Desorption of Acetone from Alkaline-Earth Exchanged Y Zeolite after Propane Selective Oxidation

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The desorption of products from a series of alkaline-earth exchanged Y zeolites after room-temperature propane selective oxidation was investigated by in situ infrared and mass spectroscopy. The intermediate product, isopropylhydroperoxide (IHP), did not desorb during temperature-programmed-desorption experiments but converted into acetone and water. Decomposition rate of IHP, produced from propane and oxygen at room temperature, into acetone increased in the order BaY < SrY < CaY (<MgY), which was attributed to the number of acid sites in the samples. TPD results on the CaY zeolite point to two acetone adsorption sites, which are tentatively assigned to Brönsted acid sites and $Ca(OH)_x$ species. Acetone mainly desorbs at higher temperatures (>250 °C) under dry conditions. Addition of water, however, results in gas phase acetone already at room temperature. From the results it can be concluded that water clearly facilitates acetone desorption, most likely via shielding of the electrostatic field and creation of additional sites.

Introduction

Partial oxidation of small alkanes is increasingly important for application of natural gas and volatile petroleum fractions as new feedstock.[1−4] In most cases, molecular oxygen is the only economically viable oxidant. Unfortunately, direct oxidation by O_2 is very unselective for most small hydrocarbons. As a result, existing methods generate large amounts of unwanted products. Lack of selectivity is often caused by the free radical nature of the reaction, high exothermicity or further oxidation of the desired product. The free mobility of the radical intermediates results in indiscriminate attack on starting hydrocarbon and primary oxidation products. Moreover, under thermal conditions, in the liquid or gas phase, oxygen attacks partially oxidized products more easily than starting hydrocarbons, resulting in overoxidation. As products accumulate, the lack of control gets worse, which limits conversion to a few percent in most practical processes.[4−6]

Recently, Frei et al.,[7−12] Grassian et al.,[13] Vanoppen et al.,[14] and our group[15] have demonstrated that (earth) alkali exchanged Y zeolite selectively oxidizes alkanes (ethane, propane, isobutene, and cyclohexane) at room temperature. Reaction activity of gas-phase cyclohexane and propane oxidation was found to increase in order NaY < BaY < SrY < CaY attributed to the increasing electrostatic field of the cations.[14,15] Complete selectivity was reported at conversions as high as about 35%.[7,8] The reaction mechanism proposed by Frei involved a charge-transfer complex, $[(C_nH_{2n+2})^+O_2^-]$. They hypothesized that the charge-transfer complex is stabilized by the electrostatic field of exchanged cations in the zeolite, and this stabilization allows one access to the charge transfer state by visible light irradiation or by thermal activation.[7−12]

The selectivity of this partial oxidation by molecular oxygen is unprecedented. The high selectivity is attributed to the strong adsorption of polar carbonyl products inside the zeolite pores, preventing overoxidation. Nevertheless, to turn this type of

selective oxidation into a practical process, the barrier for product desorption has to be overcome. At present, release of small oxygenated hydrocarbons from zeolite Y is only achieved by extraction with polar organic solvents.[16] A solvent free method would be environmentally and economically preferable. So the critical problem is to achieve continuous desorption of products from the zeolite. Use of a carrier gas and modestly elevated temperature have been proposed to give chance to desorb polar products at acceptable rates.[8] However, desorption data are still absent for those reactions. Moreover, selectivity will face a challenge due to over-oxidation of oxygenates by increasing temperature.

The present paper reports on temperature-programmed-desorption (TPD) of propane partial oxidation products using in situ FTIR and MS. The effect of additional water on the desorption patterns was investigated as well.

Experimental Section

Materials. Alkaline-earth cation (Mg, Ca, Sr, and Ba) exchanged Y-zeolites were prepared from NaY (Akzo Nobel, sample code: 1122-207) with Si/Al ratio of 2.5. The parent zeolite was exchanged three times with a 0.1 M solution of respectively magnesium chloride, calcium chloride, strontium nitrate, or barium chloride (Merck) for 20 h at 90 °C under stirring. The resulting alkaline-earth exchanged Y zeolite was washed three times with distilled water, filtered, and dried at 100 °C overnight. The chemical composition of catalysts was analyzed by X-ray fluorescence. The M^{2+} (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+})/Al ratio was 0.34, 0.43, 0.45, and 0.35 for MgY, CaY, SrY, and BaY, respectively. Powder X-ray diffraction gave no indication for collapse of zeolite structure, even not after calcination at 650 °C.

