UV-Vis Spectroscopy of Iodine Adsorbed on Alkali-Metal-Modified Zeolite Catalysts for Addition of Carbon Dioxide to Ethylene Oxide

Eric J. Doskocil, Shailendra V. Bordawekar, Brian G. Kaye, and Robert J. Davis*

Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22903-2442

Received: March 30, 1999; In Final Form: May 24, 1999

The basicity of alkali-metal-exchanged (Na, K, Cs) zeolites X and Y was probed by UV—vis diffuse reflectance spectroscopy of adsorbed iodine. The observed blue shift in the visible absorption spectrum of adsorbed iodine, compared to gaseous iodine, correlated well with the negative charge on the framework oxygen atoms calculated from the Sanderson electronegativity equalization principle. The blue shifts associated with iodine adsorbed on classical catalytic supports like silica, alumina, and magnesia suggest that the iodine adsorption technique for probing basicity is applicable to a wide variety of solids. Iodine was also adsorbed on X and Y zeolites containing occluded cesium oxide formed by decomposition of impregnated cesium acetate. However, the iodine appeared to irreversibly react on these strongly basic samples, possibly forming an adsorbed triiodide ion. As a complement to the adsorption studies, the activity of alkali-metal-containing zeolites for the base-catalyzed formation of ethylene carbonate from ethylene oxide and carbon dioxide was investigated. Among the ion-exchanged zeolites, the cesium form of zeolite X exhibited the highest activity for ethylene carbonate formation. The catalytic activity of a zeolite containing occluded cesium was even higher than that of a cesium-exchanged zeolite. The presence of water adsorbed in zeolite pores promoted the rate of ethylene carbonate formation for both cesium-exchanged and cesium-impregnated zeolite X.

Introduction

Zeolites that have been modified by ion exchange of alkalimetal cations or by decomposition of an occluded alkali-metal salt have emerged as interesting solid bases. They are known to catalyze many reactions, including double-bond isomerization of olefins, side-chain alkylation of aromatics, dehydrogenation of alcohols, and Knoevenagel condensation of aldehydes.^{1–5} The base strength of alkali-metal ion-exchanged zeolites increases with increasing electropositivity of the exchange cation, and occlusion of alkali-metal oxide clusters in zeolite cages via decomposition of impregnated alkali-metal salts results in a further increase in the basicity of these materials.^{1,3,6–9} The base sites in alkali-metal-modified zeolites are commonly characterized by IR spectroscopy and/or temperature-programmed desorption of adsorbed probe molecules such as carbon dioxide,^{3,10–13} pyrrole,^{14–16} and chloroform.^{17–19}

The nature and strength of an active site are important to understand base catalysis on a molecular level. One of the major problems encountered in studying surface basicity is that many commonly used probe molecules decompose or react upon interaction with the basic site and, therefore, do not effectively interrogate the catalyst surface. Thus, the search for a unique, widely applicable adsorbate molecule to probe the surface basicity of heterogeneous catalysts is an ongoing process.

A sample that has an exposed ionizable electron acts as a Lewis base with respect to I_2 ,²⁰ and the use of I_2 as a molecular probe of electron donor strength associated with the gas phase^{21–26} and solvated molecules^{20,27–41} has been well documented in the literature. Many researchers have correlated the

blue shift in the visible absorption band of an iodine donor-acceptor complex to its heat of formation.^{27,29,42}

Mulliken predicted the use of iodine adsorption to probe the donor strength of solids,²⁸ and sorption of iodine in zeolites has been investigated in the past.^{43,44} These early studies reported on the heat of sorption and the location of iodine in various zeolites. The results from these works confirm that iodine interacts with the basic framework oxygen and not the charge-balancing cation.^{43,44}

Recently, the visible absorption spectrum of iodine has been used to rank the donor strength of the basic oxygens in various zeolites.⁴⁵ Choi et al. have shown that a blue shift occurs in the visible spectrum of adsorbed iodine with increasing electropositivity of the alkali-metal counterion from Li to K, as well as with increasing aluminum content in the zeolite framework.⁴⁵ These observations are consistent with the ranking of zeolite basicity determined by infrared studies¹⁵ and alcohol decomposition reactions.⁴⁶

