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Selective photooxidation reactions in zeolites X, Y and ZSM-5

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The focus of this study is to develop photooxidation in zeolites as an environmentally benign alternative to conventional liquid phase oxidation of industrially important chemicals. Here we demonstrate that photooxidation in zeolites is a general technique and, therefore, synthetic strategies can be developed using the shape-selective and chemical properties of different zeolites. The photooxidation of toluene to benzaldehyde and propylene to acrolein were explored in three different zeolites – X, Y and ZSM-5. Photooxidation of toluene and propylene in zeolites other than Y has not hitherto been previously reported.

Keywords: selective oxidation, photooxidation, propylene oxidation, toluene oxidation, zeolites, FT-IR spectroscopy

1. Introduction

Recently, Frei and coworkers have demonstrated that hydrocarbons in zeolite Y can be selectively oxidized by visible light [1–7]. The basis for the selectivity is the hydrocarbon·O_2 charge transfer state which is formed in the zeolite after irradiation with visible light. The hypothesis is that the electrostatic field of the zeolite stabilizes the charge transfer state. The use of visible rather than ultraviolet irradiation allows access to this low energy pathway, eliminates many secondary photoprocesses and leads to the remarkable selectivity. The implications of this methodology for environmentally benign synthesis of chemicals are twofold. The increased selectivity of the oxidation reaction will decrease the production of unwanted side products. In addition, a zeolite catalyst and gas phase reactants and products will eliminate use of expensive and environmentally toxic solvents. The focus of this study is to develop photooxidation in zeolites as an environmentally benign alternative to conventional liquid phase oxidation of industrially important chemicals. Here, we demonstrate that photooxidation in zeolites is a general technique and, therefore, synthetic strategies can be developed using the shape-selective and chemical properties of different zeolites. The selective photooxidation of toluene to benzaldehyde and propylene to acrolein was explored in three different zeolites – X, Y and ZSM-5. Selective photooxidation of toluene and propylene in zeolite Y has been reported by Frei and coworkers [2,6] but has not hitherto been reported in other zeolites.

2. Experimental

Infrared spectroscopy was used to investigate the photooxidation of toluene and propylene in zeolites BaX, BaY and BaZSM-5. A Mattson RS-10000 infrared spectrometer equipped with a narrowband MCT detector was used in these studies. Each spectrum was recorded by averaging 1000 scans at an instrument resolution of 4 cm^{-1}. The infrared cell has been described previously [8,9]. Briefly, the zeolite is sprayed from a water slurry onto a photo-etched tungsten grid held at 40°C. The zeolite fills the holes of the tungsten grid. After an overnight oxidation in air at 200°C to remove any carbonaceous impurities, the tungsten grid with zeolite is mounted on a set of nickel jaws that is attached to a Cu feedthrough. The entire assembly is mounted inside of a 2 3/4″ stainless steel cube. The temperature is measured by a thermocouple wire attached to the tungsten grid. After the zeolite sample is prepared and mounted inside of the stainless steel cube, the cube is evacuated by a turbomolecular pump to a pressure of 1×10^{-7} Torr. For zeolites BaX and BaY, the zeolites are then heated under vacuum to 200°C and kept at that temperature overnight to remove water from the sample. For BaZSM-5, the zeolite is heated under vacuum to 350°C overnight.

Zeolites BaX, BaY and BaZSM-5, were prepared from NaX (Acros Organics), NaY (Aldrich) and NaZSM-5 (Zeolyst) by standard ion-exchange procedures using $BaCl_2$ (Aldrich) solutions. The Si/Al ratios for BaX, BaY and BaZSM-5 were determined to be 1.4, 2.9 and 19, respectively. The Ba/Al ratios for BaX, BaY and BaZSM-5 were determined to be 0.33, 0.53 and 0.26, respectively. Toluene (Fisher; 99.5%), acrolein (Aldrich; 97%) and benzaldehyde (Aldrich; 99%) were subjected to several freeze–pump–thaw cycles prior to use.

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Propylene (Matheson; 99.6%), CO (Matheson; 99.99%) and O_2 (Air Products; 99.6%) were used as received.

A 500 Watt mercury lamp (Oriel Corp.) with a water filter was used as the light source in these experiments. A broadband long pass filter (%T = 0 at 300 nm) was placed in front of the lamp. The broadband light was then reflected off of an aluminum-coated mirror and then turned by a 1″ quartz prism onto the sample. The quartz prism is mounted inside of the FT-IR sample compartment so that the dry air purge was not broken during irradiation.

