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Ring-Opening and Dimerization Reactions of Methyl- and Dimethyloxiranes on HZSM-5 and CuZSM-5 Zeolites

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Ring-opening and dimerization reactions of methyloxirane and *cis*- and *trans*-2,3-dimethyloxirane were studied on CuZSM-5, prepared by various methods, and HZSM-5 zeolites in a closed static recirculation reactor at 363 K in reductive atmosphere. On these materials two main reaction types, ring-opening and dimerization, could be observed. For methyloxirane the major transformation pathways were ring opening and dimerization, producing various dioxolane and dioxane derivatives. In addition to these routes 2,3-dimethyloxiranes underwent deoxygenation and rearrangement as well. The activities and selectivities of the transformations toward these pathways were found to be significantly different depending on the stereochemistry of the substrates as well as the nature of the catalysts. Suggestions for the active sites and transformation mechanisms are also offered. © 1999 Academic Press

Key Words: **CuZSM-5; HZSM-5; methyloxirane; *cis*- and *trans*-2,3-dimethyloxirane, ring opening; dimerization; zeolites.**

INTRODUCTION

Acid-catalyzed transformations are common in making and breaking bonds in organic chemistry (1). The reactions are most often conducted in solution, where Brønsted (most often mineral acids) or Lewis acids (like $AlCl_3$ or other transition or early transition metal halides) or their combination (which are often superacids like, e.g., HF/SbF_5) may be used. A lot of these reactions are catalytic, i.e., huge amounts of these materials are not necessary; therefore, postreaction treatment of the acidic mixture is not too problematic on a laboratory scale. However, it can be extremely complicated in pilot plants, let alone on an industrial scale. Recycling is difficult and waste disposal causes serious environmental hazards. No wonder that replacement of liquid acids by solids is in the focal point of research and development for a long time. Various kinds of materials have been tried and in spite of occasional failures considerable success has been achieved. Zeolites belong to one class of the success substances. Beside the application of natural zeolites many different zeolite types with varying Si/Al ratios and crystal structures were synthesized (2). One of them, which was proved to be industrially useful, is ZSM-5 (3). Although it is a high-silica zeolite, it contains exchangeable ions as well. It can be transformed to the H-form routinely. Either this or the starting material may be used for exchanging other ions like, e.g., Cu^{2+} into the structure. When the H-form is the starting material for further ion exchange the resulting material will contain Brønsted as well as Lewis acid centers. Their ratio may be varied when different methods like wet or solid-state ion exchange are applied. Consequently, catalysts with differing properties may be expected. These acidic materials may be used as catalysts in many acid-catalyzed reactions. Ring-opening and subsequent transformations like dimerization of epoxides typically belong to this class of reaction. In this contribution results obtained for methyloxirane and 2,3-dimethyloxirane stereoisomers on HZSM-5 and two types of CuZSM-5, prepared by either wet or solid-state ion exchange, are described. Although CuZSM-5 catalysts are popular materials as deNO_x catalysts (for recent reviews, see (4, 5)), to our knowledge, they have never been studied in ring-opening reactions. Moreover, they were rarely used in reactions (6–10) other than those for nitric/nitrous oxide removal.

EXPERIMENTAL

Materials

The starting material in the preparation of HZSM-5 was NaZSM-5 (Si/Al = 13.8). It was transformed first to the ammonium form by the wet ion-exchange method. A fourfold exchange was performed in 1 mol/dm^3 aqueous NH_4NO_3 solution. The duration of one exchange was 12 h and it was carried out at ambient temperature. The degree of ion exchange after the fourth repetition was nearly 100%. Then, the resulting NH_4ZSM-5 was deammonized by calcination in vacuum for 6 h at 873 K. It was the starting material for

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wet ion exchange as well as for ion exchange in the solid state. Wet ion exchange was performed by 5 wt% $CuCl_2$ solution in the same way as it was done in the preparation of HZSM-5 from NaZSM-5. At the end of ion exchange the material was washed free of chloride and then dried at 373 K. This material will be called CuZSM-5(l). Solid-state ion exchange was performed as suggested by Karge and Beyer (11). Certain amount (5 mol%) $CuCl_2$ was intimately mixed with well-powdered HZSM-5 in an agate mortar. The mechanical mixture was heat treated at 873 K for 8 h in air. The product was cooled to ambient temperature and washed free of chloride and then dried at 373 K. This material will be called CuZSM-5(s).

