

Effect of Water and Alkali Modifications on ETS-10 for the Cycloaddition of CO₂ to Propylene Oxide[†]

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Sodium oxide (NaO_x) impregnated Engelhard Titanosilicate-10 (ETS-10) molecular sieve catalysts were prepared to enhance the basicity associated with ETS-10 and subsequently investigated for the cycloaddition of carbon dioxide to propylene oxide to produce propylene carbonate. For dry NaO_x-modified ETS-10 catalysts that contained no adsorbed water, a maximum yield of propylene carbonate was achieved at a loading of 2.0 excess NaO_x species per unit cell. However, the greatest enhancements in the rate of reaction were observed when small amounts of water were adsorbed onto the unmodified ETS-10 catalyst immediately prior to reaction. Surface-bound water appears to enhance the surface Bronsted acidity of the unmodified ETS-10 catalyst via the formation of surface –OH groups at lower water loadings, producing a surface of better-tuned acid–base bifunctional characteristics for the cycloaddition reaction. At levels of hydration greater than 12.5% by mass, the yield of propylene carbonate was further enhanced, but at a smaller rate than that observed at lower rehydration levels, which is more indicative of an enhanced transport effect. Adsorption microcalorimetry of carbon dioxide indicated that, at loadings less than 2.0 NaO_x per unit cell, the total uptake of the CO₂ adsorption sites required for the reaction were less than in the parent ETS-10 material. However, at higher levels of NaO_x occlusion, where the total uptake and strength of the adsorption sites exceeded those observed for the as-received ETS-10 material, the cycloaddition activity of this catalyst suffered due to the reduced pore volume and surface area. It appears that precise tuning of both the surface acidity and basicity is crucial in creating an effective acid–base bifunctional ETS-10 catalyst for the cycloaddition reaction investigated.

Introduction

Engelhard Titanosilicate-10 (ETS-10) is a molecular sieve containing TiO₆ octahedra and SiO₄ tetrahedra linked through bridging oxygens. Extra framework cations (typically Na⁺ and K⁺) are used to neutralize the –2 charge associated with each TiO₆ unit. Exchanging these charge-compensating cations with other metal cations affects the acid–base character of the ETS-10 framework. When exchanged with alkali metal cations, these materials have unique catalytic functions for reactions that require strong basic character such as aldol-type reactions,¹ transesterification of soybean oil,² alcohol dehydration,^{3–5} oxidation of amines,⁶ and substituted-benzene isomerizations.⁵ In fact, Philippou et al. have indicated that the basicity of ETS-10 is comparable to that of Cs₂O occluded in zeolite CsX,⁴ which is considered to be one of the most highly basic zeolitic catalysts.

Solid base catalysts that are prepared using zeolite and molecular sieve materials have been typically prepared by occluding various alkali containing precursors into the pores of the material and thermally treating the resultant material to decompose the precursor to an “alkali oxide” of unknown stoichiometry.^{7–16} The resulting alkali oxide species that are formed help neutralize surface acidity as well as create new base sites. It has been proposed that these active sites are alkali oxides of the form M₂O, where M is an alkali metal.^{11,15} However, other studies have indicated that incomplete decom-

position of the supported alkali salt to M₂O occurs, implying that the nature of the occluded species is still in question.^{17,18} Regardless of knowing the exact composition of the supported alkali species, their presence enhances the surface basicity of the material.

Carbon dioxide, which is slightly acidic in nature, is a commonly used probe to investigate surface basicity via IR, temperature-programmed desorption (TPD), and adsorption microcalorimetry. However, applying the investigated behavior of CO₂ to that of actual reactants is a delicate proposition since, in most cases, the reactants are dissimilar in molecular size compared to the CO₂ probe. The cycloaddition of carbon dioxide to epoxides to form cyclic carbonates requires strong basicity in which carbon dioxide is itself a reactant, making it an ideal probe reaction for investigating solid basicity when using CO₂ to determine the basic character of the catalyst surface. This reaction represents an ideal case of “green chemistry” for the chemical fixation of sequestered carbon dioxide, which is a greenhouse gas, into chemicals that can be used as solvents or as valuable reaction intermediates. While effective homogeneous catalysts have been identified,^{19–23} the discovery of a highly active heterogeneous catalyst is necessary for ease of catalyst separation. More recent advances in solving catalyst separation issues have dealt with using ionic liquids,^{24,25} supported alkali salts,^{26,27} polymer-supported zinc halide catalysts,²⁸ and lanthanide oxychlorides.²⁹ In addition, cycloaddition reactivity studies have been performed with numerous epoxides over mixed oxides consisting of various zeolite, smectite, and hydrotalcite-based catalysts.^{30–32}

