

TRANSFORMATION PATHWAYS OF 2,2-DIMETHYLOXIRANE ON ALUMINOSILICATES: THE EFFECTS OF CATALYST STRUCTURE AND REACTION CONDITIONS

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ABSTRACT

The ring transformation reactions of 2,2-dimethyloxirane were studied over various aluminosilicates (HZSM-5, CuZSM-5, HY, AIMCM-41 or NaN₃-loaded AIMCM-41) in a pulse reactor at 423 K. The main reactions identified were isomerisation and cyclic dimerisation. The product formation selectivities could be tuned by varying the pore size of the molecular sieves and/or altering the reaction parameters. Large pore size and mild conditions favoured isomerisation, while an optimally constrained environment and overloading the catalyst with the epoxide (increased pulse size) was advantageous for cyclic dimerisation.

Keywords: Ring transformations; Aluminosilicates; 2,2-Dimethyloxirane; Reaction mechanisms.

INTRODUCTION

Epoxides are extremely useful synthons in the synthesis of various complex organic molecules and macromolecules [1,2]. Their versatility lies in the fact that the ring may be opened by acids [3] or bases [4] in catalytic reactions as well as by electrophiles [5] or nucleophiles [6] in stoichiometric reactions. The epoxide ring can be opened on solids and for this purpose various oxides [7], zeolites [8-12] and even supported transition [13] or early transition [14] metals may be used. Over the solid materials ring opening may occur by the scission of either C-O bond. This single ring opening may give open-chain isomers, cyclic dimers saturated alcohols over the transition metals in the presence of hydrogen and in principle, linear oligomers too. Occasionally, double C-O scission, oxygen loss that is, also takes place. The actual product distribution depends very much on the nature of the solid substances and experimental conditions, particularly on the reaction temperature. Generally, higher temperature favours deoxygenation, and the sterically less hindered C-O bond tends to be ruptured on solids of higher acidity. On acidic porous materials dimerisation was found to be the preferred transformation pathway [8-12] for methyloxirane and 2,3-dimethyloxirane. Curiously, this reaction only occurred for the *cis* isomer [8]. This fact points to the significance of steric factors, therefore it may be of interest whether a geminally substituted derivative can undergo such a reaction and whether varying the pore size and acidity of the molecular sieves influences transformation selectivity.

In this contribution the transformations of an epoxide (2,2-dimethyloxirane) over various molecular sieves are described and the effects of the catalyst structure and the reaction variables on the proportion of the reaction pathways are elaborated.

EXPERIMENTAL

Materials

The catalysts applied were HZSM-5 (Si/Al = 13.8), CuZSM-5, HY (Si/Al = 2.31), AIMCM-41 (Si/Al = 40.0) or NaN₃-loaded AIMCM-41 molecular sieves.

The H-zeolites were prepared by wet ion exchange starting from the Na-forms (NaY – Union Carbide, NaZSM-5 – home made following the description in ref. [15]). Fourfold ion exchange was performed in 1 mol/dm³ aqueous NH₄NO₃ 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 ammonium forms were deammonised by calcination in vacuum for 6 h at 873 K.

The MCM-41 derivative was synthesized in our laboratory following recipes published in the literature [16-19]. Sodium silicate and aluminium isopropoxide were the silica and the alumina sources, respectively. Hexadecyltrimethylammonium bromide was used as the surfactant. NaOH and sulfuric acid solutions were applied for adjusting the pH. The resulting gels were crystallised for 6 days under autogenous conditions at 373 K. Then, they were filtered and washed by distilled water, dried at 373 K and, finally, calcined at 773 K for 10 h to burn the template off.

For the preparation of NaN_3 -loaded AlMCM-41 the azide was introduced into MCM-41 (5 w%) in methanolic solution. After drying the sample at 523 K the azide was decomposed by heat treatment (slow heating by 3 degrees/min up to 653 K in nitrogen atmosphere). This procedure facilitates the transformation of maximum amount of NaN_3 into sodium metal clusters making a basic zeolite (basicity was not quantified) and leaves the structure of the host material largely intact [20].

