Cycloaddition of CO₂ to Epoxides over Solid Base Catalysts

Mai Tu and Robert J. Davis¹

Department of Chemical Engineering, University of Virginia, 102 Engineers Way, Charlottesville, Virginia 22904-4741

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The cycloaddition of carbon dioxide to various epoxides (ethylene oxide, epoxybutene, and epoxypropylbenzene) over solid base catalysts (KX zeolite, Cs-loaded KX zeolite, Cs-doped alumina, and MgO) was performed in a batch autoclave reactor at 423 K and with excess CO₂. Catalysts were characterized by elemental analysis, N₂ physisorption, and CO₂ adsorption microcalorimetry. The combination of results from elemental analysis and microcalorimetry showed that the occluded base sites on the Cs/KX were actually composed of occluded Cs and K species that could be removed by washing with water. The activity of the zeolite catalysts for ethylene oxide conversion to ethylene carbonate depended on the basicity of the sample, with the sample containing occluded alkali metal oxides being the most active. In addition, the site-time yields of ethylene carbonate formation, based on CO₂ adsorption capacity, over Cs/KX, Cs/Al₂O₃, and MgO were similar to each other and were within a factor of 4 of the site-time yield seen with the homogeneous catalyst $[N(C_2H_5)_4]$ Br. The rates of epoxypropylbenzene conversion over the solid base catalysts were much lower than the rates of ethylene oxide conversion, presumably due to steric hindrance of the bulky side group on the former. Rate measurements with a mixture of ethylene oxide and epoxypropylbenzene over Cs/KX and MgO indicated that most of the basic sites on Cs/KX are located in the zeolite micropores. A high catalytic activity of Cs/Al₂O₃ for all of the epoxides studied suggests that proximity of surface Lewis acid sites to surface base sites is needed for the cycloaddition reaction. In the case of a zeolite catalyst, addition of a small amount of water enhanced the rate ethylene oxide reaction without significant formation of glycol side products. © 2001 Academic Press

Key Words: zeolite, basic; expoxide, reaction of; carbon dioxide, addition of; magnesia; alumina, Cs-doped; catalysis, base.

INTRODUCTION

Cyclic carbonates synthesized by the addition of CO_2 to epoxides are useful as highly polar solvents and reagents in polymer synthesis (1–6). Many organic and inorganic compounds, including onium halides, phosphines, amines, and metal halides, catalyze the reaction of CO_2 with epoxides under mild conditions to give high yields of cyclic carbonate (1–3). Solid bases such as MgO, calcined hydrotalcite (Mg–Al mixed oxide), and basic zeolites have also been explored as possible catalysts for the reaction (4-6). Interestingly, stereospecific addition of CO₂ has been reported over the Mg-based solid oxides (4, 5).

Basic zeolites have attracted attention recently primarily due to their environmentally benign character and their potential use in fine chemical synthesis (7–9). The basicity of zeolites can be developed by ion-exchange with heavy alkali metal cations (8–11). Stronger base sites can be incorporated in the zeolite pores by decomposing an occluded alkali metal salt such as cesium acetate (8–11). Basic zeolites have been tested in various reactions such as toluene alkylation with methanol, oxidative methylation of toluene with methane, dehydrogenation of alchols, double bond isomerization, and aldol condensation (7–19). Despite these extensive studies, the nature of occluded bases in zeolite pores and the structure of the active sites are unknown (7, 9).

In a previous paper, we reported that alkali-modified zeolites were catalytically active in the reaction of ethylene oxide with CO_2 to make ethylene carbonate (6). The activity increased with the electropositivity of the countercation and with incorporation of extraframework cesium oxide.

In the present work, we investigate the reactions of CO_2 with ethylene oxide, epoxybutene, and epoxypropylbenzene over a series of base catalysts, including X zeolites, Cs-loaded alumina, and magnesia. For comparison, pure Al_2O_3 and tetraethylammonium bromide were also studied. These reactions are illustrated in Fig. 1.