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In this work, the basic character of ETS-10 was enhanced by occluding sodium oxide in the pores in an attempt to enhance the cycloaddition of propylene oxide and carbon dioxide to produce propylene carbonate in the absence of a solvent. The effect of water on carbonate yield was also investigated since, contrary to previous results for these materials in other reactions, water was found to enhance the product yield. In addition, the CO₂ adsorption properties of these catalysts were investigated using adsorption microcalorimetry in an attempt to relate CO₂ adsorption strength and site number to catalytic activity.

Experimental Methods

Preparation of ETS-10 Catalysts Containing Occluded Alkali. ETS-10, with a unit cell composition of Na_{21.9}K_{7.5}Ti_{16.5}Si_{77.5}O₂₀₈, was obtained from the Engelhard Corporation (Iselin, NJ) and used as received. Initially, a powdered sample of ETS-10 was heated to 500 °C in flowing air at a rate of 4 °C min⁻¹ and subsequently held at that temperature for 10 h to remove any adsorbed water and thus determine the dry mass of ETS-10 for that sample. The dried sample was placed in a high humidity chamber to slowly reintroduce water into the pores prior to incipient wetness impregnation of a distilled–deionized water solution containing dissolved sodium acetate (Aldrich, 99.99%). ETS-10 catalysts with nominal loadings of 0.8, 1.2, 1.6, 2.0, 2.4, and 2.8 excess “sodium oxide (NaO_x)” per unit cell were prepared. Each supported catalyst was then dried overnight in air at 100 °C. Decomposition of the supported precursor was carried out by heating the supported sample to 500 °C in flowing air at a rate of 4 °C min⁻¹ and holding at that temperature for 10 h to form the supported oxide catalyst (NaO_x/ETS-10). Each of the NaO_x/ETS-10 catalysts were stored in a desiccator to minimize adsorption of water.

After each sample was outgassed for 12 h at 200 °C, the BET surface areas and pore volumes for the NaO_x/ETS-10 molecular sieves were determined from N₂ adsorption isotherms at -196 °C measured on a Porous Materials Incorporated gas sorption analyzer. The pore volume of the ETS-10 molecular sieves are reported as the liquid volume associated with the nitrogen uptake at $P/P_0 \sim 0.30$. Using a TA Instruments Q50 TGA, the initial water content of the as-received ETS-10 was determined by heating a fresh sample at 30 °C for 1 h to remove any loosely bound water, followed by heating the sample in flowing air to 500 °C at a rate of 4 °C min⁻¹ to remove the more strongly bound waters of hydration.

Cycloaddition of Carbon Dioxide to Propylene Oxide. To prepare the ETS-10 catalysts for use in reactivity studies, the NaO_x/ETS-10 samples were thermally treated overnight at 200 °C in air. About 1.00 g of freshly dried catalyst (size selected to <60 mesh) was used as a basis for all reactivity studies presented in this work. For studies investigating the role of adsorbed water, the freshly dried catalyst was placed in a weigh boat and subsequently placed in a high humidity chamber to slowly introduce adsorbed water to the catalyst. In some cases, the amount of adsorbed water was determined from the difference between the pre- and post-adsorption masses. Changing the exposure time resulted in materials that were rehydrated to various levels. The catalysts rehydrated overnight were found to contain roughly 25% excess water by mass compared to the initial dry mass of catalyst used.

The cycloaddition of CO₂ to propylene oxide was carried out in a 300-mL stainless steel autoclave (Parr Instrument Company) in the absence of any solvent. The vessel was kept at room temperature in a desiccator prior to loading with catalyst in order to minimize any contamination due to water. When loading the