Methyloxirane (MOX) and *cis*- and *trans*-2,3-dimethyloxirane (diMOX) were commercial products (Fluka) and were used as received, except for some freeze–evacuation–thaw cycles before reactions.

Characterization

Every catalyst was characterized by X-ray diffractometry and BET measurements and the metal content was determined by X-ray fluorescence spectroscopy.

X-ray diffractograms were registered on well-powdered samples with a DRON 3 diffractometer in order to check crystallinity.

BET measurement was performed in a conventional volumetric adsorption apparatus at the temperature of liquid N_2 (77.4 K). Prior to measurement the samples were pretreated in vacuum at 573 K for 1 h.

The ratio of Brønsted to Lewis acid sites was determined by pyridine adsorption followed by FT-IR spectroscopy. Self-supported wafers were pressed and degassed *in situ* in the optical cell at 573 K for 1 h. Then, they were cooled to 473 K and pyridine was loaded. The wafers were kept in pyridine for 1 h followed by evacuation at the same temperature.

For determining crystallinity from IR measurements the ratio of bands in the range of 440–480 and 550–650 cm^{-1} was used (12). For samples of good crystallinity the value should be around 0.72.

FT-IR measurements were performed with a Matson Genesis spectrometer and 128 scans were collected for one spectrum.

Characteristic data on the catalysts collected by the different methods are displayed in Table 1.

Reactions and Analytical Method

The reactions were run in a static closed recirculation reactor. A mixture of 1.33 kPa of the respective oxiranes and 20 kPa of H_2 (in order to retard the formation of deactivating coke) was prepared and allowed to react on 20 mg of the dehydrated zeolite (1 h evacuation at 573 K). The reaction temperature was 363 K. Samples were withdrawn at 5 and 15 min and the mixture was analyzed by the GC-MS method (Hewlett Packard (HP) 5890 gas chromatograph equipped with a HP 5970 quadrupole mass selective detector; 50-m long HP-1 or carbowax capillary column, 523 and 423 K as the temperature of the injector and the oven, respectively). Since not all the products were available in sufficient amounts for calibration, relative area percentage values were used for characterising the progress of the reactions.

TABLE 1

Characteristic Data on the Catalysts

Characteristics	HZSM-5[a]	CuZSM-5[a]	
		Liquid (l)	Solid (s)
Cu^{2+} content (wt%)	—	2.3	2.7
BET surface area ($m^2\ g^{-1}$)	336	270	318
Crystallinity[b] (%)	89	83/75	83/79
Brønsted/Lewis[c]	0.88	0.36	0.09
Degree of exchange (%)	100	73	46

[a] Si/Al = 13.8.
[b] By XRD/by IR.
[c] By pyridine adsorption.

Single ring-opening, deoxygenation products were identified using clean compounds. The identity of the dimers were determined by the combination of their molecular weight (by MS), fragmentation pattern (applying the NBS/NIH/EPA/MSDC reference library), chemical evidence, and experiences collected previously on dioxolone and dioxane derivatives by other members of our department (13). All the dimers formed in the reactions studied here have already been described in the chemical literature (14, 15).

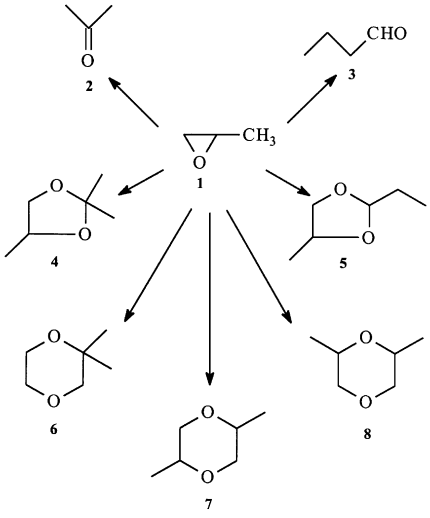
RESULTS

Reactions of Methyloxirane

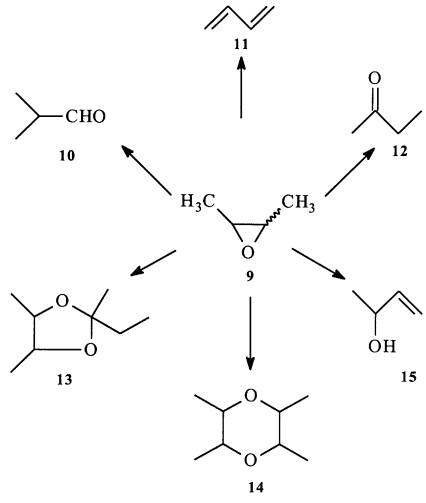
This compound underwent various transformations in the presence of HZSM-5, CuZSM-5(l), and Cu-ZSM-5(s) catalysts (Scheme 1).

