction of chemisorbed water with the Lewis acid sites. On the average one chemisorbed water molecule can poison two active Lewis sites in USY, while on alumina one Lewis site is poisoned.

It is tempting to relate this stoichiometry to the nature of the water chemisorption process. On the zeolite the loss in the Lewis sites can be assigned to the molecular water. The bending vibration at 1650 cm^{-1} (figure 1) is, indeed, characteristic for the molecular water. On alumina, dissociative chemisorption of water cures the oxygen vacancies created by thermal activation. Even if the aluminum coordinations in NFAl look quite similar to those observed in nanosized alumina particles, the effect of water is quite different, as shown in figure 8. So far, and only for mordenite dealuminated at 600 °C has it been shown that a Lewis site consists of two aluminum atoms [26]. For instance, ammonia, on such a site, would be coordinated to two aluminum atoms, the average Al–N distance being 2 ± 0.05 Å.

Molecular modeling has shown that such pairs of sites could exist in transition alumina [27]. There may be a correlation between these observations and the difference in the slope observed in figure 8. Experiments are in progress to elucidate this intriguing point. Whatever the solution will be, the result of this study on the poisoning of the catalytic sites which are active in the acetone condensation reaction has led to two main conclusions. Namely:

1. The Lewis acid sites are the catalytic sites; and
2. The loss of the Lewis acid site upon poisoning by water is in line with previous estimates of their content, but the stoichiometry and the mechanism of the poisoning reaction is not the same in zeolites (at least USY) and in alumina.

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