autoclave with catalyst and epoxide, the catalyst was placed in the vessel followed immediately by 20 mL of propylene oxide (Aldrich, 99%), after which time the vessel was immediately sealed. To remove any air from the vessel and minimize the evaporation of propylene oxide, which has a significant vapor pressure at room temperature, the sealed vessel was cooled to 0 °C using an ice–water bath prior to and during three 200-psig purge cycles with carbon dioxide (Lin weld, UHP). After removal of the ice–water bath, the autoclave was pressurized with CO₂ to 500 psig at room temperature. The reactor was heated to the reaction temperature at a rate of 1.7 °C min⁻¹. Reported reaction times are normalized to the amount of time the reactor operated at 150 °C. After reaction, the reactor was cooled to 0 °C using an ice–water bath and subsequently vented to atmosphere. While all efforts were made to minimize the loss of propylene oxide prior to analysis, significant losses of the reactant were observed due to its relatively high vapor pressure and the necessary purging prior to and immediately after performing the reaction. After opening the vessel, the reaction mixture was extracted with acetone (Fisher, HPLC grade) and a known quantity of decane (Aldrich, 99%) was added as an external standard for quantification. The product mixture was analyzed by flame ionization detection using a Thermoquest Trace GC fitted with a Supelcowax column. Over all modified ETS-10 catalysts, propylene carbonate was the primary product obtained.

Adsorption Microcalorimetry of Carbon Dioxide. Adsorption microcalorimetry of carbon dioxide was performed using a Calvet-type microcalorimeter, which consisted of an assembly of an aluminum block with two integral thermoelectric enclosures (International Thermal Instrument Company, model no. CR-100-1). A high-temperature silicone oil (Acros Organics) was used to improve the thermal contact between the cell wall and the inner wall of the cavity of the microcalorimeter. The microcalorimeter unit was located in a well-insulated forced-air oven to isolate the system from the environment. Between 1 and 2 g of catalyst was placed in the sample cell to form a catalyst bed a few millimeters thick. Each catalyst was pretreated under dynamic vacuum by heating at a rate of 2 °C min⁻¹ to 500 °C, where the temperature was held for 10 h. Once pretreatment was completed, the sample was allowed to cool to room temperature and the gas-dosing manifold was charged with CO₂ to a pressure ranging between 9.5 and 10.0 Torr. Manifold pressures were measured using a 615A high-accuracy Baratron absolute pressure sensor (MKS Instruments). A Lab-View programmed Virtual Instrument was used to control the sequential dosing of CO₂ to the sample and record the evolved heat and manifold pressures required for determining the total heat of adsorption and the amount adsorbed. The dry catalyst mass was used to determine the differential heats of adsorption as a function of CO₂ uptake per gram of catalyst.

Results

A summary of the NaO_x/ETS-10 catalysts investigated can be seen in Table 1. The surface areas and pore volumes for the occluded samples decrease significantly with increased NaO_x loading. The highest occluded sample, which contained nearly 3 excess NaO_x molecules per unit cell, lost roughly one-third of its total surface area and one-quarter of its original pore volume due to the presence of the occluded NaO_x species inside the ETS-10 pores. Attempting to enhance surface basicity via this method clearly results in a loss of effective reaction volume that, as will be seen, reduces the effectiveness of the catalyst for the cycloaddition reaction investigated.

TABLE 1: Physical and Cycloaddition Reactivity Characteristics Associated with Investigated ETS-10 Molecular Sieves Containing Occluded NaO_x

NaO _x loading per Unit Cell	surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	yield of propylene carbonate ^a (mmol)	total CO ₂ uptake ^b (μmol g ⁻¹ cat ⁻¹)
0	326	0.159	14.5	59.6
0.8	298	0.143	14.4	40.4
1.2	257	0.142	15.6	40.8
1.6	255	0.141	19.7	42.5
2.0	245	0.135	21.7	47.6
2.4	222	0.122	20.2	46.8
2.8	214	0.118	15.1	69.2

^a After 24 h at 150 °C over 1 g of dry catalyst. ^b From CO₂ adsorption microcalorimetry at 25 °C.