Infrared Spectroscopy. The zeolite powder was pressed into a self-supporting wafer and analyzed in-situ during reaction and desorption by means of transmission FTIR spectroscopy using a Bruker Vector22 FTIR spectrometer with a MCT detector. A miniature cell, equipped with CaF_2 transparent windows, which

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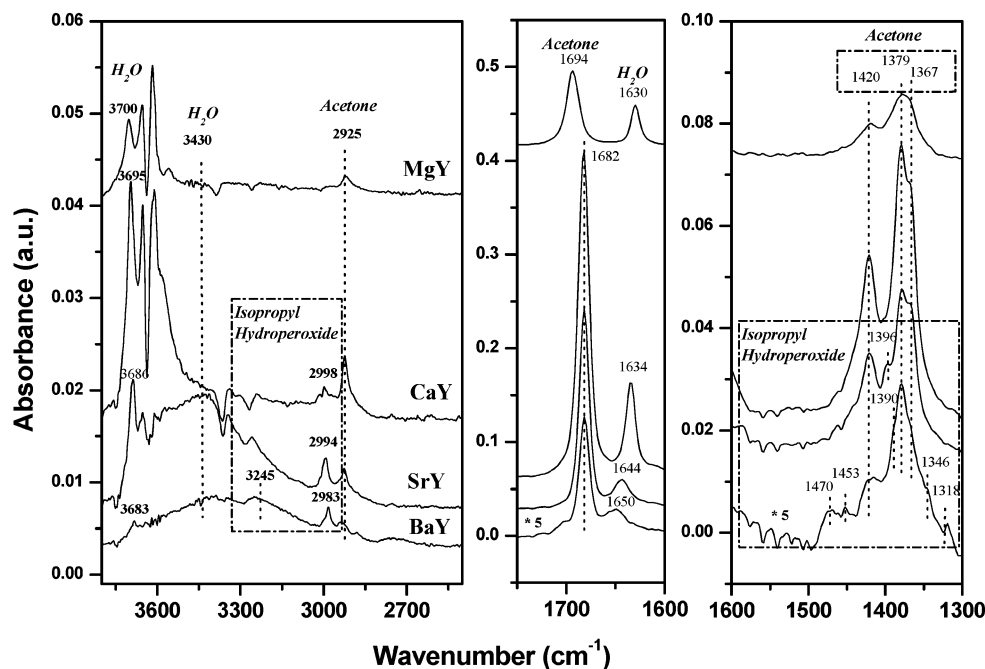
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Figure 1. Different FTIR spectra after 20 h propane oxidation, followed by 1 h evacuation.

can be evacuated to pressures below 10^{-7} mbar was used for the in situ experiments. The temperature is variable from room temperature to 500 °C. Each spectrum consists of 32 scans taken at 4 cm^{-1} resolution. The spectra were corrected for absorption of the activated zeolite (for details see ref 15).

Temperature Programmed Desorption (TPD). The infrared cell was used as a batch reactor for propane oxidation at 1 mbar propane and 40 mbar oxygen pressure. After 20 h reaction, followed by evacuation for 1 h, the remaining adsorbed molecules were removed by temperature programmed desorption (rate 10 °C/min, up to 500 °C). Infrared spectra were taken simultaneously with on-line mass spectroscopy for detection of gas-phase species.

Results

Surface Species after Propane Oxidation. Figure 1 shows the FTIR spectra after 20 h reaction of propane and oxygen followed by 1 h evacuation for different exchanged Y-zeolites. The observed vibrations can be attributed to acetone (2925, 1694, 1682, 1420, 1379, 1367 cm^{-1}), water (3700, 3695, 3686, 3683, 3430, 1650, 1644, 1634, 1630 cm^{-1}), and isopropyl hydroperoxide (IHP) (3245, 2998, 2994, 2983, 1470, 1453, 1396, 1390, 1346, 1318 cm^{-1}).[9,10,15] On MgY only acetone and water were observed.

Figure 2 reports the change in band intensity for IHP and acetone to illustrate the effect of evacuation at room temperature. About 4%, 7%, and 25% of IHP converted into acetone and water on BaY, SrY, and CaY, respectively, after 1 h evacuation. No products could be detected in the gas phase by on-line MS spectroscopy during evacuation at room temperature.