EXPERIMENTAL METHODS

Potassium-exchanged zeolite X (KX) was prepared by triply exchanging NaX (UOP, Lot No. 07483-36) with 1 M aqueous solutions of KNO₃ (Alfa, 99.0%). The NaX was slurried in the aqueous solution for 2 h during each exchange and then vacuum filtered. The exchanged sample was then washed with distilled water until the filtrate was neutral. The resulting material was dried overnight and then calcined in flowing air at 773 K for 5 h. The heating rate was 4 K min⁻¹ from room temperature to 773 K except that the sample was held at 423 K for 1 h during the ramping period.

Cesium was loaded into the KX by incipient wetness impregnation of aqueous solution of cesium acetate (Aldrich,



¹ To whom correspondence should be addressed, rjd4f@virginia.edu.



FIG. 1. Cycloaddition of carbon dioxide to various epoxides used in this work.

99.99%) (10). After drying overnight, the sample was calcined in flowing air at 773 K for 5 h with the same temperature program as for the KX. The resulting sample is denoted as Cs/KX(I). Another cesium-loaded zeolite X sample was prepared by identical procedures and is denoted as Cs/KX(II). Some of the Cs/KX(I) sample was added to distilled water, slurried for 2 h, and then filtered, dried, and calcined. All the conditions were identical to those described above for the KX. This washed sample is referred to as Cs/KX(W). Elemental analysis of the zeolite samples was performed by Southern Testing, NC. In addition, an alumina-supported cesium oxide (Cs/Al₂O₃) was prepared by incipient wetness impregnation following the procedures used for the preparation of the Cs/KX samples. The γ -alumina was provided by Mager Scientific Inc. and the magnesia (Grade 500A) was donated by Ube.

The BET surface areas and micropore volumes of the samples were evaluated from N_2 adsorption isotherms at 77 K measured on a Coulter Omnisorp 100CX instrument. Prior to measurement, a sample was outgassed overnight at 573 K. The micropore volume of the zeolite samples is reported as the liquid volume of N_2 adsorbed at a relative pressure of 0.3. The micropore volume of the Cs-loaded alumina and magnesia was evaluated by a *t*-plot analysis of the adsorption data. The magnesia sample was found to be nonmicroporous.

The basicity of the samples was measured by CO_2 adsorption microcalorimetry (20, 21). The details of the microcalorimeter used in this work are described in a previous paper (22). About 1.5 g of sample was loaded into the microcalorimeter and evacuated at 773 K for 5 h before cooling to 373 K. The adsorption was performed at 373 K.

Reactions of epoxides with CO_2 were carried out at 423 K in a 50-ml high-pressure, stainless steel, stirred autoclave from Parr Instrument Co. To give approximately the same base site loading in each run, about 50 to 150 mg of catalyst was loaded into the reactor prior to introduction of about 2 to 2.5 g of epoxide (ethylene oxide, Messer, 99.9%; epoxybutene, donated by Eastman Chemical Co.; 2, 3-epoxypropylbenzene, Aldrich, 98%). The reactor was then pressurized with about 550 psig CO_2 (BOC Gases, 99%) at ambient temperature. Prior to reaction, the catalyst was dried in flowing He at 623 K for 2 h and then immediately transferred to the reactor. After a reaction time of 3 h, products were extracted with acetone. A weighed amount of dodecane (Aldrich, 99+%) was added as an external standard to the product mixture, which was analyzed on a Hewlett Packard 6890 GC/MS with a 50-m HP-1 column. In a few experiments, catalysts were loaded with water by exposing them to air at 100% relative humidity at ambient temperature and pressure.

RESULTS

Results from elemental analysis, N_2 physisorption, and CO_2 chemisorption are summarized in Table 1. Each unit cell of the Cs/KX(I) contains 80 potassium cations and 20 extra cesium cations, which translates to a loading of about 2.5 Cs cations per supercage. Elemental analysis of Cs/KX(W) revealed that only 65 potassium cations and 15 cesium cations remained in the unit cell. Washing the Cs-loaded zeolite removed the extraframework alkali metal cations, since the total number of Cs and K cations was the same as the Al content in the unit cell. However, only 25% of the cesium atoms that were loaded into the sample were eliminated. Evidently, 75% of the added cesium exchanged with potassium ions already in the zeolite, thus allowing some of the potassium to be washed out of the sample. The high surface areas and micropore volumes of all zeolite