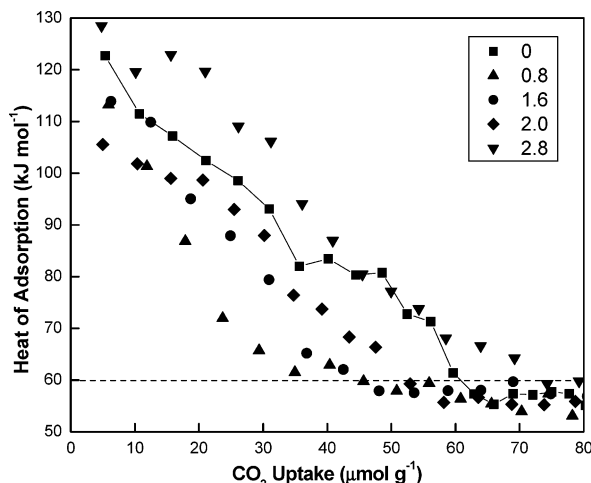


Figure 1. Effect of loading on the differential heat of adsorption as a function of carbon dioxide uptake at 25 °C for ETS-10 molecular sieves containing occluded NaO_x. The lines connecting the points for adsorption heats for the unmodified ETS-10 are used to aid the eye. The dotted line at 60 kJ mol⁻¹ indicates the cutoff energy associated with counting the number of CO₂ chemisorption sites as stated in ref 17. To avoid plot congestion, not all NaO_x-modified ETS-10 samples have been included.

Differential heats of adsorption as a function of CO₂ uptake for microcalorimetry studies of the NaO_x-modified ETS-10 catalysts can be found in Figure 1. Unmodified ETS-10 exhibited a significant uptake of carbon dioxide of about 60 μmol CO₂ g⁻¹. Surprisingly, a lower total CO₂ uptake was observed after incorporating 0.8 excess NaO_x per unit cell into the ETS-10 pores. In fact, this loading exhibited the lowest uptake of carbon dioxide of all samples investigated here.

At increased occlusion loadings of NaO_x, a greater uptake of carbon dioxide is observed compared to the 0.8 NaO_x loading; this increase can be attributed solely to the incorporation of additional surface base sites. The total CO₂ uptake, however, remains at a level lower than that for the unmodified ETS-10 until about 2.8 excess NaO_x species per unit cell have been incorporated. At this loading, not only is the total CO₂ uptake larger than that of the unmodified ETS-10 material but the heats of adsorption at a lower coverage are larger as well, indicating that the incorporated CO₂ adsorption sites are stronger. In fact, at this level of NaO_x occlusion, uniform sites at strengths near 120 kJ mol⁻¹ are observed, whereas nonuniform sites were observed at lower occlusion levels. For determination of the amount of catalytically relevant adsorption sites, we followed the criterion set by Tu and Davis to count the number of useful adsorption sites by assuming that the active species are the chemisorbed species formed when observed heats of adsorption are greater than 60 kJ mol⁻¹.³¹ The number of CO₂ chemisorption sites are given in Table 1.

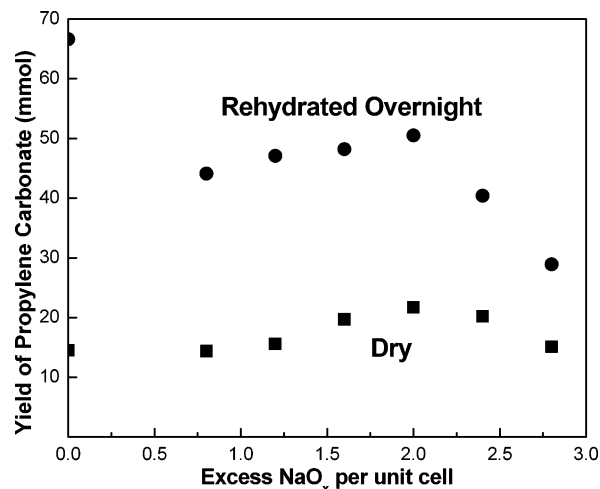


Figure 2. Effect of NaO_x occlusion level and overnight rehydration on the yield of propylene carbonate after 24 h at 150 °C.

The cycloaddition of CO₂ to propylene oxide at high CO₂ pressures was performed over dry and rehydrated NaO_x/ETS-10 catalysts. The effect of NaO_x occlusion level and rehydration on the yield of propylene carbonate after 24 h at 150 °C is shown in Figure 2. For the dry supported catalysts, a maximum yield was achieved at a loading of 2.0 excess NaO_x per unit cell, which corresponded to an increase of about 50% in the yield compared to the unmodified ETS-10. At loadings greater than this level, the yield dropped back to a level comparable to that of the unmodified ETS-10, indicating that these higher loadings result in a material with a more reduced pore volume, where mass transfer limitations may begin to play a role in the observed kinetics. These reduced pore volumes are clearly indicated in Table 1.