In this paper, we extend the application of iodine as a visible probe for the determination of the basic strength for zeolites to include cesium-exchanged samples as well as various metal oxides. A limitation of this technique for use with strong bases will also be presented. To correlate the characterization results with the catalytic function, the activity of alkali-metal-modified zeolites was examined for the reaction of ethylene oxide and carbon dioxide to produce ethylene carbonate, an important intermediate in the manufacture of rubber chemicals and textile agents, as well as a precursor in the production of high-purity ethylene glycol.^{47–51} The usual catalysts employed in this reaction are homogeneous bases such as sodium hydroxide, tertiary amines, or quaternary ammonium compounds. To ease the separation of product from the catalyst, we have explored the possibility of using alkali-metal-modified zeolites as het-

 $[\]ast$ To whom correspondence should be addressed. E-mail: rjd4f@ virginia.edu.

zeolite	unit cell comp	no. of excess alkali metal atoms	BET surface area, $m^2 g^{-1}$	pore vol, mL g^{-1}
NaX	H _{8.9} Na _{78.8} Si _{104.3} Al _{87.7} O ₃₈₄	0.0	766	0.288
KX	H _{6.8} Na _{8.2} K _{73.0} Si _{104.0} Al _{88.0} O ₃₈₄	0.0	652	0.245
CsX	H _{14.0} Na _{27.8} Cs _{47.7} Si _{102.5} Al _{89.5} O ₃₈₄	0.0	399	0.160
CsO_X/CsX	Na _{27.0} Cs _{62.7} Si _{108.3} Al _{83.7} O ₃₈₄	6.1	270	0.111
NaY	$H_{0.4}Na_{53.6}Si_{137.9}Al_{54.1}O_{384}$	0.0	863	0.325
KY	H _{4.8} Na _{2.8} K _{50.0} Si _{134.5} Al _{57.5} O ₃₈₄	0.0	867	0.331
CsY	H _{3.9} Na _{14.7} Cs _{39.0} Si _{134.4} Al _{57.6} O ₃₈₄	0.0	623	0.232
CsO _X /CsY	$Na_{15.1}Cs_{50.1}Si_{138.5}Al_{53.5}O_{384}$	11.7	373	0.141

erogeneous base catalysts for this reaction. The spectroscopic results from iodine adsorption studies and the catalytic activities of the zeolite catalysts have been used to rank their basicities.

Experimental Methods

Catalyst Preparation. Potassium- and cesium-exchanged zeolites were obtained by triply-ion-exchanging NaX (Union Carbide, Lot No. 943191060078) and NaY (Union Carbide, Lot No. 955089001010-S) in 1 M solutions of potassium nitrate (Mallinckrodt, reagent grade) and cesium acetate (Aldrich, 99.9%), respectively. The exchanged samples were then washed with an aqueous solution of the corresponding alkali-metal hydroxide (pH = 13.3), unless otherwise noted. The exchanged samples were then contacted with distilled-deionized water in an attempt to remove excess alkali metal that might have been occluded in the zeolite cages during ion exchange. The resultant ion-exchanged materials were dried overnight in air at 373 K. The zeolites were then heated in flowing air at 4 K min⁻¹ to 773 K and subsequently held at that temperature for 5-10 h. If a sample was to be impregnated with excess cesium after heat treatment, it was placed in a high-humidity vessel to slowly reintroduce water to the zeolite before impregnation with an aqueous cesium acetate solution of the appropriate concentration. The impregnated catalyst was then calcined in an identical manner to the ion-exchanged materials in order to decompose the occluded acetate. The impregnated samples, which are referred to as CsO_X/CsX and CsO_X/CsY, contain between 6 and 16 excess Cs atoms per unit cell. Elemental analyses of the alkali-metal-exchanged zeolites were performed by Galbraith Laboratories, Inc., Knoxville, TN. The additional materials used in this study were pure mesoporous silica (Si-MCM-41) prepared from an established procedure,⁵² y-alumina (Mager Scientific AP-312), magnesia obtained from the decomposition of Mg(OH)₂,⁵³ and cesium-doped (8 wt % Cs) mesoporous alumina.5 The BET surface areas and pore volumes were obtained from dinitrogen adsorption isotherms measured at 77 K on a Coulter Omnisorp 100CX instrument after outgassing for 10-12 h at 573 K.