TABLE 1

Characterization of Zeol	ites, Cs/Al ₂ O ₃ ,	and MgO
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Catalyst	Composition	BET surface area (m ² g ⁻¹)	Micropore volume (ml g ⁻¹)	${ m CO_2}\ { m adsorption}\ { m capacility}^a\ (\mu { m mol}\ { m g}^{-1})$
КХ	_	467	0.234	80
Cs/KX(I)	Cs20K80Al80Si112O384	313	0.154	87
Cs/KX(II)	_	346	0.153	145
Cs/KX(W)	Cs15K65Al80Si112O384	366	0.181	45
Cs/Al ₂ O ₃	13.1 wt% Cs	69	0.008^{b}	123
MgO	_	42	_	45

 aBased on results from microcalorimetry; only sites stronger than 60 kJ mol^{-1} were counted.

^bBased on *t*-plot analysis.



FIG. 2. Differential heats of adsorption as a function of CO₂ uptake on basic zeolites.

samples suggest that incorporation of cesium did not extensively damage the crystalline framework. The Cs/Al₂O₃ and MgO catalysts had relatively low surface areas and no micropores detected by *t*-plot analysis.

Figure 2 shows the differential heat of CO₂ adsorption as a function of the loading on the zeolite samples. Carbon dioxide adsorbed on KX with a ΔH_{ads} of about 70 kJ mol⁻¹ up to a loading of about 80 μ mol g⁻¹. Addition of cesium to the zeolites increased both the heat of adsorption (to greater than 100 kJ mol⁻¹) and the maximum loading of CO2. The stronger basicity of the Cs/KX can be attributed to the occluded alkali metal oxide species, which may be either cesium or potassium oxide. The values of ΔH_{ads} on Cs/KX samples were similar to those reported previously for Cs loaded into CsX using analogous synthesis procedures (17). The CO_2 adsorption sites on the water-washed, cesium-containing zeolite, Cs/KX(W), were 10 kJ mol⁻¹ stronger than those on KX, probably due to the Cs cations that remained in the washed sample. The adsorption sites with ΔH_{ads} greater than 90 kJ mol⁻¹ were removed by washing a cesium-loaded zeolite, which confirmed that the strongest base sites were associated with the occluded alkali metal oxides.

The basicity of the MgO and Cs/Al₂O₃ samples was also determined by CO₂ adsorption microcalorimetry and results are summarized in Fig. 3. The MgO had the strongest adsorption sites (160–170 kJ mol⁻¹), but the total uptake of CO₂ was less than 50 μ mol g⁻¹ due to its low surface area. The adsorption sites on Cs/Al₂O₃ were energetically similar to those on MgO, but the total adsorption capacity of about 150 μ mol g⁻¹ was much higher. Results from microcalorimetry revealed a significant difference between adsorption sites of Cs/Al₂O₃ and cesium-loaded zeolites (Cs/KX and Cs/CsX (17)), indicating a significant support effect on the nature of cesium oxides.

The reaction of epoxide with CO_2 prefers cyclization rather than polymerization due to the thermodynamic stability of five-membered cyclic carbonate (1). In all of our



FIG. 3. Differential heats of adsorption as a function of CO_2 uptake on Cs/Al_2O_3 and MgO compared to Cs/KX.

experiments with dry catalysts, monocyclic carbonate was the only product detected by GC/MS. The catalytic activity is reported in this work as a site-time yield, which was calculated from the molar product yield after 3 h and the CO₂ adsorption capacity measured by microcalorimetry (Table 1). The CO₂ adsorption capacity was determined somewhat arbitrarily as the number of adsorption sites with $\Delta H_{ads} \ge$ 60 kJ mol⁻¹. The reaction temperature and time were chosen to give reasonable yields of product.

Table 2 compares the reactivity results for synthesis of 1,3-dioxolan-2-one (also called ethylene carbonate) from ethylene oxide over basic zeolites. The site-time yield of ethylene carbonate increased in the order of KX < Cs/KX(W) < Cs/KX, consistent with the order of the basicity of the samples determined by microcalorimetry. This result suggests that the catalyst basicity plays an important role in the addition reaction.