Studies were performed to investigate the effect of adsorbed water on the cycloaddition activity of the NaO_x/ETS-10 catalysts. Surprisingly, the yield of propylene carbonate over rehydrated ETS-10 materials was 2–5 times higher when compared to the dry catalysts over the range of NaO_x loadings investigated. Figure 2 shows that, while the maximum yield for the rehydrated samples containing occluded NaO_x coincided with that observed for the dry catalysts, the rehydrated ETS-10 that did not contain any occluded NaO_x showed the highest yield under identical reaction conditions. This yield was reproducible for three separate reaction trials over the unmodified ETS-10 catalyst.

To investigate the role of hydration level on unmodified ETS-10, samples were rehydrated to various levels of excess water by mass and the reaction was performed under identical reaction conditions. The observed yield as a function of rehydration level is seen in Figure 3. As can be seen in the figure, a direct relationship between yield and rehydration level is seen at excess water levels below 12.5% by mass. In addition, a direct

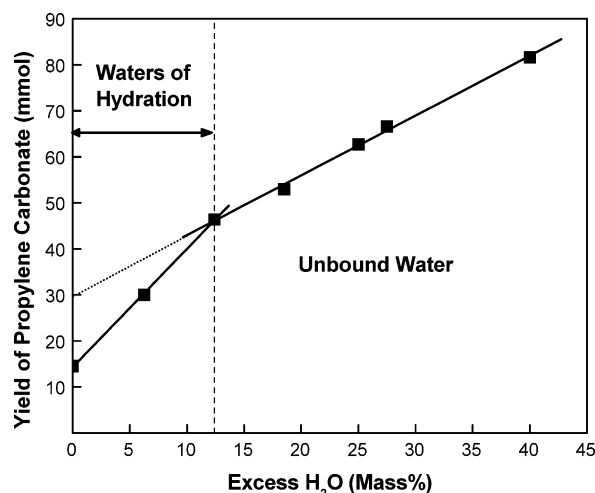


Figure 3. Yield of propylene carbonate as a function of rehydration level over as-received ETS-10 catalysts after 24 h at 150 °C.

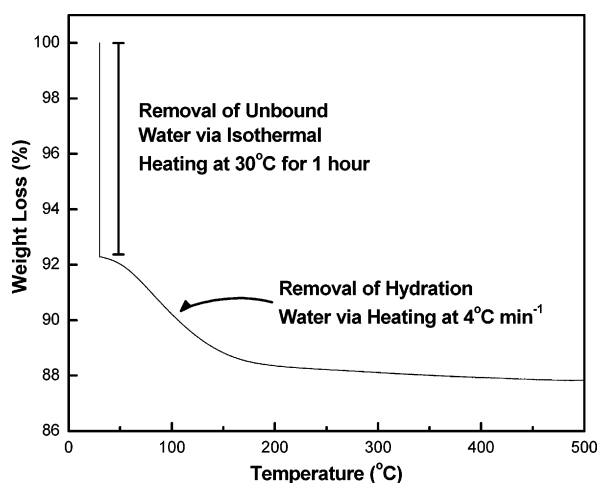


Figure 4. Dehydration behavior of as-received ETS-10.

relationship between yield and rehydration level is also observed at excess water levels above 12.5% by mass but at a lower rate of catalytic enhancement. As seen in Figure 4, this transitional level of hydration coincides with the level of hydration present in the as-received ETS-10 material since, after heating an as-received ETS-10 sample in flowing air to remove adsorbed water, roughly 12% of the initial mass was lost after heating to 200 °C. This hydration level is consistent with thermogravimetric analysis (TGA) and TPD analysis performed by many authors.^{33–35} Therefore, the transition in the rate enhancement appears to occur at a hydration level consistent with that found in the as-prepared material, where water helps to stabilize the structure.

Discussion

Clearly, the state in which CO₂ exists on the catalyst surface plays a key role in the cycloaddition reactivity for these catalysts. By use of Fourier transform IR spectroscopy of adsorbed CO₂, Llabrés i Xamena and Zecchina have shown that carbon dioxide forms some carbonate-like species when adsorbed on Na-ETS-10 at room temperature, which are associated with basic framework oxygen atoms.³⁶ In addition, a contribution due to linear adsorption of CO₂ on cations to form Na⁺...O=C=O adducts in significant quantities were also observed, interactions which have been assigned to Lewis acidity.^{37,38} From the microcalorimetry results presented in Figure 1, the total CO₂