Iodine Adsorption. Iodine adsorption was performed in a U-shaped quartz tube with a quartz frit to support the sample. Each catalyst sample was pressed between 2000 and 3000 psig, ground, and size separated (+40/-60 mesh) to facilitate transfer into a uvonic cuvette attached to the U-tube. About 0.5 g of sample were heated in vacuo to 773 K at a rate of 3 K min⁻¹ and held at that temperature for 10 h, unless stated otherwise. The ultimate pressure reached at 773 K was less than 3.3×10^{-5} mbar for each sample. A separate quartz reservoir containing crystalline iodine (EM Science, 99.8%) was attached by Cajon ultra-Torr fittings between the vacuum system and the sample holder and evacuated to less than 1.2×10^{-5} mbar. Iodine was dosed to the sample by opening the reservoir to the evacuated assembly and subsequently exposing it to the solid sample in the U-tube. The sample bed turned a bright color

after introduction of iodine vapor to the solid. The sample containing I₂ was allowed to equilibrate for at least 30 min before spectroscopy was performed. The mass of iodine adsorbed onto the sample was determined gravimetrically. Desorption of iodine was accomplished by heating an iodine-loaded sample in vacuo to 773 K at a rate of 3 K min⁻¹ and holding at that temperature for 5–8 h.

Diffuse reflectance UV-visible spectra were recorded on a Varian Cary 3E spectrophotometer equipped with a Labsphere integrating sphere (DRA-CA-30) with a Labsphere Spectralon reflectance standard (USRS-99-020). After the sample tube was inverted to load the cuvette with sample, multiple UV-vis spectra were recorded and averaged after each sample treatment.

Reaction of Ethylene Oxide with Carbon Dioxide To Make Ethylene Carbonate. The reaction was carried out in a 50-mL high-pressure batch reactor supplied by Parr Instrument Co. About 150 mg of catalyst were loaded into the reactor, after which a measured liquid volume of ethylene oxide was introduced to the reactor. The vessel was pressurized with carbon dioxide to about 400 psig at ambient conditions and then heated to 423 K with constant stirring of the reaction mixture. After heating, the pressure in the reactor increased to about 1500 psig. The reaction was stopped after 3 h. The product was extracted in acetone and analyzed by gas chromatography using a 50-m HP-1 capillary column and decane as an external standard.

Results and Discussion

Iodine Adsorption on Zeolites. The unit cell compositions for zeolites used in the iodine adsorption study, expressed in terms of an ideal zeolite unit cell having 384 oxygen atoms bridging Si and Al tetrahedra, are summarized in Table 1. Protons were added to the unit cell formulas in order to balance the framework charge. Additional oxygen atoms present from the decomposition of the occluded acetate are not included in the unit cell composition. Based on the unit cell compositions obtained from elemental analysis, potassium- and cesiumexchanged zeolites appeared to contain no excess alkali metal after ion exchange. Exchanging the Na cations with heavier alkali metals resulted in a moderate decrease in the surface area of the zeolites. Observed pore volumes, determined from the liquid volume of dinitrogen adsorbed at a relative pressure of 0.3, indicated a small decrease in specific pore volume with exchange of heavy alkali metal, mostly due to their higher atomic weights and their larger cation radii. Decomposition of cesium acetate in the pores of the zeolites resulted in 0.8 and 1.5 excess cesiums per supercage for CsX and CsY, respectively.