The results from CO_2 addition to ethylene oxide (EO), epoxypropylbenzene (EPBz), and epoxybutene (EpB) on various catalysts are reported in Table 3. The Cs/KX, Cs/Al₂O₃, and MgO catalysts were active in the synthesis of ethylene carbonate (D) with site-time yields ranging from 208 to 325 h⁻¹. Although the total base site density

TABLE 2

Catalytic Activity of Basic Zeolites in the Addition of CO₂ to Ethylene Oxide^a

Catalyst	$\Delta H_{\rm ads}$ of CO ₂ (kJ mol ⁻¹) ^b	Ethylene carbonate yield (%)	Site-time yield (h ⁻¹)
КХ	70	1.8	27
Cs/KX(I)	110	14	250
Cs/KX(W)	80	3.0	70

 a Reaction conditions: 423 K, initial CO₂ pressure 550 psig at 293 K, reaction time = 3 h.

^bBased on microcalorimetry.

TABLE 3

Addition of CO₂ to Epoxides over Solid Base Catalysts^a

Catalyst	Reactant ^b	Product ^b	Carbonate yield (%)	Site-time yield (h ⁻¹)
$[N(C_2H_5)_4]Br$	EO	D	74	812
	EPBz	BzD	41	239
	EpB	ED	87	345
Cs/KX(I)	EO	D	14	250
	EPBz	BzD	3.1	15
C _S /KX(II)	EO	D	19	208
	EpB	ED	0.3	3
C _S /Al ₂ O ₃	EO	D	24	325
	EPBz	BzD	20	56
	EpB	ED	28	231
Al_2O_3	EpB	ED	0	0
MgO	EO	D	19	309
-	EPBz	BzD	4.0	26
	EpB	ED	0.9	10

 a Reaction conditions: 423 K, initial CO₂ pressure 550 psig at 293 K, reaction time = 3 h.

^bEO, ethylene oxide; D, 1,3-dioxolan-2-one (ethylene carbonate); EPBz, epoxypropylbenzene; BzD, 4-benzyl-1,3-dioxolan-2-one; EpB, epoxybutene; ED, 4-ethenyl-1,3-dioxolan-2-one.

of Cs/KX(I) and Cs/KX(II) was different (see Table 1), the site-time yield for ethylene carbonate synthesis varied by only 17%, demonstrating the reproducibility of the reaction protocol. The homogeneous catalyst, $[N(C_2H_5)_4]Br$, was about 2.5 to 4 times more active than all the solid base catalysts for ethylene carbonate production. The reactivity of the larger epoxides was more complicated than that of ethylene oxide. For example, the cycloaddition of CO_2 to bulky epoxypropylbenzene was very slow over Cs/KX(I) with a site-time yield 16 times less than that measured with the homogeneous catalyst, presumably due to the steric restrictions around the basic sites located in the zeolite micropores. The site-time yields for epoxypropylbenzene reaction over nonmicroporous Cs/Al₂O₃ (56 h⁻¹) and MgO (26 h⁻¹) were greater than that over Cs/KX(I) (15 h⁻¹). Epoxybutene (EpB), which is larger in size than ethylene oxide but smaller than epoxypropylbenzene, was also tested in the cycloaddition reaction. As seen in Table 3, the sitetime yield of the EpB reaction over Cs/KX(II) $(3 h^{-1})$ was more than 100 times lower than that found with the homogeneous catalyst (345 h^{-1}). The olefinic functionality apparently plays a significant role in reactivity of EpB on solid bases. Interestingly, the site-time yield of the EpB reaction on Cs/Al₂O₃ (231 h^{-1}) was within a factor of 2 of the homogeneous catalyst (345 h^{-1}) and 23 times greater than that on MgO (10 h^{-1}). The surprisingly high activity of the Cs/Al₂O₃ catalyst led us to check the reactivity of the support alumina without added cesium. As illustrated in Table 3, no reaction of EpB was observed over pure alumina. It should be noted that ethylene oxide was the most reactive epoxide, regardless of the catalyst used.