uptake is initially reduced when the NaO_x species are occluded in the ETS-10 pores. Therefore, it appears that the incorporation of excess NaO_x in the ETS-10 pores are in close proximity to or bond to the charge-compensating cations, blocking access to these cationic sites and reducing the Lewis acidity, thereby resulting in a lower uptake of CO₂. For a variety of zeolites and microporous materials, less than a 1:1 ratio between CO₂ uptake and occluded alkali oxide loading has been observed in prior studies.^{8,17} Since we would expect that a 1:1 ratio would occur for the linearly adsorbed adducts, the observed reduction in CO₂ uptake at lower NaO_x occlusion levels must be due to blocking of the charge-compensating cation by the occluded NaO_x species. Adsorption microcalorimetry of CO₂, therefore, gives an indirect determination of how these Lewis acid sites are affected after occlusion of NaO_x. Therefore, the high uptake of CO₂ in the unmodified ETS-10 cannot be attributed solely to surface basicity. The linear interactions with the cations compete with the basic oxygen active sites for CO₂ adsorption and may even enhance CO₂ access to the active site by acting as a localized CO₂ storage site located in close proximity to the actual surface active sites responsible for cycloaddition. We have presented a more thorough investigation of CO₂ adsorption on the charge-compensating cations elsewhere for various alkali and alkaline-earth-exchanged ETS-10 materials.³⁹

To gain a better understanding of why water could exhibit such a significant effect on the yield, we must better understand the mechanism of the cycloaddition reaction. Most heterogeneous catalysts that have been used for the cycloaddition of carbon dioxide to epoxides have been considered to be primarily “basic” in nature.^{27,31,32,40} However, Yamaguchi et al. have shown that substitution of aluminum as Lewis acid sites into a magnesium oxide structure in a Mg:Al ratio of 5:1 acts in a cooperative manner with surface basic sites, enhancing the cycloaddition reactivity compared to pure MgO, while high substitution levels result in an inactive catalyst.³⁰ Therefore, effective tuning of the acidity and basicity in terms of strength and number of sites is critical for this reaction.

For ETS-10 molecular sieves, this criterion was clearly shown by Philippou et al. using the decomposition of 2-propanol as a probe of surface acidity and basicity, who found that Cs-ETS-10 exhibited about a 50% lower conversion to propene than ETS-10 while the conversion to base-catalyzed acetone decreased only slightly, indicating that ion-exchanging Cs into the ETS-10 structure does not significantly affect the overall basicity associated with the catalyst but does reduce the surface acidity.⁴ While Philippou et al. varied the acid–base character of the ETS-10 via ion exchange, similar effects on the acid–base site density must account for the yields observed for the cycloaddition reaction presented here, where the acid–base character was altered by incorporation of supported NaO_x as well as by the incorporation of water.

From the reactivity analysis, it is apparent that enhancement of the reaction on a dry basis can be affected by incorporating additional sites of surface basicity into the ETS-10 pores. However, to produce a higher conversion to propylene carbonate, introducing adsorbed water prior to starting the reaction has a greater effect. Because of this, the ETS-10 catalyst requires no special handling of the catalyst in order to keep the catalyst moisture-free. Henceforth, introducing surface base sites alone cannot effectively tune the ETS-10 catalyst to perform this reaction. From our observations, it appears that water can play four roles in creating this higher conversion: (1) by enhancing the Brønsted acidity associated with the ETS-10 surface, (2) by producing localized carbonic acid sites that take part in the

reaction, (3) by enhancing the transport of reactants to the interior active sites, or (4) by significantly modifying the supported oxide to produce sites of higher turnover.

The rate transition in the yield observed at a rehydration level of 12.5% by mass observed in Figure 3 occurs at a level consistent with the stabilized structure for as-prepared ETS-10.^{33–35} Below this transition point, roughly one-third of this water exists as highly bound water that bonds with the cations present in the structure, while the remaining hydration water is speculated to be due to hydrogen-bonded water interacting with surface oxygen atoms.³⁵ From the cycloaddition reactivity analysis, the observed rate enhancement does not appear to be dependent solely on either the strongly or weakly bound water but rather due to a combination of these two adsorption modes. Above this transition, where the amount of water exceeds that initially present in the as-received material, the adsorbed water is not as effective in enhancing the conversion to propylene carbonate and clearly plays a different role in enhancing the conversion.