Infrared Study of Desorbing Species. The TPD profiles of IHP, acetone, and water as observed in the infrared spectra for SrY are compiled in Figure 3. The band intensity of IHP (band at 2994 cm^{-1}, Figure 3a) decreased with rising temperature. A dramatic decrease of intensity occurred from 80 °C. The IHP band totally disappeared at 170 °C. Concurrently, the acetone ($\nu_{C=O}$ at 1682 cm^{-1}) and water (δ_{H_2O} at 1644 cm^{-1}) intensities also varied. For acetone (Figure 3b), the C=O stretch intensity increased until the temperature reached about 170 °C. Then it
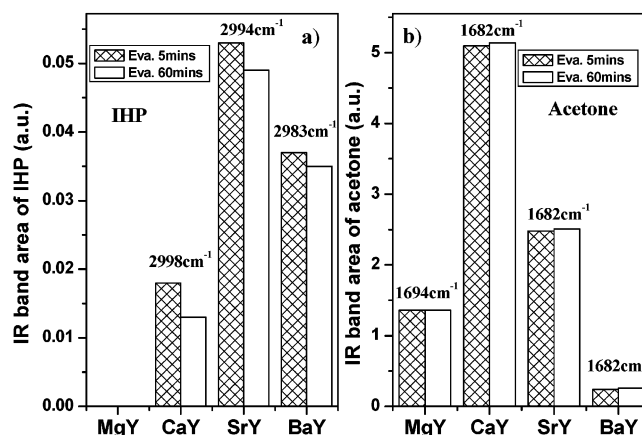

Figure 2. Infrared intensity change of IHP and acetone before and after 1 h at room temperature under vacuum
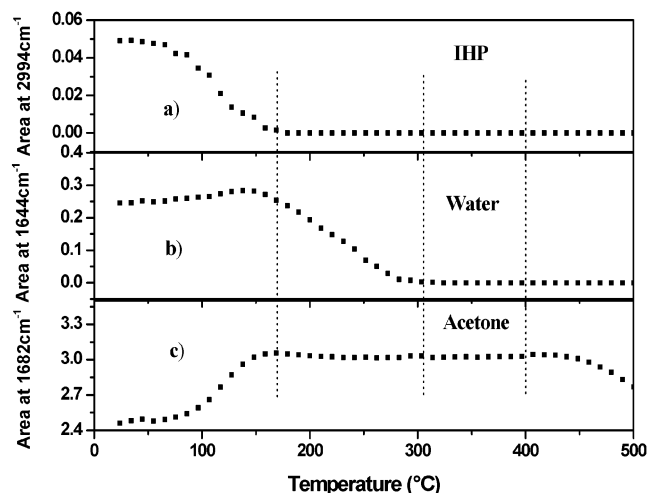

Figure 3. Change of FTIR band intensity (integrated area) of products on SrY zeolite during TPD.

was constant up to 400 °C. Subsequently, decreasing acetone intensity was found if temperature increased further. A similar behavior of water, the water signal (δ_{H_2O}, Figure 3c) first

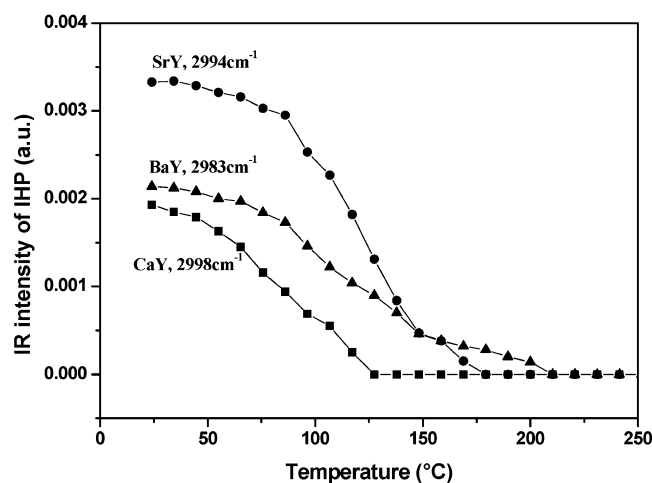**Figure 4.** Change of FTIR band intensity of IHP on alkaline-earth exchanged Y zeolites during TPD.