Figures 1 and 2 compare the UV-vis spectra of the various zeolites containing adsorbed iodine. The large absorption feature in the deep ultraviolet region is known as the charge-transfer band associated with the formation of an iodine donor-acceptor complex. In our work, we focus on the low-energy bands depicted by the arrows in Figures 1 and 2. For both X and Y zeolites, a blue shift was observed in these low- energy bands when sodium was exchanged with potassium. Choi et al. found



Figure 1. UV-Vis diffuse reflectance spectra for iodine adsorbed on various X zeolites at room temperature. The spectra shown are for the iodine doses given in Table 2, except for CsX, in which the dose is 6.6 mg of $I_2 g^{-1}$.



Figure 2. UV-Vis diffuse reflectance spectra for iodine adsorbed on various Y zeolites at room temperature. The spectra shown are for the iodine doses given in Table 2.

 TABLE 2: Results from UV-Vis Spectroscopy of I2

 Adsorbed on Zeolites

Z	eolite X		Z	eolite Y	
sample	loading, mg g ⁻¹	$\lambda_{\max},$ nm	sample	loading, mg g ⁻¹	$\lambda_{\max},$ nm
NaX	19.1	410	NaY	27.8	473
KX	20.1	359	KY	26.8	419
CsX	19.4	362	CsY	20.5	419
CsO _X /CsX	26.3	349	CsO _X /CsY	23.6	359

similar results for analogous zeolites.⁴⁵ In addition, the peak maximum of the X zeolites was always located at higher energies (lower wavelengths) than analogous Y zeolites. The wavelengths of these low-energy features are reported in Table 2 for iodine loadings near 20 mg of $I_2 g^{-1}$. The cesium-exchanged X and Y zeolites had absorption features at almost the same wavelengths as their corresponding potassium-exchanged zeolites

Figure 3 shows the correlation of the partial negative charge on the framework oxygen atoms and the energy shift of the iodine absorption maximum with respect to I_2 in the gas phase. The partial negative charge on oxygen was calculated from the Sanderson intermediate electronegativity principle, which is based solely on the overall sample composition.⁵⁴ A linear relationship between energy shift and partial negative charge on oxygen was observed for the alkali-metal zeolites. The incomplete levels of Cs exchange account for the similar absorption features for CsX and KX as well as CsY and KY.

In the case of I_2 adsorbed in CsY, a peak at 350 nm is observed together with the usual visible absorption band at 419 nm. This 350-nm band is not present in the spectrum of iodine



Figure 3. Partial negative charge on oxygen as a function of energy calculated from the blue shift of adsorbed iodine in relation to gaseous iodine.

on KY, but a similar feature at 359 nm is found for I_2 on CsO_X/CsY . For CsY and CsO_X/CsY , an additional UV absorption band occurs at 280 and 290 nm, respectively. Awtrey and Connick⁵⁵ and Buckles et al.⁵⁶ have shown that the I_3^- ion gives an absorption maximum at 365 nm and another band at 295 nm, which supports the possible formation of a cesium triiodide salt upon iodine adsorption on CsY and CsO_X/CsY. The formation of the I_3^- ion is possible only if dissociation of I_2 takes place initially. Since complete dissociation of an iodine molecule requires a strong base site, samples revealing an absorption spectrum consistent with triiodide most likely expose strong donor sites. Unfortunately, the formation of I_3^- limits the ability of this technique to accurately rank the base strength by simple comparison of UV-vis absorption bands.