The CuZSM-5 catalyst was prepared by solid-state ion-exchange method as described in the literature [21]. Certain amount (5 w%) 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.

2,2-Dimethyloxirane (**1**, for the structure, see Figure 1) was a commercially (Fluka) available compound and was used as received. Hydrogen (the carrier gas) was produced in a Matheson generator. The high purity nitrogen (for decomposing the azide) contained less than 0.0001% contamination.

Characterisation

The catalysts were characterized by powder X-ray diffractometry, BET surface area measurements, pyridine adsorption followed by FT-IR spectroscopy (Table 1).

Table 1. Characterising data of the molecular sieves.

Mol. sieves	d_{001}^a (nm)	BET surface areas (m^2g^{-1}) ^a	Bronsted/Lewis sites ^b
HZSM-5	-	336	0.88
CuZSM-5	-	318	0.09
HY	-	604	8.67
AlMCM-41	4.059	932	0.62

a - calcined samples (for conditions, see text); b - calculated on the basis of IR spectra of adsorbed pyridine

X-ray diffractograms were registered on well-powdered samples with a DRON 3 diffractometer in order to determine pore diameters. BET measurements were performed in a conventional volumetric adsorption apparatus cooled to the temperature of liquid nitrogen (77.4 K). Prior to measurements the samples were pretreated in vacuum at 573 K for 1 h.

The acid-base properties were studied by pyridine adsorption followed by IR spectroscopy (Mattson Genesis I FT-IR spectrometer, 128 scans for one spectrum, WIN-IR software package). Self-supported wafers (10 mg/cm^2 thickness) were pressed from the aluminosilicate samples. They were pretreated in the optical cell at 573 K for 2 h in vacuum. 1.33 kPa of pyridine was adsorbed on the activated samples at 363 K for 1 h followed by cooling to room temperature under continuous evacuation. Bands at 1540 cm^{-1} and 1450 cm^{-1} were used for calculating Bronsted and Lewis acidities, respectively.

The reaction and the analytical method

The reactions of 2,2-dimethyloxirane were studied in a pulse reactor system applying hydrogen as carrier ($45 \text{ cm}^3/\text{min}$ gas flow). The reaction temperature was set to 423 K after probing the AlMCM-41 catalysts with a pulse sequence in the 363–423 K temperature range. The pulse size was varied between 1–10 μl . In most of the experiments, to overload the catalyst with the epoxide and providing higher surface concentration, thus giving a chance for larger variety of transformations to take place, 10 μl was chosen. Sixty minutes were allowed to pass between the pulses. In all measurements 10 mg of catalyst was used.

Analysis of the product mixture was done by a GC-MS system (Hewlett Packard 5890 gas chromatograph equipped with a HP 5970 quadrupole mass selective detector). Good separation was achieved on a 50-m long CPWAX 52CB coated CHROMPACK WCOT fused silica capillary column by applying a temperature program (303 K for 15 min, 323 K for 20 min and 473 K for 10 min). Product identification was based on the NBS/NIH/EPA/ MSDC database and clean samples.

RESULTS

2,2-Dimethyloxirane **1**) underwent various reactions on the molecular sieves. Single ring opening resulting in an isomerisation product (isopropyl aldehyde, **3**), dimerisation leading to a dioxane derivative (2,2,5,5-tetramethyl-1,4-dioxane, **4**) and double C-O scission facilitating deoxygenation (2-methyl-1-propene, **2**) were the three major transformation pathways observed (Figure 1).

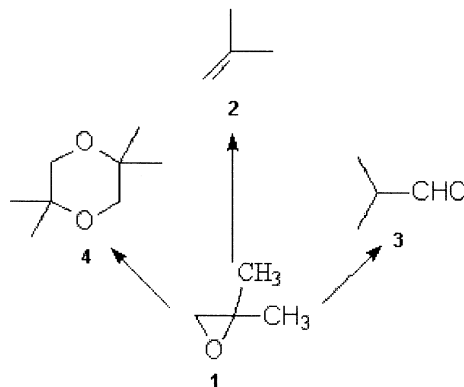


Figure 1. Transformation routes of 2,2-dimethyloxirane.