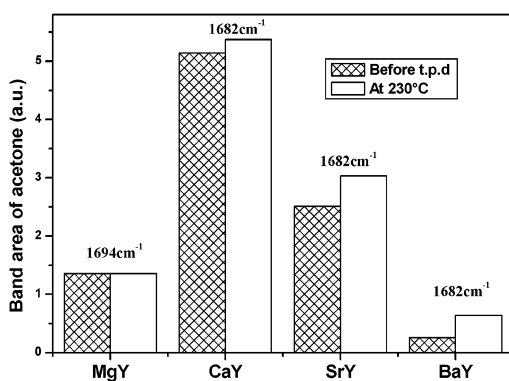**Figure 6.** Infrared spectra of adsorbed species on SrY at conditions: (a) after 20 h propane oxidation, followed by 1 h evacuation; (b) TPD experiment at temperature 500 °C; (c) after TPD, dwell 30 min, followed cooling to 25 °C.

Figure 5. Infrared intensity of acetone before TPD and at temperature 230 °C during TPD

Figure 7. Change of acetone after TPD, followed 500 °C half hour heating under vacuum on alkaline-earth exchanged Y zeolites.

increased when the temperature was raised. The maximum intensity was observed at 140 °C, from where it reduced and totally disappeared at 320 °C.

The IHP decomposition profile in the infrared spectra during TPD for alkaline earth exchanged Y zeolite is given in Figure 4. It was found that IHP decomposition on BaY was slower than on CaY and SrY. Figure 5 displays the difference in infrared intensity for acetone ($\nu_{C=O}$, integrated area) before TPD and at 230 °C during TPD. As indicated above, with rising temperature, IHP decomposition was observed, and simultaneously acetone and water (not shown) amounts increased on CaY, SrY, and BaY. The ratio of converted IHP (integrated area at 2998 cm^{-1} for CaY, 2994 cm^{-1} for SrY, and 2983 cm^{-1} for BaY in Figure 1) and produced acetone ($\nu_{C=O}$, integrated area, in Figure 5) was 0.06 ± 0.03, 0.09 ± 0.01, and 0.09 ± 0.01 for CaY, SrY, and BaY, respectively. The large error for CaY is caused by the very small amount of IHP for which, in addition, the vibrations overlap with acetone, which is present in a large amount. For SrY and BaY there clearly is less acetone and more IHP, resulting in a smaller error. At 230 °C, IHP fully decomposed for all catalysts, but no acetone desorbed yet. Temperatures at which water totally desorbed were 280 °C for BaY, 320 °C for SrY, and 400 °C for both CaY and MgY.

Figure 6 shows the infrared spectra of adsorbed species on SrY before TPD (Figure 6a), at 500 °C during TPD (Figure 6b), and after TPD, dwell 30 min at 500 °C, and subsequent cooling to room temperature (Figure 6c). On the basis of the spectra, water and only part of acetone desorbed. No other oxidation or dimerization products (e.g., mesityl oxide) were found in the infrared spectra for the zeolites studied.
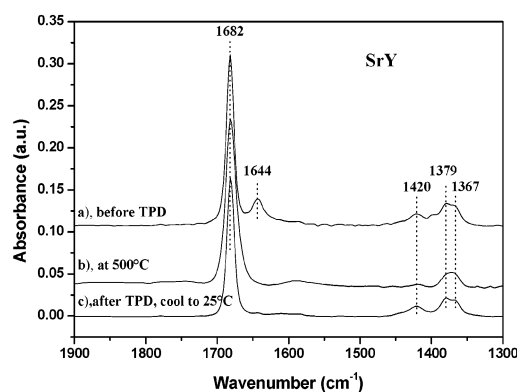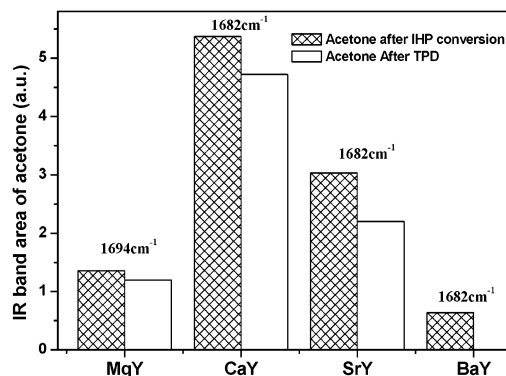
Interestingly, it was found that most of the acetone was still on the surface of MgY, CaY, and SrY, but from BaY completely desorbed after temperature-programmed desorption, subsequent evacuation at 500 °C for 30 min, and cooling to room temperature under vacuum (Figure 7). About 10% acetone for both MgY and CaY, about 25% acetone from SrY and 100% acetone from BaY desorbed during this experiment.