The low reactivity of the bulky epoxypropylbenzene over Cs/KX(I) compared to that of ethylene oxide suggests that diffusional limitations inside the zeolite micropores may be limiting the mobility of the large reagent and/or product near the basic sites. To test this hypothesis, the CO₂ cycloaddition reaction was carried out with a mixture of ethylene oxide and epoxypropylbenzene. The results are shown in Table 4 for epoxide mixtures converted over Cs/KX(I) and MgO. Over the nonmicroporous MgO catalyst, the site-time yield of the bulky carbonate (BzD) was about the same as that observed with only epoxypropylbenzene (Table 3) and the STY of ethylene carbonate in the reaction mixture was slightly depressed by a factor of 1.6 over the pure component run (Table 3). Over the microporous Cs/KX(I), the rate of bulky carbonate formation was unaffected by the presence of ethylene oxide whereas the rate of ethylene carbonate formation was decreased by a factor of 8 by the presence of bulky epoxypropylbenzene. These reaction mixture experiments demonstrated that the bulky epoxide or its reaction product blocks access of ethylene oxide to the interior of the zeolite where most of the catalytically active basic sites are located.

Since ethylene carbonate can also catalytically decompose to form ethylene oxide and CO_2 (23), it is possible that ethylene carbonate formed in a mixed epoxide reaction (Table 4) participated in the reaction to form the bulky carbonate of epoxypropylbenzene. Therefore, we decomposed ethylene carbonate (Aldrich, 98%) in the presence of epoxypropylbenzene and 550 psig N₂. The results in Table 5 clearly show that decomposition of ethylene carbonate on the solid bases provided an alternative source of CO_2 for the epoxypropylbenzene. The site-time yields of BzD were 30 and 13 h⁻¹ on the MgO and the Cs/KX(I), respectively, and were similar to those obtained with CO_2 as a carbonate source. For comparison, the site-time yield of BzD was only 4.3 h⁻¹ with the homogeneous catalyst.

In a previous study, we found that exposing the cesiumcontaining zeolite X to a humid atmosphere before reaction

TABLE 4

Addition of CO₂ to Epoxide Mixtures over Cs/KX and MgO^a

Catalyst	Reactant ^b	Product ^b	Carbonate yield (%)	Site-time yield (h^{-1})
Cs/KX(I)	EO and EPBz	D BzD	3.5 5.6	31 14
MgO	EO and EPBz	D BzD	16 12	189 29

 a Reaction conditions: 423 K, initial CO₂ pressure 550 psig at 293 K, reaction time = 3 h.

^bEO, ethylene oxide; D, 1,3-dioxolan-2-one (ethylene carbonate); EPBz, epoxypropylbenzene; BzD, 4-benzyl-1,3-dioxolan-2-one.

TABLE 5

Reaction of Ethylene Carbonate and Epoxypropyl Benzene on Various Catalysts^a

Catalyst	BzD yield ^b (%)	Site-time yield (h ⁻¹)
MgO	9.3	30
Cs/KX(I)	5.3	13
$[N(C_2H_5)_4]Br$	9.0	4.3

^{*a*}Reaction conditions: 423 K, initial CO₂ pressure 550 psig at 293 K, reaction time = 3 h. Amount of ethylene carbonate was ~1.8 g for runs with solid catalysts and 2.9 g for the run with $[N(C_2H_5)_4]Br$. The standard amount of EPBz (~2 g) was used.

^bBzD, 4-benzyl-1,3-dioxolan-2-one.

promoted the production of ethylene carbonate from ethylene oxide (6). We have performed similar experiments with water-containing Cs/KX (I) and MgO and the results are reported in Table 6. Although the base site density of the wet catalysts has not been measured, an influence of water on the reaction rate can be seen in the site-time yield based on the dry catalyst base site density and the product selectivity. The site-time yield of ethylene carbonate increased to $705 h^{-1}$ over the wet Cs/KX(I) compared to $250 h^{-1}$ under dry conditions. A trace amount of ethylene glycol was the only side product detected. The site-time yield of ethylene carbonate on wet MgO was reduced to $56 h^{-1}$ compared to $309 h^{-1}$ on dry MgO because large amounts of mono-, di, and triethylene glycols were formed.