The absorption features associated with strongly basic samples suggest that iodine may react with the solids, so the reversibility of iodine adsorption was investigated. After a complete iodine dosing cycle (typically ~ 100 mg of I₂ g⁻¹), zeolites NaY, KY, CsY, and CsO_X/CsY were heated in vacuum to 773 K and held at that temperature for over 5 h under vacuum to obtain a final pressure of less than 10^{-5} mbar in an attempt to remove the adsorbed iodine from the zeolite. In each case, the visible color initially present on the I₂-dosed sample disappeared. For NaY, the iodine was completely removed by heating the dosed sample (53.2 mg of I_2 g⁻¹) for 5.5 h at 773 K. However, for the KY and CsY cases, a small fraction of the iodine (0.7 and 1.5 mg of $I_2 \ g^{-1}$ respectively) did not desorb under identical treatment conditions; the residual iodine loading corresponded to 0.7 and 2.4 I₂ molecules per 1000 alkali-metal atoms, respectively. Because the KY and CsY zeolites were prepared using a hydroxide wash, a very small amount of occluded alkali metal may interact irreversibly with the adsorbed iodine. Since the amount of residual iodine is very low compared to the total amount of K and Cs cations in the samples, it is clear that iodine does not interact irreversibly with the ions located in standard ion-exchange positions. For cesium impregnated on CsY, however, a large fraction of iodine, equivalent to 18.6 mg of I_2 per g of CsO_X/CsY , remained on the sample after heating at 773 K for 9 h, which corresponds to a residual loading of 1.35 I_2 molecules per unit cell (0.12 I_2 molecule per excess Cs atom). Clearly a strong interaction between sorbed iodine and occluded cesium exists, but the stoichiometry did not indicate complete conversion of the occluded cesium species to cesium iodide. Bulk cesium iodide (CsI, Acros, 99.9%) did not reveal any visible absorption bands in our UV-vis spectrometer, indicating that the visible absorption band observed after iodine adsorption onto the zeolite is not due to formation of cesium iodide. It is



Figure 4. Effect of iodine loading on the low-energy absorption band location for various X zeolites.



Figure 5. Effect of iodine loading on the low-energy absorption band location for various Y zeolites.

TABLE 3: Results from UV–Vis Spectroscopy of I_2 Adsorbed on Various Oxides

sample	λ_{max} , nm	$I_2 \ loading, \ mg \ g^{-1}$	BET surf area, $m^2 g^{-1}$
Si-MCM-41	508	17.0	802
γ -Al ₂ O ₃	410	27.2	87
MgO	366	19.4	77
CsO _X /Al ₂ O ₃	360	24.5	370

possible that the occluded cesium oxide clusters are sufficiently large to restrict an iodine interaction with each occluded cesium atom.

A gradual red shift in the visible absorption band with increasing adsorption of iodine on the sample has been observed by Choi et al.45 The location of the low-energy band as a function of iodine loading can be seen in Figures 4 and 5 for various X and Y zeolites, respectively. Each of the Y zeolites studied showed a red shift with increasing iodine loading. For NaX, a significant red shift in the visible absorption band with increasing iodine sorption was observed over the entire range of iodine loading. For the KX and CsX zeolites, however, there was little change in the location of the visible absorption band at loadings exceeding 40 mg of I_2 g⁻¹. It is quite possible that, for strongly basic materials, the iodine adsorption is not equilibrated with the sample. From Figure 4, it is clear that KX has a greater blue shift and thus stronger basicity than the cesium X zeolite at small I₂ doses, indicating that KX contained a few stronger adsorption sites than the CsX zeolite.

Iodine Adsorption on Other Catalytic Materials. The use of iodine as a visible probe for donor strength was then extended to other metal oxides typically used as catalyst supports. Table 3 shows the peak locations for the low-energy absorption band for various metal oxides with similar loadings of iodine. Silica MCM-41 had an absorption band at 508 nm, which is close to

 TABLE 4: Properties of Zeolites^a Used for Catalytic Reaction

zeolite	unit cell comp	BET surf area ($m^2 g^{-1}$)
NaX	H _{8.9} Na _{78.8} Si _{104.3} Al _{87.7} O ₃₈₄	766
KX	H _{3.4} Na _{6.1} K _{79.9} Si _{102.6} Al _{89.4} O ₃₈₄	609
CsX	H _{8.4} Na _{28.2} Cs _{50.6} Si _{104.9} Al _{87.2} O ₃₈₄	398
NaY	H _{0.4} Na _{53.6} Si _{137.9} Al _{54.1} O ₃₈₄	863
CsY	$H_{2.2}Na_{15.7}Cs_{39.2}Si_{134.9}Al_{57.1}O_{384}$	502

^a Hydroxide washed, except for Na zeolites.