Mass Spectroscopy Study of Desorbing Species. Simultaneously with infrared data, mass spectra were taken to detect gas-phase compounds during TPD (Figure 8a,b). It was observed that water desorption started at 60 °C with BaY, 80 °C with SrY, 110 °C with CaY, and 140 °C with MgY.

Acetone desorption initiated in the same order, namely at 230, 300, 300, and 350 °C for BaY, SrY, CaY, and MgY, respectively. Desorption did not reach a maximum at 500 °C (max. temperature for FTIR cell) on these catalysts except for BaY, where the acetone maximum intensity occurred at around 425 °C.

With mass spectrometry also no other oxidation or dimerization products could be detected.

Effect of Water on Acetone Desorption. After 25 h reaction of propane and oxygen on CaY, the reaction system was evacuated for 10 min (Figure 9a). Subsequently, 0.5 mbar water was introduced into the infrared cell and kept for 30 min, after which the system was evacuated for 1 h (Figure 9b). After water was added to CaY, the water bending mode was appreciably broader and several bands were observed (1634, 1644, 1622 cm^{-1}). Influenced by the adsorbed water, the acetone C=O stretch vibration shifted from 1682 cm^{-1} to 1689 cm^{-1}, but acetone CH$_3$ deformations (1420, 1379, 1367 cm^{-1}) did not change.

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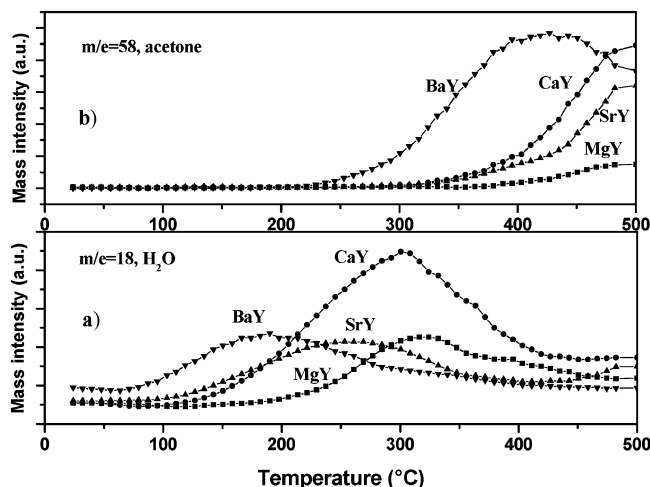*J. Phys. Chem. B, Vol. 108, No. 1, 2004* **221**

Figure 8. TPD-MS of products desorption after propane oxidation on alkaline-earth exchanged Y zeolites.
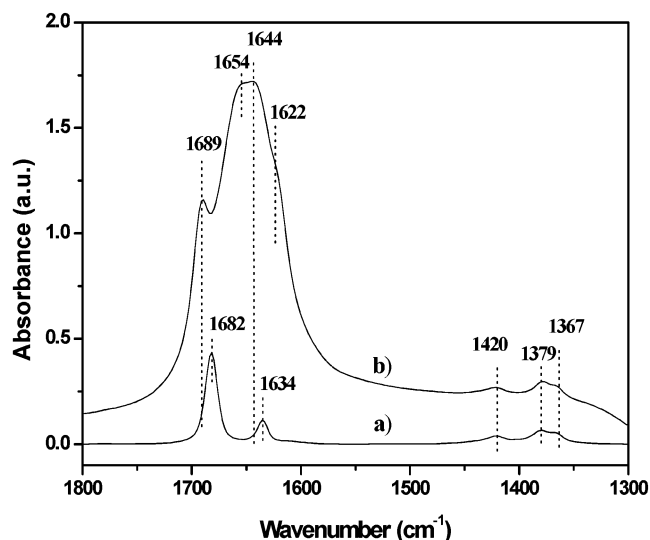

Figure 9. FTIR spectra of (a) after 25 h propane oxidation, followed by 10 min. evacuation; (b) after adding 0.5 mbar water, 30 min dwell and evacuation for 1 h, all at room temperature.