3. Results and discussion

Propylene was introduced into the infrared cell at a pressure of approximately 25 Torr and allowed to equilibrate for 1 h. Gas-phase propylene was then pumped out leaving propylene molecules trapped inside the zeolite cages [10]. Molecular oxygen was then added to the infrared cell at a pressure of 750 Torr. The reaction mixture was left for 1.5 h to equilibrate the system and to ensure that a dark reaction did not occur. Subsequently, the sample was irradiated with a broadband lamp. A 490 nm broadband filter (Oriel filter 59492) was placed at the output of the lamp so that only wavelengths above 490 nm were incident on the sample. The lamp power at the sample was measured to be 89 mW/cm^2. Figure 1 shows the difference spectra in the spectral region extending from 1850 to 1350 cm^{-1} following irradiation of the charge transfer band of propylene·O_2 complexes in zeolites BaX, BaY and BaZSM-5 at room temperature. The difference spectra were made by spectral subtraction of the spectrum recorded prior to irradiation from the spectrum recorded after irradiation. Product bands are apparent in the spectrum near 1668 and 1365 cm^{-1} for BaX and BaY. These two bands match the bands observed for acrolein in these two zeolites. For BaZSM-5, a broad product is apparent near 1664 cm^{-1} and another band at 1358 cm^{-1}. A similar spectrum is observed for acrolein in BaZSM-5. In general, the infrared bands of the photoproducts in ZSM-5 were broader than those in zeolites X and Y. Under the conditions of this study, acrolein is observed as the sole hydrocarbon photooxidation product in BaX, BaY and BaZSM-5. Propylene oxide has been observed for propylene photooxidation in zeolite Y at higher loadings of propylene [5]. Water is also formed in the reaction, as indicated by the shoulder at 1645 cm^{-1} in the spectrum. At shorter wavelengths, $\lambda < 490$ nm, both formaldehyde (major peak near 1703 cm^{-1}) and CO_2 (2352 cm^{-1}) form in zeolites BaX and BaY. It is clear that CO_2 is trapped inside of the zeolite from the infrared band structure since a single sharp band appears near 2352 cm^{-1} in the photoproduct spectrum at shorter wavelengths. The rovibrational band structure, i.e. the doublet feature, observed for gas-phase CO_2 is not observed.

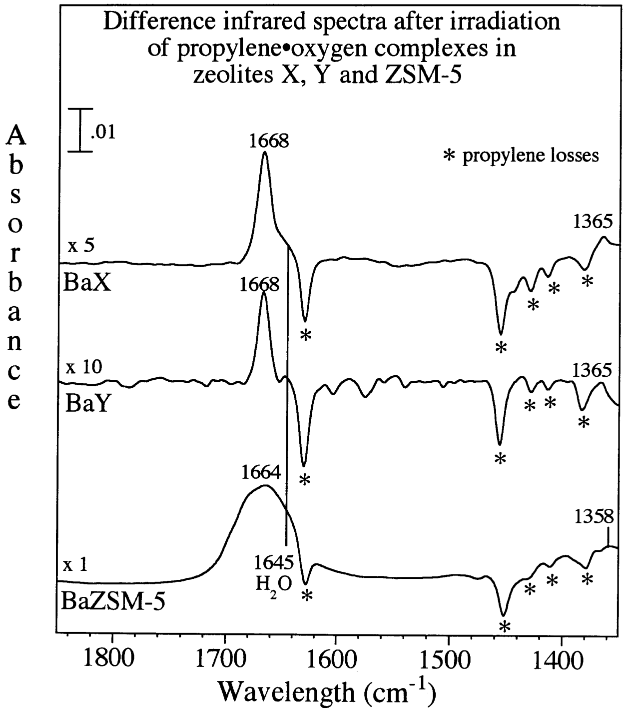


Figure 1. Difference infrared spectra following one hour of broadband irradiation ($\lambda > 490$ nm) of propylene·O_2 complexes in zeolites BaX, BaY and BaZSM-5. Acrolein is the sole hydrocarbon product for this reaction in all three zeolites. Propylene losses are indicated by an asterisk.