 TABLE 5: Activity of Alkali-Metal-Modified Zeolites for

 Ethylene Carbonate Formation

catalyst	yield of ethylene carbonate, ^a %
NaX	1.4
$\mathbf{K}\mathbf{X}^b$	2.7
KX	20.9
CsX^b	10.5
CsX	26.6
CsO_X/CsX^b	33.4
NaY	0.0
CsY	0.3
CsO_X/CsY^b	11.9

 a Yield reported after 3 h at 423 K and about 1500 psig. b Not hydroxide washed.

that observed for gaseous I_2 (520 nm), indicating that the interaction with amorphous silica is relatively weak. Similar values have been seen as well for zeolitic materials with high Si/Al ratios.45 Alumina exhibited a significant blue shift of the low-energy absorption peak to 410 nm, indicating a similar donor strength of the Al₂O₃ oxygen to that of framework oxygen in NaX at a similar coverage. Microcalorimetry results obtained in our laboratory indicate that alumina contains base sites capable of adsorbing carbon dioxide at room temperature.⁵⁷ Magnesia, a classic basic oxide, gave adsorbed I₂ an even more significant blue shift to 366 nm, confirming the high donor strength of its surface. The low-energy absorption band for iodine adsorbed on cesium-modified mesoporous alumina (8 wt % Cs) exhibited a significant blue shift to 360 nm compared to that for the γ -alumina under identical pretreatment conditions. This result is similar to the blue shift observed for the CsO_X / CsY sample mentioned previously. Clearly, the UV-vis spectrum of adsorbed iodine can be used to study solids other than zeolites.

Catalytic Activity. A separate series of basic zeolite materials was prepared for the study of catalytic probe reactions. The elemental compositions of these alkali-metal X and Y zeolites can be found in Table 4. Since both water-washed and hydroxide-washed zeolites exhibited similar elemental compositions, only the results for the hydroxide-washed samples are shown in Table 4. Cesium oxide occluded in zeolites X and Y contained about 16 excess cesium atoms per unit cell.

The catalytic activity of alkali-metal-modified zeolites for ethylene carbonate formation is reported in Table 5. In all of the experiments, ethylene carbonate was the only product detected by gas chromatography. The yield of ethylene carbonate after 3 h of reaction at 423 K increased with increasing electropositivity of the exchange cation. Increased electropositivity of the exchange cation results in a higher negative charge on the framework oxygen atoms, thereby making the material more basic. This is reflected in the higher activity of KX compared to NaX. As seen in Figure 3, the partial negative charge on the framework oxygen atoms of CsX is nearly identical to that of KX, which could explain why the activities of these two catalysts are similar. The NaY sample showed no activity for ethylene carbonate formation, whereas CsY revealed

 TABLE 6: Effect of Adsorbed Water on the Activity of Alkali-Metal-Modified Zeolites^a for Ethylene Carbonate Formation

catalyst	yield of ethylene carbonate, ^b %
CsX	10.5
dehydrated CsX	3.0
rehydrated CsX	10.4
CsO_X/CsX	33.4
dehydrated CsO _X /CsX	3.1

^a Not hydroxide washed. ^b Yield reported after 3 h at 423 K and about 1500 psig.

some activity for the reaction. However, the catalytic activity of CsY was much lower than that of CsX. The rank of catalytic activities of the ion-exchanged X and Y zeolites compares very well to the expected order of basic strength reported in Figure 3.