DISCUSSION

The results from elemental analysis and microcalorimetry provided insights into the nature of the occluded species in the basic zeolites. The basic species formed by decomposition of occluded cesium acetate was easily removed by washing in water, presumably through a hydrolysis process. In addition, most of the cesium that was impregnated as extraframework cations exchanged with potassium ions already present in the zeolite. To obtain occluded cesium species, a basic zeolite should be ion-exchanged with ce-

TABLE 6

Effect of Trace	e Water on th	e Addition of	f CO ₂ to	Ethylene	Oxide ^a
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Catalyst ^b	Ethylene carbonate yield (%)	Site-time yield (h^{-1})	By-product ^c
Cs/KX(I)	54	705	Trace amount EG
MgO	3.7	56	EG, DEG, TEG

 $^a Reaction$ conditions: 423 K, initial CO2 pressure 550 psig at 293 K, reaction time = 3 h.

^bExposed to 100% relative humidity prior to reaction.

 $^c\mathrm{Detected}$ by HP 6890 GC/MS. EG, ethylene glycol; DEG, di-ethylene glycol; TEG, triethylene glycol.

sium cations prior to impregnation beyond ion-exchange capacity.

The reactivity results indicate that basicity and porosity affect the rate of cycloaddition of carbon dioxide to epoxides. For example, the rate of ethylene carbonate formation over basic zeolites increased with increasing basicity as evaluated by carbon dioxide adsorption microcalorimetry. Clearly, the basic strength of a catalyst cannot be too great or carbon dioxide will be adsorbed too strongly to react. The catalysts used in this study are of appropriate base strength that allows for both CO_2 adsorption and reaction.

The porosity of the catalyst affected the conversion of the sterically hindered epoxypropylbenzene. Rates of reactions with both the pure component epoxides (Table 3) and mixed epoxides (Table 4) are consistent with the majority of the active sites on the zeolites being located in the micropores instead of on the external surface. For the mixed epoxide experiments (Table 4) both epoxypropylbenzene and its cyclic carbonate could retard the diffusion of ethylene oxide into the zeolite pores, leading to the severely reduced production of ethylene carbonate. However, the bulky reactant and product negligibly affected the rate of ethylene carbonate production over nonmicroporous MgO. These results provide clear evidence that most of the basic sites of zeolite catalysts containing occluded alkali metal oxide species are within the micropore network and suggest their use as shape-selective base catalysts.

Shape-selective catalysis is important for synthesis of fine chemicals and for processing of petroleum fractions. Most of the applications of shape selectivity are based on reactions catalyzed by acidic zeolites. Recently, researchers have started to explore the potential shape selectivity of basic zeolites (8). Rodriguez et al. studied the reaction of benzaldehyde with ethyl cyanoacetate over zeolites X and Y containing cesium oxide prepared by decomposition of occluded cesium acetate (24). They found that Knoevenagel condensation proceeded, but the product did not undergo the subsequent Michael addition. The lack of further addition reactions may be due to inadequate base strength of the catalyst or due to the limited space inside the zeolite cavities. Corma and Martin-Aranda also studied Knoevenagel condensation reactions on basic zeolites and suggested that the lack of Michael addition products is due to geometrical constraints in the zeolite (12). In a related work, Ballini et al. performed nitroaldolic condensation of aromatic aldehydes with nitroalkanes over basic zeolites (19). The lower levels of Michael addition products with larger reactants were again attributed to steric restrictions in the zeolite pores. In our work, we found a "reverse" reactant shape selectivity of the Cs/KX catalyst since cofeeding bulky epoxypropylbenzene with relatively small ethylene oxide almost totally inhibited the reaction of the small molecule. This is most likely a consequence of the relatively low reaction temperatures that do not favor desorption of the bulky reactants and products from the zeolite micropores, thus blocking access to the basic sites.

The influence of CO_2 availability at the active site is illustrated in Table 5. The decomposition of ethylene carbonate was used to provide carbon dioxide for epoxypropylbenzene. The site-time yields over MgO and Cs/KX(I) were greater than the homogeneous catalyst and were similar to the reactions in the presence of carbon dioxide. Evidently, the virtual pressure of carbon dioxide on the solid bases is quite high since reasonable site-time yields were observed. The CO_2 may even remain adsorbed on the solid bases until it is reacted away. For the case involving the homogeneous catalyst, a low site-time yield was probably due to the very low partial pressure of CO_2 in the reaction vessel due to ethylene carbonate decomposition.