Very surprisingly, acetone was observed in the gas phase during evacuation at room temperature, whereas for the dry zeolite no acetone could be detected (Figure 10, Part A).

After evacuation, TPD experiments were performed (Figure 10a). A small amount of acetone was detected in the gas phase for temperatures from 50 to 160 °C (see inset of Figure 10). The onset of a second desorbing acetone species was 200 °C, about 100 °C lower than in experiments without preadsorbed water (Figure 10b,c). In addition, mass spectroscopy showed large amounts of water present in the gas phase when acetone was desorbing. Moreover, without added water, mainly at one temperature, desorbing acetone species were observed, and only a very small amount was detected around 120 °C.

Figure 11 displays the relative amount of desorbed acetone for experiments with and without preadsorbed water prior to TPD. After TPD and subsequent half an hour isothermal heating at 500 °C, about 20% of the total amount of acetone had desorbed when water was added compared to 10% of acetone from dry zeolite, irrespective of the acetone coverage. Additional experiments (not shown) have indicated that higher quantities of water increase the amount of desorbed acetone.

Because acetone desorbed from CaY zeolite is enhanced by water, additional experiments were carried out in a glass batch
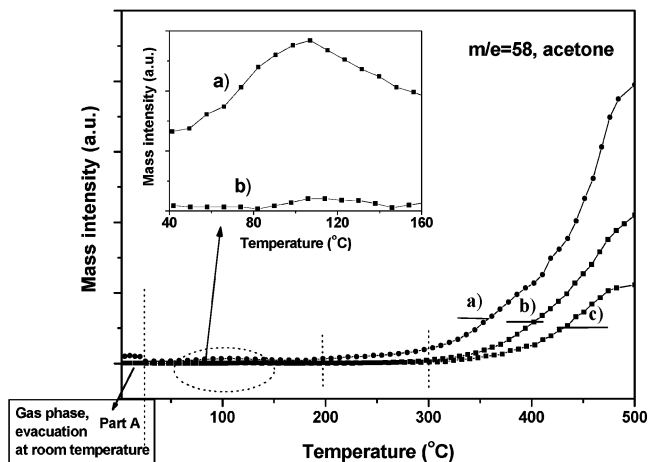

Figure 10. TPD acetone desorption on CaY at conditions: (a) after 25 h reaction, evacuated 10 min, followed adding 0.5 mbar water; (b) after 35 h reaction; (c) after 20 h reaction.
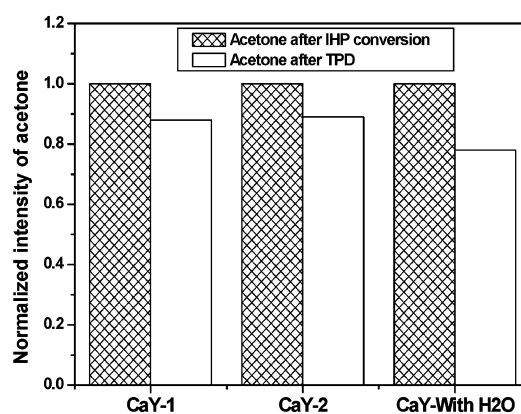

Figure 11. Change of acetone ($\nu_{C=O}$, normalized) intensity after TPD, and evacuation at 500 °C for half an hour for CaY zeolite with and without adding water after reaction. (CaY-1, 20 h reaction; CaY-2, 35 h reaction; CaY-with H2O, 25 h reaction, evacuated for 10 min at room temperature, followed by adding 0.5 mbar H_2O).

reactor with 0.15 bar propane, 1.5 bar oxygen, and 80 mg of activated MgY, CaY, SrY, and BaY zeolites, respectively. After 20 h reaction at room temperature in the dark, no acetone was detected in the gas phase by mass spectrometry in all cases. After 15 min evacuation, followed by injection of 0.5 mL of water, a significant concentration of acetone was detected in the gas phase above each of the four catalysts, in agreement with the low-pressure experiment in the infrared cell on CaY zeolite. After these experiments, the samples were taken out and infrared spectra were recorded; no acetone could be observed anymore in each of zeolite samples.