Among these reactions there were single ring-opening routes leading to either acetone (**2**) or aldehyde (**3**). Various dimers were also formed. They were either 1,3-dioxolane (**4**, **5**) or 1,4-dioxane (**6**, **7**, **8**) derivatives. Product distribution and selectivity (percentage of MOX molecules taking part in the formation of various products) data are displayed in Tables 2 and 3, respectively.

Data in these tables reveal that the behavior of HZSM-5 and CuZSM-5(1) was similar, while CuZSM-5(s) proved to be significantly more active. A dimerization product, not found on the other two catalysts, also appeared here. It was generally true that dimerization pathways were more important than those of single ring opening. Other general features are the lack of deoxygenation and ether formation



SCHEME 1. Transformation pathways of methyloxirane on HZSM-5 and CuZSM-5 zeolites.



SCHEME 2. Transformation pathways of 2,3-dimethyloxiranes on HZSM-5 and CuZSM-5 zeolites.

(i.e., the C–C bond in the ring is not cleaved). Demethylation was not observed either. It is also to be noted that during dimerization the two ring types were formed with about the same selectivities. However, there were characteristic differences in the distribution of specific dioxane derivatives between the catalysts prepared by wet ion exchange (HZSM-5 and CuZSM-5(l)) and that made by ion exchange in the solid sate, especially at the initial stages of the reactions (at the first sampling). Acetone also appeared on each catalyst; nevertheless, the predominant single ring opening route was the scission of the sterically more hindered C–O bond, in accordance with expectations. The carbocationic intermediate is more stable in this case than that would form after the rupture of the 1,3 C–O bond. The accurate stereochemistry of compounds **5**, **7**, and **8** could not be determined due to separation problems. A comparison of the diameter of the channel openings and the diameter of the stereoisomeric compounds may indicate stereochemical preferences. This problem will be treated under Discussion.

Reactions of cis- and trans-2,3-Dimethyloxiranes

The stereoisomeric 2,3-dimethyloxiranes behaved differently from methyloxirane and also from each other (Scheme 2).

Product distribution and selectivity (percentage of diMOX molecules taking part in the formation of various products) data are displayed in Tables 4 and 5, respectively.

Data in the tables reveal two major features. First, there was no *cis* ⇄ *trans* isomerization. Second, the most important dividing line here is not between the catalysts but the isomers, quite possibly because of stereochemical reasons. Therefore, first, the general features are detailed along with those differences which are rooted in stereochemistry. Then

TABLE 2

Product Distribution in the Zeolite-Catalyzed Reactions of Methyloxirane (MOX) under Reductive Atmosphere (20 mg Catalyst, 1.33 kPa MOX, 20 kPa H_2, 363 K)

	Composition (relative area %)						
		5 min			15 min		
	0 min	HZSM-5	CuZSM-5(l)	CuZSM-5(s)	HZSM-5	CuZSM-5(l)	CuZSM-5(s)
1	100	70.5	83.5	23.6	63.6	80.9	5.6
2	0	1.3	0.7	4.1	2.8	1.5	5.7
3	0	6.7	3.6	12.3	9.6	5.2	17.3
4	0	0	0	1.8	0	0	2.3
5	0	10.4	5.6	24.7	11.3	6.1	30.0
6	0	8.0	4.3	14.5	8.5	4.6	16.9
7	0	0.7	0.5	8.1	0.9	0.4	9.7
8	0	2.4	1.8	10.9	3.3	1.3	12.5

TABLE 3

Percentage of Methyloxirane (MOX) Molecules Taking Part in Product Formation Channels (20 mg Catalyst, 1.33 kPa MOX, 20 kPa H_2, 363 K)

	Selectivity (%)					
	5 min			15 min		
	HZSM-5	CuZSM-5(l)	CuZSM-5(s)	HZSM-5	CuZSM-5(l)	CuZSM-5(s)
2	2.5	2.5	3.0	4.6	4.8	3.4
3	13.1	12.5	9.0	15.9	16.5	10.4
4	0	0	2.6	0	0	2.8
5	40.8	39.0	36.2	37.4	38.7	36.2
6	31.4	30.0	21.3	28.2	29.2	20.4
7	2.7	3.5	11.9	3.0	2.5	11.7
8	9.5	12.5	16.0	10.9	8.3	15.1

variations, which are possibly due the nature of the catalysts (counterion and/or differences in the method of preparation), are described.