The hydroxide-washed KX and CsX catalysts were more active for ethylene carbonate formation than their water-washed counterparts (Table 5). As discussed earlier, washing the ion-exchanged zeolite with alkali-metal hydroxide is likely to introduce trace amounts of excess alkali metal in the zeolite cages, which can enhance activity. Indeed, Engelhardt et al. have shown that washing alkali-metal-exchanged zeolites with water introduced some acidity in the materials, leading to increased selectivity for acid-catalyzed products in the alkylation of toluene with methanol.⁵⁸ However, treatment of the ion-exchanged zeolite with alkali-metal hydroxide solution resulted in improved selectivity to the base-catalyzed products.⁵⁸

Occlusion of cesium oxide in the X and Y zeolites improved the activity for ethylene carbonate. Tsuji et al.³ and Kim et al.⁷ have reported an increase in the activity of CsX for 1-butene isomerization upon incorporation of occluded cesium oxide clusters. Similarly, Hathaway and Davis found that occlusion of cesium oxide clusters in CsY resulted in an increase in selectivity to acetone, the product primarily formed over base sites, in the decomposition of 2-propanol.¹ Our activity results for ethylene carbonate formation are consistent with these observations.

The activity of CsX (water washed) for ethylene carbonate formation showed a linear increase with time, reaching a yield of 31.6% after 10 h. For comparison purposes, the yield of ethylene carbonate after 3 h in a homogeneously catalyzed reaction using tetraethylammonium bromide was 76.3%. Thus, the yields reported for alkali-metal-modified zeolites in Table 5 are not limited by thermodynamic equilibrium.

To ensure that the reaction between ethylene oxide and CO_2 was heterogeneously catalyzed, the reaction mixture from a run with CsX (water washed) was used in a subsequent experiment after removal of the zeolite catalyst. A fresh feed of ethylene oxide was added to the reaction mixture, and the vessel was pressurized with CO_2 and heated at 423 K for 3 h. The yield of ethylene carbonate in this experiment was negligible, indicating that the reaction predominantly occurs in the presence of the zeolite.

Each zeolite catalyst reported in Table 5 was exposed to the atmosphere after calcination at 773 K. As a result, these catalysts adsorbed a significant amount of ambient water. To study the effect of adsorbed water on the catalytic activity of the zeolites, CsX (water washed) was dehydrated at 523 K in flowing He for 2 h prior to the reaction. The dehydrated sample showed reduced activity for ethylene carbonate formation (Table 6), compared to CsX exposed to atmosphere. As seen in Table 5, rehydration of a dehydrated CsX sample, using a flowing stream of helium saturated with water, recovered the activity of the

sample for ethylene carbonate formation. Dehydration of CsO_X/ CsX (water washed) also decreased its activity to ethylene carbonate (Table 6). These results indicate that adsorbed water plays an important role in the catalytic activity of alkali-metalmodified zeolites for ethylene carbonate formation. Haw et al. have shown that coadsorbed nitromethane in HZSM-5 increased the activity of the zeolite for 2-propanol dehydration, conversion of methanol to hydrocarbons, and conversion of acetone to acetic acid.59 They claim that nitromethane adsorbed on HZSM-5 behaves in a manner similar to polar solvents and promotes proton transfer by stabilizing ion-pair structures, leading to increased catalytic activity. In our case, adsorbed water in alkalimetal-modified zeolites enhanced the activity for ethylene carbonate formation, possibly through a hydroxide-mediated path. Ongoing studies in our laboratory are probing the interesting role of water in this reaction.

Conclusions

The adsorption of iodine as a probe for surface basicity has been shown to be effective in determining the relative basicity for alkali-metal-exchanged zeolites. Blue shifts in the visible absorption spectra of iodine correlated well with the basic strength of alkali-metal-exchanged zeolites. Extending this technique to supported alkali-metal species in zeolite pores and on oxide surfaces has yielded mixed results. Occluded alkali species apparently interacted irreversibly with iodine yet still exhibited a visible absorption band near 360 nm. Alkali-metal ion-exchanged zeolites were active for the reaction of ethylene oxide with carbon dioxide to make ethylene carbonate, and the activity increased with the electropositivity of the exchange cation. Incorporation of the occluded cesium oxide species in the ion-exchanged zeolites via decomposition of impregnated cesium acetate further promoted their catalytic activity. Water adsorbed in zeolite pores played a critical role in ethylene carbonate formation.

Acknowledgment. This work was supported by the Department of Energy (Basic Energy Sciences, Grant DEFG05-95ER14549) and the Virginia Academic Enhancement program.

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