The reaction of epoxybutene requires special discussion since it contains an additional olefinic functionality. It is unknown at this time why it is unreactive for cycloaddition of CO_2 in the basic zeolites. This result requires further study. Another interesting observation is that EpB was rapidly converted over Cs/Al₂O₃ but not over MgO. Since the heat of CO₂ adsorption on MgO is about the same as that on Cs/Al₂O₃, the high catalytic activity of Cs/Al₂O₃ for EpB conversion indicates that a factor other than basicity should be considered.

It has been reported that the calcined hydrotalcite (Mg-Al mixed oxide) was more active than the MgO in the reaction of CO₂ with epoxides because of the coexistence of Lewis acid sites on the former (5). These acid sites are believed to stabilize the adsorbed epoxide prior to addition of carbon dioxide. Therefore, the proximity of Lewis acid sites to basic sites capable of adsorbing carbon dioxide may be required to catalyze the cycloaddition reaction. A possible reaction mechanism for the addition of CO₂ to epoxides over solid base catalysts, shown in Scheme 1, has been suggested by Yamaguchi et al. (5). Carbon dioxide is adsorbed on Lewis basic sites (i.e., O^{2-}) to form a surface carbonate species. The strength and number of the surface base sites is likely to be very important for the activation of CO₂. The epoxide is adsorbed on a neighboring Lewis acid site, most likely an exposed cation. The carbonate surface anion reacts with the less sterically hindered carbon atom of the adsorbed oxirane to generate the oxyanion, which subsequently yields the cyclic carbonate product.

For the basic zeolites, a large number of exchangeable cations in the zeolite provide adequate coordination sites for the reacting epoxides. The case is likely to be different on the MgO and Cs/Al₂O₃ catalysts. Magnesia is a classic solid base with rather poor Lewis acidity whereas Cs/Al₂O₃ likely exposes Lewis acidic aluminum cations in the vicinity of the basic cesium "oxide" sites. The Cs/Al₂O₃ catalyst probably has an acid–base character analogous to that of the Mg–Al mixed oxides mentioned above. The accessibility of Lewis



SCHEME 1. Postulated mechanism for cycloaddition of CO_2 to an epoxide on a basic metal oxide surface. M represents a metal cation (Lewis acid) and O represents a surface oxygen (Lewis base).

acid cations becomes more important as the size of the reacting epoxide increases. Indeed, Cs/Al_2O_3 was more active than MgO for both epoxybutene and epoxypropyl benzene. However, the large difference between the two catalysts for EpB conversion is also likely due to the presence of the double bond. Further investigations are needed to clarify this point.

The beneficial effect of water observed for the Cs/KX catalyst may now be understood in light of the mechanism described in Scheme 1. Introduction of water into the zeolite pores generated basic hydroxyl groups that are highly mobile compared to the occluded alkali metal species. Thus, the reaction proceeds more like a homogeneously catalyzed process in which the acid–base sites are not constrained to a surface. Interestingly, the low level of water in the pores and the limited space available for reaction prevented the formation of glycol byproducts that were seen on wet magnesia catalysts.

CONCLUSIONS

The cycloaddition of CO₂ to various epoxides on a series of solid bases (KX, Cs/KX, Cs/Al₂O₃, and MgO) was influenced by base strength, porosity, and Lewis acidity of the catalysts. Decomposition of impregnated cesium acetate precursor on zeolite KX produced a zeolite with basic sites inside the zeolite micropores. The occluded moieties were composed of both Cs and K oxides due to ion-exchange during the synthesis procedure. The heat of carbon dioxide adsorption on the Cs/KX zeolites was about 50 kJ mol⁻¹ lower than that on either MgO or Cs/Al₂O₃. Nevertheless, CO₂ addition to ethylene oxide was effectively catalyzed by Cs/KX, MgO, and Cs/Al₂O₃. Porosity

and Lewis acidity appeared to influence the reactivity of epoxybutene (an epoxide containing a carbon–carbon double bond) and epoxypropylbenzene (a bulky epoxide) more than that of ethylene oxide. Finally, zeolites appear to provide a unique reaction environment that allows water to play a beneficial part in base catalysis involving carbon dioxide cycloaddition reactions.

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