In contrast to methyloxirane, deoxygenation reaction could be detected. It was the major single-product transformation pathway for the *trans* compound in all but one case (CuZSM-5(s), 15 min sampling), and it was significant for the *cis* molecule as well. It is to be noted that this latter compound was less reactive toward this reaction route on every catalyst than the other stereoisomer.

Molecules from single ring opening were also found on each catalyst. The straightforward product was 2-butanone. Isobutyraldehyde was detected too. It must have been formed by ring opening and simultaneous rearrangement. Selectivity toward this product was higher for the *trans* than for the *cis* compound (Table 3). The allyl alcohol analog 3-butene-2-ol was formed exclusively from the *trans* isomer. Interestingly, however, only the *cis* isomer was active in dimerization. Once again, the accurate stereochemistry of certain dimers could not be determined. However, stereochemical preferences may be revealed, taking into account the thermodynamic stabilities and the molecular dimensions of the stereoisomeric compounds as well as steric effects.

Although the catalysts in this case did not differ so much as when methyloxirane was the reactant, here too, as far as their behavior in these reactions are concerned, HZSM-5 and CuZSM-5(l) resembled to each other more than any of them to CuZSM-5(s). The most important difference is, perhaps, that among the dimers, the formation of 1,3-dioxolane derivative was significantly more important than that of the 1,4-dioxane on CuZSM-5(s) than on the other two.

DISCUSSION

Although the acid-catalyzed ring-opening reaction under homogeneous conditions (conducted in solution) is very well known and even taught in fundamental organic chemistry courses (16), interestingly, heterogeneous acidic catalysts were only sporadically used to promote this reaction. When they were, oxides (Al_2O_3, Al_2O_3–SiO_2, ZnO, WO_3, ZrO_2, CaO, BeO, Nb_2O_5, etc. (17, 18)) or Nafion-H (19)

TABLE 4

Product Distribution in the HZSM-5- or CuZSM-5-Catalyzed Reactions of *cis*- and *trans*-2,3-Dimethyloxirane (diMOX) under Reductive Atmosphere (20 mg Catalyst, 1.33 kPa diMOX, 20 kPa H_2, 363 K)

	Composition (relative area %)													
			5 min						15 min					
	0 min		HZSM-5		CuZSM-5(l)		CuZSM-5(s)		HZSM-5		CuZSM-5(l)		CuZSM-5(s)	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
9	100	100	96.2	76.4	79.9	73.6	60.5	86.9	89.4	64.7	59.3	54.4	13.7	68.1
10	0	0	0.2	3.0	1.4	4.0	1.7	2.3	0.5	4.4	3.2	7.8	4.7	5.9
11	0	0	1.1	11.0	2.0	12.5	1.6	4.5	3.4	16.3	5.0	20.1	4.2	9.5
12	0	0	1.1	4.6	7.8	6.0	18.6	4.1	3.4	7.3	19.2	10.1	42.8	10.9
13	0	—	0.9	—	3.1	—	16.5	—	2.4	—	5.4	—	32.2	—
14	0	—	0.5	—	5.8	—	1.1	—	0.9	—	7.9	—	2.4	—
15	—	0	—	5.0	—	3.9	—	2.2	—	7.3	—	7.6	—	5.6

TABLE 5

Percentage of *cis*- or *trans*-2,3-Dimethyloxirane (diMOX) Molecules Taking Part in Product Formation Channels (20 mg Catalyst, 1.33 kPa diMOX, 20 kPa H_2, 363 K)