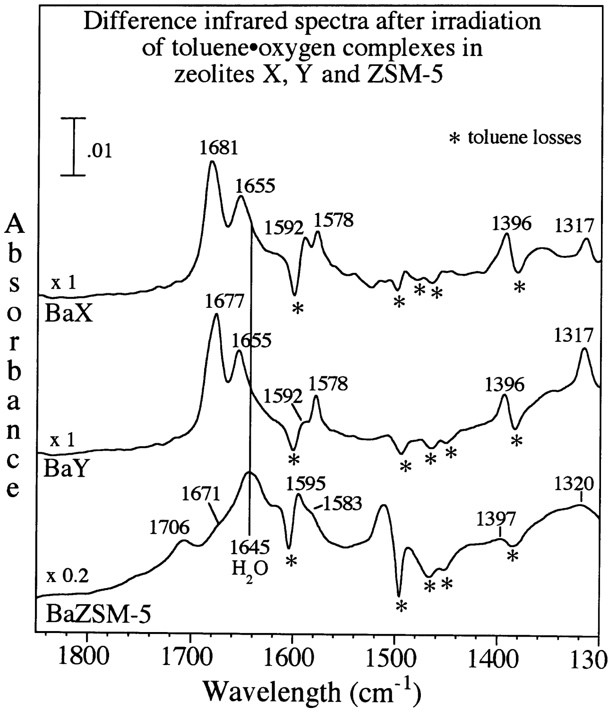
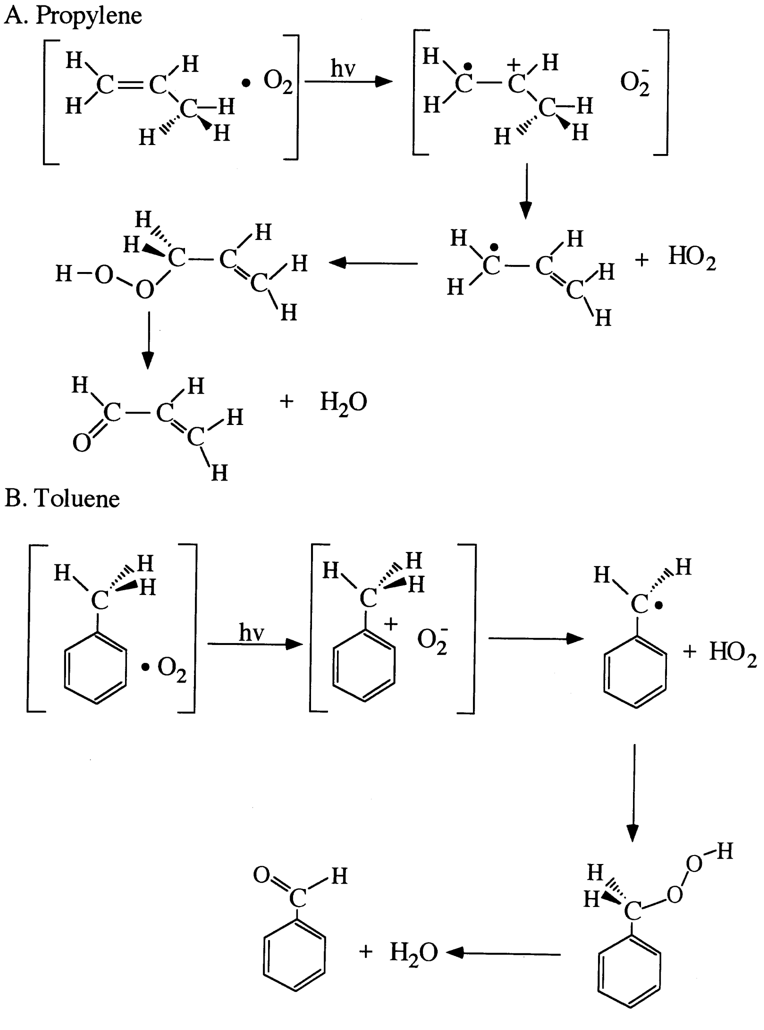


Figure 2. Difference infrared spectra following one hour of broadband irradiation ($\lambda > 340$ nm) of toluene·O_2 complexes in zeolites X, Y and ZSM-5. Benzaldehyde is the sole hydrocarbon product for this reaction in all three zeolites. Toluene losses are indicated by an asterisk.

Two other points should be made concerning the photooxidation of propylene in BaZSM-5. First, the infrared spectrum for propylene in BaZSM-5 is somewhat more complicated than the spectrum observed for propylene in zeolites BaX and BaY. There are some additional bands in the C–H stretching region that could be due to some propylene molecules that have reacted with acid sites, perhaps on the exterior surface of the zeolite. However, the photoproducts observed in the difference spectrum are from photooxidation of propylene molecules inside of the zeolite cages. Second, in separate experiments, it has been shown that background water readily adsorbs on BaZSM-5, thereby enhancing the intensity of the water band at 1645 cm^{-1} in the BaZSM-5 spectrum.