AIMCM-41 was chosen to screen the effect of changing the reaction parameters and to pick those conditions, which seem to be appropriate to compare the performance of the various molecular sieves. Results are displayed in Table 2.

Table 2. The effects of reaction parameters on the ring-transformation reactions of 2,2-dimethyloxirane over AIMCM-41 (data corresponding to the reactant are in italics).

Temperature/K	Pulse size/ μ l	Composition/mol%			
		<i>1</i> (epoxide)	<i>2</i> (olefin)	<i>3</i> (aldehyde)	<i>4</i> (cyclic dimer)
363	1	<i>100</i>	0	0	0
393	1	<i>100</i>	0	0	0
423	1	<i>0.3</i>	0.4	99.3	0
423	3	<i>8.0</i>	0.5	71.9	19.6
423	5	<i>9.4</i>	0.3	67.0	23.3
423	10	<i>4.0</i>	1.6	89.8	4.6
423	10	<i>4.1</i>	1.4	89.6	4.9
423	10	<i>4.0</i>	1.0	89.1	5.9
423	10	<i>3.8</i>	0.4	87.9	7.9

It is to be seen that 423 K can be a good choice as far as reaction temperature is concerned, since here the catalysts was highly active. Varying the pulse size influenced conversion as well as product distribution. The activity was fairly steady when the size of the pulse was the largest. At each pulse size the main product was isopropyl aldehyde (**3**) and it was almost exclusively formed in the first pulse at 423 K. On increasing the pulse size dimerisation became appreciable still leaving isomerisation the main transformation pathway. There seems to be an optimum pulse size (5 μ l that is) for maximising the quantity of the dioxane derivative. Double C-O scission (deoxygenation that is) was not a significant transformation pathway irrespective to the size of the pulse. It is to be noted that the scission of the sterically less hindered C-O bond did not occur and

dioxolane (five-membered ring with two non-adjacent oxygens in the ring) derivatives, typical for methyloxirane over aluminosilicates [8, 10], were not found either.

For further experiments 423 K was chosen as the reaction temperature and, because of the steady activity for AIMCM-41, 10 μ l as the pulse size. Product distribution over the other aluminosilicates are summarised in Table 3.

Table 3. Composition of the reacting mixture in the ring-transformation reactions of 2,2-dimethyloxirane at 423 K (data corresponding to the reactant are in italics).

Catalysts	Pulse No.	Composition/mol%			
		<i>1 (epoxide)</i>	<i>2 (olefin)</i>	<i>3 (aldehyde)</i>	<i>4 (cyclic dimer)</i>
HY	1	<i>6.1</i>	1.5	58.7	33.7
	2	<i>9.0</i>	0.9	60.1	30.0
	3	<i>11.6</i>	0.6	60.2	27.6
	4	<i>13.5</i>	0.7	60.7	25.1
HZSM-5	1	<i>3.6</i>	0.1	87.3	9.0
	2	<i>28.2</i>	0.1	61.3	10.4
	3	<i>33.4</i>	0.1	55.4	11.2
	4	<i>40.4</i>	0	47.5	12.1
CuZSM-5	1	<i>41.9</i>	0.1	54.6	3.4
	2	<i>44.4</i>	0.4	51.7	3.5
	3	<i>47.1</i>	0.3	49.0	3.6
	4	<i>49.8</i>	0.1	46.4	3.7

There was no new reaction on these catalysts not seen on AIMCM-41. Single and double C-O scissions leading to isomerisation and deoxygenation, respectively, as well as dimerisation were the prevailing transformation pathways. Single C-O scission producing isopropyl aldehyde (**3**) remained the main reaction on the zeolites of various pore sizes and differing acidities as well, however, the catalysts were less active (especially on subsequent pulses) than AIMCM-41 was. Upon subsequent pulses the activity decreased over the H-form zeolites appreciably, but it just slightly changed over CuZSM-5. While double C-O scission (deoxygenation) activity was low throughout the experiments, the dimerisation reaction pathway was significant and varied considerably from catalyst to catalyst. Its proportion was the highest over HY, a zeolite with pore size between that of AIMCM-41 and ZSM-5. Reactions missing on AIMCM-41, ring opening *via* the rupture of the sterically less hindered C-O bond and dimerisation giving dioxolane derivative(s) they are, did not take place on the other molecular sieves of this study either.