	Selectivity (%)											
	5 min						15 min					
	HZSM-5		CuZSM-5(l)		CuZSM-5(s)		HZSM-5		CuZSM-5(l)		CuZSM-5(s)	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
10	3.8	12.7	4.8	15.2	3.0	17.6	3.6	12.5	5.9	17.1	3.9	18.5
11	21.2	46.6	6.9	47.3	2.8	34.4	24.5	46.1	9.3	44.1	3.5	29.8
12	21.2	19.5	26.9	22.7	32.6	31.3	24.5	20.7	35.5	22.1	35.4	34.2
13	34.6	—	21.4	—	57.7	—	34.5	—	20.0	—	53.2	—
14	19.2	—	40.0	—	3.9	—	12.9	—	29.3	—	4.0	—
15	—	21.2	—	14.8	—	16.7	—	20.7	—	16.7	—	17.5

were mainly applied (for a recent review, see (20)). Very few publications could be located where zeolites were chosen to catalyze the ring opening reaction (21–27) and none where the zeolite was CuZSM-5. In most cases the reaction was used for synthetic purpose (23–27). Mechanistic type of investigations are only described in the earlier works (20, 21). HZSM-5 was occasionally the zeolite of choice and this material helped in achieving excellent stereoselectivities in ring opening (25-27). Rearrangement was also observed (27), but dimerization reactions have not been reported yet.

In our hands methyloxirane and *cis*-2,3-dimethyloxirane (stereoisomeric simple oxiranes, to the best of our knowledge, have never been used as probe molecules in zeolite catalysis) gave appreciable amounts of dimerized products. It is to be noted that dimerization did not occur with the *trans* isomer. This lack of dimerization helps in narrowing the many possible stereoisomers of 2,3,5,6-tetramethyl 1,4-dioxanes and 2-ethyl-2,4,5-trimethyl 1,3-dioxolanes down to two for both products. First, let us point out that dimerization occurs inside the zeolite and not on the external surface. If it were taking place on the outer surface, the *trans* isomer should also dimerize, while in a constrained environment (inside the channels) there is not enough room for two bulky molecules to interact with the acid sites (whether they are Brønsted or Lewis centers) and each other. Second, due to the limited space in the channels *cis–trans* isomerization cannot take place either. Third, the existence of different transformation pathways for the stereoisomers indicates that the mode of adsorption is also different. The *cis* isomer adsorbs parallel to the surface (flat adsorption), while the *trans* does so in an edgewise manner.

From these considerations it follows that those dimers are only probable in which the original *cis* position of the methyl groups is retained. Therefore, two dioxane derivatives remain, which contain the four methyl groups in equatorial–axial–equatorial–axial (**14a**) or equatorial–axial–axial–equatorial (**14b**) positions. They are diastereomers. Because of steric reason the formation of the latter is more probable; however, the first cannot be ruled out (Fig. 1, compounds **14a** and **14b**).

On similar grounds the 4,5-methyl groups of dioxolane should be *cis*, but these methyl groups can be on either the ethyl or the methyl side of position 2 of the ring. Choosing between them cannot be done on the basis of molecular dimensions (*cis*-2-ethyl-*trans*-2-methyl-*cis*-4,5-dimethyl-1,3-dioxolane (**13a**): $4.76 \times 4.10 \times 7.01$ Å; *trans*-2-ethyl-*cis*-2,4,5-trimethyl-1,3-dioxolane (**13b**): $4.98 \times 3.84 \times 7.55$ Å, both based the AM1 (28) optimized structures). One needs to take into consideration that on cleaving the C–O bond resulting the ethyl substituent, there is more space for turning above the ring (the bottom is occupied by active site, which is part of channel wall of the zeolite); thus, there is more chance for the formation of *cis*-2-ethyl-*trans*-2-methyl-*cis*-4,5-dimethyl-1,3-dioxolane (Fig. 1).

For the dimerization of methyloxirane choosing between the possible stereoisomer dimers is more ambiguous. The variety is smaller; however, certain isomers cannot be ruled out in the way it could be done in the case of 2,3-dimethyloxirane stereoisomers. Energetic and molecular size considerations may be used for indicating the more plausible products. The *trans* isomers of the 1,4-dioxane derivatives proved to be thermodynamically more stable than the *cis* isomers by AM1 semiempirical quantum chemical calculations. Moreover, the molecular dimensions of these isomers make them easier to form and diffuse through the channels of the zeolite than the others (*trans*- and *cis*-2,6-dimethyl-1,4-dioxane [**8a** and **8b**], respectively): $3.97 \times 2.83 \times 6.62$ Å and $4.18 \times 3.31 \times 6.03$ Å, respectively; *trans*-and *cis*-2,5-dimethyl-1,4-dioxane [**7a** and **7b**, respectively]: $4.37 \times 2.99 \times 6.66$ Å and $4.38 \times 3.54 \times 6.01$ Å, respectively). The opposite stability order was calculated for the 1,3-dioxolane derivatives; however, the molecular dimension still may favor the diffusion of the *trans* isomer