Discussion

During evacuation at room temperature under dry conditions, no products were observed in the gas phase. Only slight decomposition of isopropyl hydroperoxide (IHP) into acetone and water was found (Figure 2). With increasing temperature, IHP intensity decreased and disappeared before the temperature reached 230 °C for CaY, SrY, and BaY, as observed in the infrared spectra (Figure 4). Simultaneously, the acetone intensity increased in similar ratios to the original amount of IHP on the catalyst surface. The low value of the IHP to acetone ratio is caused by the fact that the absolute intensity decrease for IHP is much lower than the absolute growth of acetone, due to the different extinction coefficients for IHP (C−H) and acetone

(C=O) vibrations. The intensity of acetone was constant above 230 °C until the desorption temperature was reached (Figure 3c). For MgY the amount of acetone was constant from the start of TPD up to desorption temperature, because no IHP was present to be converted.

These results support the two-step reaction path for propane selective oxidation to acetone and water over alkaline earth exchanged zeolite as proposed in our previous paper:[15]

$$CH_3CH_2CH_3 + O_2 \rightarrow CH_3C(OOH)HCH_3 \rightarrow$$
$$CH_3COCH_3 + H_2O$$

Additionally, on BaY clearly more IHP than acetone was present after 20 h reaction, because conversion of IHP results in a total amount of acetone that is over twice (2.4 times) the original amount of acetone produced from propane and oxygen (Figure 5a). Consequently, total propane conversion over BaY at room temperature is 2.4 times higher than previously reported, which was based on the amount of acetone observed.[15] IHP converted much slower into acetone over BaY than for CaY and SrY (Figure 4).

On the basis of the IR band positions of adsorbed IHP and acetone on the zeolite, we proposed that IHP formation and decomposition into acetone occur at different active sites.[15] The cation site directs the reaction from propane into IHP whereas Brönsted acid sites seem to be involved in the decomposition of IHP into acetone. The present observation that the relatively higher amount of IHP after 20 h reaction (Figure 5) and its slower conversion over BaY, which hardly has any Brönsted sites (Figure 4), supports our previous finding of the importance of Brönsted acid sites for the IHP decomposition. We reported previously that the Brönsted acidity increases in the order BaY < SrY < CaY < MgY on the basis of direct observations on the intensity of the OH vibrations.[15] Moreover, the present results suggest that the exceptional acetone desorption behavior of BaY can also be attributed to the lower acidity of this sample. Acetone desorption initiated at 230, 300, 300, and 350 °C on BaY, SrY, CaY, and MgY, respectively. Acetone adsorption obviously is so strong that it only partially desorbed from MgY, CaY, and SrY, even after isothermal heating at 500 °C for half hour (Figure 7). Completely desorption of acetone under the above condition was only achieved for BaY. No obvious relation was found between acetone desorption temperature or quantity and its C=O stretch frequency (Figure 1), indicating that the C=O stretch vibration cannot be used as a measure for the acetone binding strength in the studied zeolite.

The starting temperature of water desorption observed in the infrared spectra for SrY was 140 °C (Figure 3), whereas mass spectroscopy already detected water desorption at 80 °C (Figure 8). This can be easily explained, because during a TPD experiment two reactions simultaneously take place:

$$CH_3C(OOH)HCH_3(ad) \rightarrow CH_3COCH_3(ad) + H_2O(ad) \quad (1)$$

$$H_2O(ad) \rightarrow H_2O(g) \quad (2)$$
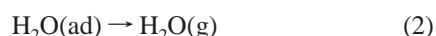
If the IHP decomposition rate is higher than the water desorption rate, the infrared intensity of water will increase whereas simultaneously desorbed water will be detected in gas phase.

The strong adsorption of partially oxidized hydrocarbons was proposed to be responsible for the high selectivity toward oxygenates.[8,13] However, it is also causing the desorption problem in this type of samples. Interestingly, the present study clearly shows that acetone can be desorbed in the gas phase even at room temperature by simple addition of water to the