Toluene photooxidation was also investigated in BaX, BaY and BaZSM-5. Similar gas pressures used for propylene photooxidation were used for toluene photooxidation. Figure 2 shows the difference spectra in the region extending from 1850 to 1300 cm^{-1} following broadband irradiation ($\lambda > 340$ nm – Oriel filter 59460; lamp power = 143 mW/cm^2) of the charge transfer band of toluene·O_2 complexes in zeolites BaX, BaY and BaZSM-5 at room temperature. The spectra show that new product bands have appeared in the spectrum after irradiation. For BaX, these peaks are at 1681, 1655, 1592, 1578, 1396 and 1317 cm^{-1}, for BaY, these peaks are at 1677, 1655, 1592, 1578, 1396 and 1317 cm^{-1}, and for BaZSM-5, these peaks are at 1706, 1671, 1595, 1583, 1397 and 1320 cm^{-1}. Standard infrared spectra of benzaldehyde recorded in each of these zeolites gave nearly identical spectra. Therefore, it is concluded that the exclusive hydrocarbon product for this reaction is benzaldehyde. Water is also formed in the reaction, as indicated by the band at 1645 cm^{-1} in the spectrum. The 1645 cm^{-1} peak is even more apparent in BaZSM-5 because of background water adsorption, as discussed above. At shorter wavelengths, $\lambda < 340$ nm, the bands for benzaldehyde grow in intensity and an additional band appears in the spectrum at 2352 cm^{-1} indicating that CO_2 is formed inside the zeolite cage.

It has been previously shown by Frei and coworkers



Scheme 1. Photooxidation of propylene and toluene in zeolites X, Y and ZSM-5.

that these photooxidation reactions in zeolite Y go through a hydroperoxide intermediate [1–7]. The hydroperoxide intermediate was observed at low temperatures and found to convert to the corresponding aldehyde after warming to room temperature. A similar mechanism is proposed here for the photooxidation of toluene to benzaldehyde and propylene to acrolein in zeolites X and ZSM-5, as shown in reaction scheme 1. In the first step the charge transfer state is formed. This is followed by proton abstraction and subsequent reaction to form the hydroperoxide. The hydroperoxide rearranges to afford the aldehyde.

The prototype study presented here shows that longer wavelength photooxidation of hydrocarbons in zeolites is a general phenomenon and thus the shape and size selective properties of these zeolites may perhaps be used in these reactions to design environmentally benign syntheses for industrially relevant molecules. For example, the intersecting channels of ZSM-5 are accessible to aromatics such as benzene, toluene and para-xylene, but not to ortho-xylene. ZSM-5 is an important shape-selective catalyst in many reactions, such as the disproportionation of toluene [10]. Para-xylene is the dominant product because the transport of the other isomers, ortho-xylene and meta-xylene, is restricted due to the pore size of ZSM-5.

We have used CO as a probe of the electrostatic field gradient in these zeolites as the frequency of the CO stretch increases when CO is inside a zeolite cage because of the field. The CO vibrational frequency in the different zeolites was measured to be 2170 cm^{-1} in BaX, 2178 cm^{-1} in BaY and 2184 cm^{-1} in BaZSM-5 at $T = 25°\mathrm{C}$ and a CO pressure of approximately 7.5 Torr. Pacchioni et al. have calculated a correlation with field strength and CO stretching frequency [11]. Using those calculations and a scaling factor that takes into account the Hartree–Fock correction [11,12] electrostatic field strengths of 4.8 and 6.3 V nm^{-1} are determined for BaX and BaY, respectively. The field strength for BaZSM-5 in the vicinity of the exchangeable cation is calculated to be 7.4 V nm^{-1}, over 1 V nm^{-1} higher than that found for BaX and BaY. These results suggest that longer wavelengths of light should be effective in photooxidation reactions in ZSM-5 as the charge transfer state of hydrocarbon·O_2 complexes will be stabilized to an even greater extent in ZSM-5 compared to X and Y. Measurements of the charge-transfer absorption band of hydrocarbon·O_2 complexes in the three different zeolites are currently underway. These measurements will allow for a direct measure of the threshold of the charge transfer band [4].

Lastly, we have determined that the oxidation products, benzaldehyde and acrolein, can be removed from ZSM-5 simply by heating the sample above 250°C, an important consideration in the scale-up of these reactions [7]. Higher field gradients, the ability to remove products from the zeolite once they are formed, and the shape-selective properties of the zeolite make ZSM-5 a potentially commercial zeolite for use in photooxidation reactions. Further studies of hydrocarbon photooxidation reactions in ZSM-5 and other zeolites are currently underway.

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