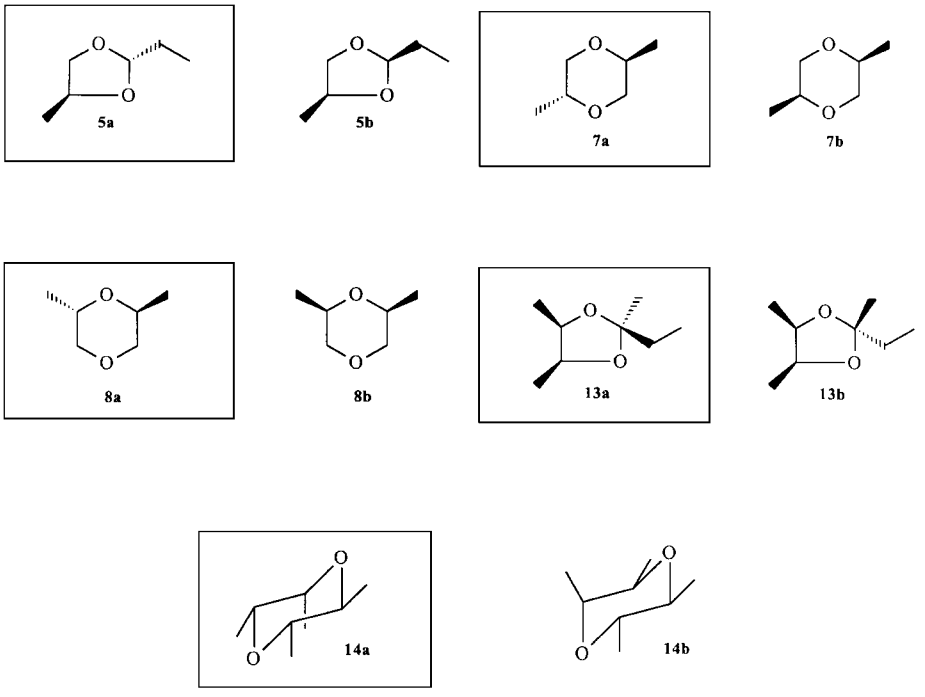
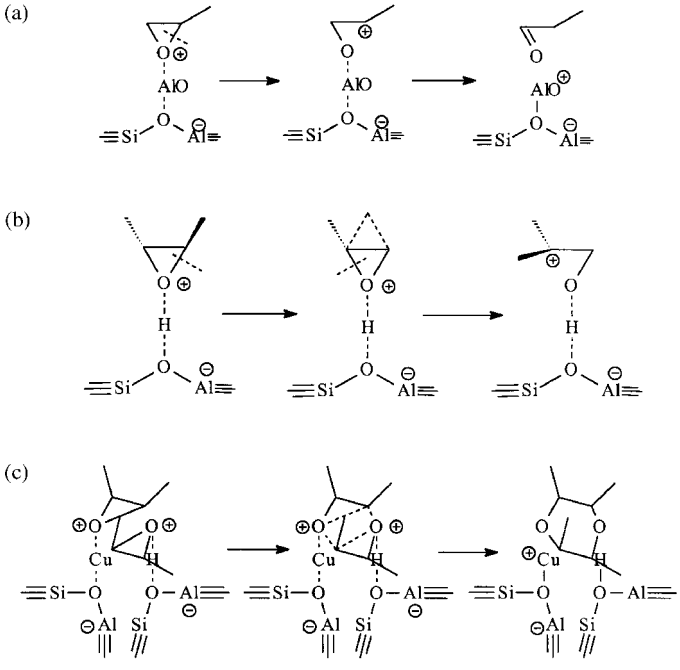


FIG. 1. Dimers forming from methyloxirane or *cis*-2,3-dimethyloxirane (the more probable diastereomers are framed).