The exact role of water above and below this transition point is unclear at this time. However, we can speculate that, at lower hydration levels, where the rate of enhancement is greatest, the presence of zeolite-type water, which is more strongly bound to the surface, is responsible to some degree for enhancing the yield. Since the fine tuning of the acid–base character of the catalyst plays such a vital role in the creation of an effective cycloaddition catalyst, one can speculate that the initial enhancement at low hydration levels must involve localized changes to the acid–base character at the surface since, as indicated by the work by Yamaguchi et al., some specific ratio of acidity to basicity must provide an optimum catalyst for the reaction. In fact, at these lower levels of hydration, surface –OH groups are produced that enhance the surface Bronsted acidity at the surface.^{34,35} Above this level of hydration, the water is present in a freer form, which does not alter the ETS-10 surface and could potentially act as a facilitator of transport to and from the active sites located in the pores of the ETS-10. A more plausible explanation would be that localized carbonic acid is formed by dissolution of carbon dioxide in the free water under the higher CO₂ pressures used for the reaction, which further enhances the acidity near the catalyst surface by forming areas of weak diprotic Bronsted acidity.

Since these studies investigated the unmodified ETS-10 material, interactions between water and NaO_x were neglected in this case. However, if we correlate the reduced activity encountered for the rehydrated NaO_x/ETS-10 catalysts to the adsorption microcalorimetry of carbon dioxide, we see that the reduction in the total CO₂ uptake at lower NaO_x occlusion levels must be attributed to the interaction of the occluded NaO_x with the charge-compensating cations and/or surface oxygen atoms responsible for the adsorption of carbon dioxide in unmodified ETS-10.

Gravimetric analysis for the adsorption of water indicates that, for 2.0 NaO_x/ETS-10, the occluded sample exhibiting the greatest reactivity on a dry basis, the amount of water adsorbed at constant humidity is statistically identical to that adsorbed on the parent ETS-10 sample on a per gram basis. Therefore, the occluded NaO_x species do not significantly reduce the total amount of water that is adsorbed in the pores of the ETS-10 and a smaller volume of adsorbed water cannot be responsible for the reduced activity observed. Likewise, microcalorimetric analysis of the adsorption of water (not shown) indicates that the heats of adsorption for water at initial doses is not enhanced by the presence of NaO_x in the pores of ETS-10 as would be

expected if water was adsorbing on the occluded sodium oxide species. Because of these observations, the reduced activity observed for the NaO_x occluded catalysts after rehydrating with water must be due to the interaction of the occluded NaO_x species with an active ETS-10 site that would normally be enhanced via the reintroduction of water into the ETS-10 pores. The most likely explanation that fits the above observations would be that the occluded sodium precursor reacts with surface hydroxyl groups present during the wetness impregnation preparation technique,⁴¹ reducing the number of potential Bronsted acid sites once the NaO_x occluded catalyst has been rehydrated, thus altering the surface acid–base characteristics required for the bifunctional reaction.

Conclusions

Various alkali modified ETS-10 molecular sieves were investigated for the cycloaddition of carbon dioxide and propylene oxide to produce propylene carbonate. For dry catalysts, the incorporation of occluded NaO_x clusters into the parent ETS-10 pores resulted in a catalyst with an increased yield of propylene carbonate, with an optimum loading of 2.0 excess NaO_x per unit cell providing a 50% yield enhancement compared to the parent ETS-10. This increased yield confirmed that the reaction is dependent on surface basicity in order to carry out the reaction. However, after rehydrating the modified and parent ETS-10 materials overnight in a high humidity chamber, the rehydrated form of unmodified ETS-10 exhibited the greatest yield for all the catalysts investigated in this study. The waters of hydration, which are bound either to the charge-compensating cations or framework oxygen atoms, appear to create surface –OH groups, which enhance the Bronsted acidity of the ETS-10 and more significantly enhance the yield of propylene carbonate. Adsorption microcalorimetry of carbon dioxide on the modified ETS-10 catalysts show that the total CO₂ uptake is initially reduced at lower loadings and does not reach a total uptake level of CO₂ greater than the as-received ETS-10 material until at least 2.8 excess NaO_x per unit cell is achieved. At this level, however, the catalyst is less effective for the cycloaddition reaction due to the reduced pore volume and surface area. Surface bound water plays a more critical role in enhancing the cycloaddition reactivity for the ETS-10 catalysts than the incorporation of excess basicity via occlusion of excess sodium oxide.

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