sample (Figures 10 and 11). Upon addition of water to CaY zeolite, the onset of the high-temperature acetone desorption was found to decrease by 100 °C. Further, an additional low-temperature acetone desorption peak was observed at about 100 °C (Figure 10). Finally, the relative amount of desorbed acetone after addition of water is significantly higher than the amount from a dry zeolite (note: the amount of water is much more than the number of cations present). As no other oxidation or dimerization products (e.g., mesityl oxide) were found in the infrared spectra and mass spectra during reaction and TPD, hydrolysis of such compounds can be excluded to contribute to the increased amounts of desorbed acetone. Moreover, acetone coverage did not affect the onset of desorption or the relative desorbed amount of acetone (Figures 10 and 11). Addition of water resulted in two clear acetone desorption peaks during TPD, one around 100 °C and one starting around 200 °C. Importantly, during acetone desorption also large amounts of water vapor were observed. For the dry zeolite only a very small amount of acetone was found to desorb around 120 °C. At present we assume this is likely caused by desorption of the small amount of water present in the zeolite after propane oxidation. Apparently, the water partial pressure is too low to facilitate acetone desorption for dry CaY, causing higher desorption temperatures and smaller desorbing quantities.

The two acetone desorption peaks suggest that acetone is adsorbed on two different sites on CaY zeolite. In addition to Brönsted acid sites, as we proposed before, small amounts of acetone may be adsorbed onto Lewis acid sites or $Ca(OH)_x$ species. In principle, different adsorption sites are expected to result in different frequencies for acetone vibrations. However, because the site contributing to the low temperature peak only covers a minor part of the total acetone amount, different acetone frequencies could not be observed.

The influence of the water in the zeolite can be explained by various interactions. First, water can shield the electrostatic field within the zeolite cages through coordination to the cations.[9] Second, adsorbed water on cations or protons changes the Brönsted and Lewis acidity of the zeolite.[17−19] Normally, addition of water to dry CaY creates more Brönsted acid sites and $Ca(OH)_x$ species, whereas Lewis acid sites are converted into Brönsted sites. At present we cannot exclude one of these effects. The observed shift in C=O stretch frequency upon addition of water (Figure 9) could be due to creation of new adsorption sites in addition to superposition of this peak on the large water signal. After TPD, the remaining C=O stretch vibration appeared at its original frequency in the infrared spectra. As expected, an increase of the Brönsted acid sites and $Ca(OH)_x$ signals was found after TPD.

It is clear that the presence of water on CaY zeolite resulted in two effects: more acetone was desorbed for both desorption peaks and the temperature onset of both desorption peaks was decreased (Figure 10). The lower desorption temperatures indicate that the abundant presence of water weakens the acetone adsorption strength. Moreover, the increased intensity of the low-temperature peak points to creation of extra sites of this particular type after addition of water. This supports the possibility that $Ca(OH)_x$ species might be responsible for the low-temperature desorption peak. Moreover, increasing the amount of water added to the zeolite after reaction from 0.015 mol/$g_{zeolite}$ (in the infrared experiment) to 0.35 mol/$g_{zeolite}$ (in the glass batch experiment) increased the amount of desorbed acetone from 20% to almost 100%.

Although addition of water to the feed of propane and oxygen rapidly deactivates the zeolite due to the high hydrophilicity of

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Y zeolite,[19] our results convincingly show that desorption of acetone at room temperature is possible by simply adding water after reaction. Because regeneration of wet zeolites can be done at much lower temperatures than for acetone-saturated zeolites, the water-assisted desorption of acetone possibly opens a route for application of these samples to produce acetone in large amounts. Although detailed studies on the effect of water on desorption of acetone have been performed only for CaY, it is evident that the observation that desorption is assisted by water holds for all alkaline earth modified Y zeolites.

Presently, experiments are performed to determine the delicate balance between good activity, selectivity, and desorption of products by tuning zeolite properties and feed composition.

Conclusion

Decomposition rate of IHP, produced from propane and oxygen at room temperature, into acetone increases in the order BaY < SrY < CaY (<MgY), which is attributed to the number of acid sites in the samples. TPD results on CaY zeolite point to two acetone adsorption sites, which we tentatively assign to Brönsted acid sites and $Ca(OH)_x$ species. Acetone mainly desorbs at higher temperatures (>250 °C) under dry conditions, only a minor amount is observed around 120 °C. Addition of water, however, results in gas phase acetone already at room temperature. Further, upon addition of water, both desorption peaks are shifted to lower temperature and show increased intensities. It can be concluded that water clearly facilitates acetone desorption, most likely via shielding of the electrostatic field and creation of additional sites. To reach practical application of this type of samples for partial oxidation of small alkanes, a balance has to be found between cations, acid sites, and the amount of water in the zeolites or reactants.

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