(*trans*- and *cis*-2-ethyl-4-methyl-1,3-dioxolane [**5a** and **5b**, respectively]: 3.60 × 3.08 × 7.63 Å and 4.18 × 3.18 × 6.53 Å, respectively). To conclude, the formation of the *trans* dimers is more probable; however, almost certainly the *cis* isomers form too (Fig. 1).

It is obvious that dimerization involves ring opening; thus, ring opening may be considered the most important transformation pathway for these oxiranes. For methyloxirane two and for 2,3-dimethyloxiranes three types of ring opening may be distinguished. Dimerization involves simultaneous bond making and breaking. Olefin formation (exclusive for 2,3-dimethyloxiranes) means double C–O bond scission. Single C–O bond cleavage leads to aldehydes and ketones and unsaturated alcohol (*trans*-2,3-dimethyloxirane). The stereoselectivity can be studied only for methyloxirane. There is no surprise; the sterically more hindered C–O bond cleaves preferentially, in accordance with the assumed cationic ring-opening mechanism. Unexpected products from single C–O bond scission emerge for 2,3-dimethyloxiranes. Both stereoisomers yield isobutyraldehyde, which may be explained by simultaneous 1,2 methyl shift and ring opening. Methyl shift is easier for the *trans* compound. Formation of the unsaturated alcohol is exclusive for the ring opening of the *trans* compound for no obvious reason.

As far as the active sites are concerned, we think that both Brønsted and Lewis centers are involved. For reasons discussed above, the reactions are thought to occur in the channels of the zeolite. This seems certain for dimerization. Single or double C–O scission possibly proceeds on the exterior as well, but this should not be the major stage of these reactions either. As was pointed out under Results, in the case of methyloxirane transformations, the behavior of HZSM-5 and CuZSM-5(l) was close to each other. Although the ratio of Brønsted to Lewis acid centers decreased upon ion exchange, Brønsted acidity still remained appreciable. The ratio is certainly higher than it should be if the degree of ion exchange is only considered. It is very probable that extra Brønsted sites are created during wet ion exchange, which should be associated to the copper ions. It is also known that even though Cu^{2+} ions are exchanged, some of them fast become Cu^{+} ions due to autoreduction. During reduction Cu–O bonds are broken and for charge compensation protons are formed (these protons are possibly originated from water, the solvent) (29). Further reduction may take place under hydrogen atmosphere producing copper metal clusters and even more protons (30). Some of these copper sites (either the one plus ions and/or the metal clusters) may be reoxidized by the adsorption of the oxygen of the oxirane ring. Therefore, the working catalyst probably contains Cu^{2+}, Cu^{+} as well as metallic Cu, and protonic sites, which are due to this redox chemistry. When the catalyst was prepared by ion exchange in the solid state, the ratio of Brønsted to Lewis sites decreased considerably. Here there was no solvent; thus, there was no source for the formation of extra Brønsted acid sites. It is also believed that the most abundant copper species is the two plus ion



SCHEME 3. Mechanistic suggestions for representative transformation routes: (a) single C–O scission on Lewis acid site (originated from extraframework aluminium ion (32)), (b) rearrangement on Brønsted acid site, and (c) dimerization on a combination of copper(I) and Brønsted sites.

(31). It was certainly transformed during the reaction and a steady-state mixture of Cu^{2+} and Cu^{+} ions should have been formed due to the interplay of the reducing effect of hydrogen and the oxygen of the oxirane ring. The behavior of this catalyst differed from that of the other two in the reactions of methyloxirane. It did not only prove to be more active but a new dimer product, not seen on the other two catalysts, appeared, although in small quantity. The differences were not so dramatic, since they almost disappeared when a stronger effect, the stereochemistry of the dimethyloxiranes, took over.

Mechanistic suggestions for representative transformation routes on various types of acid sites are depicted in Scheme 3.

CONCLUSIONS

Studying the ring-opening reactions of these simple epoxides over zeolites for the first time, it was shown that rings open in two and three major ways in the case of methyloxirane and dimethyloxiranes, respectively. Two of the routes are common; i.e., they are ring opening of one C–O bond and dimerization. The third was found for the dimethyloxiranes only, deoxygenation that is.

The HZSM-5 and the CuZSM-5(l) catalysts were similar in behavior when methyloxirane was the reactant, while CuZSM-5(s) was more active and more products were formed.

In the case of the dimethyloxiranes where stereochemical features of the reactants were predominant, all three catalysts acted rather similarly.

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