All the above aluminosilicates were acidic and they transformed 2,2-dimethyloxirane in various ways. One of the molecular sieves were made basic by loading and decomposing NaN_3 in it under controlled conditions making sure that the original structure remained largely intact. The NaN_3 -loaded AIMCM-41 was not active in the ring transformation reactions of 2,2-dimethyloxirane under conditions when the acidic molecular sieves had appreciable reactivities.

DISCUSSION

It is known from any fundamental organic chemistry course that a substituted epoxide gives a mixture of products even on simple ring opening (single C-O scission and no further reaction of the ring-opened products), when the reaction is started with the attack of an acid but a single product when the attacking agent is a base [22]. The former is a mixture of $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions, while the latter is a typical $\text{S}_{\text{N}}2$ transformation. The $\text{S}_{\text{N}}1$ reaction proceeds *via* a "free" carbenium ion, while the $\text{S}_{\text{N}}2$ does not have "free" carbenium ion intermediate but a pentacovalent transition state although being ionic in character. On solid acid or base catalysed transformation the ring opening analogous to the $\text{S}_{\text{N}}1$ reaction gives an aldehyde and that analogous to $\text{S}_{\text{N}}2$ results in a ketone. It is also well known that epoxide easily undergoes polymerisation providing polyethers of various lengths. It is a recent discovery that when propylene oxide is the reactant dimerisation occurs on acidic zeolites and zeotypes producing dioxane and dioxolane derivatives [8,10,12]. It has been established, that for this reaction to occur constrained environment is advantageous.

In principle, the ring transformation reactions of the epoxide of this study could have been catalysed by both acid and basic sites. However, in our case the reactions were catalysed only by the acid sites, since there was no activity on NaN₃-loaded AlMCM-41. The acid sites could be either Brønsted or Lewis sites, since their varying ratio did not open or close reaction pathways. Ring opening *via* the single C-O cleavage route proceeded through an S_N1-like mechanism. A carbenium ion type intermediate, a very stable tertiary carbenium ion, should have formed (Figure 2). The sterically less hindered C-O bond was not cleaved, since a primary carbenium ion like species should have formed at least initially, which would be energetically highly unfavourable.

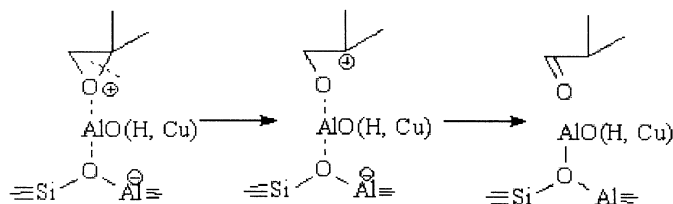


Figure 2. Single C-O scission Lewis or Brønsted acid site (S_N1-type transformation mechanism).

The second most important transformation route is dimerisation producing a six-membered ring compound, a dioxane derivative. Clearly, a confined environment is advantageous for this reaction and among the molecular sieves the pore size of the Y zeolite seems to be the most appropriate. When the transformations of methyloxirane were probed [8,10] the pore size of ZSM-5 was the best, truly, dimerisation leading to five-membered ring (dioxolane derivatives) was the major reaction pathway (even in the absolute sense). No wonder smaller pore size was optimal. Beside the confined environment, increased pulse size (overloading the catalyst with the epoxide) is also advantageous for dimerisation to occur, since the higher surface concentration facilitates the build-up of the relatively complex and organised arrangement of the dimerised product. The predominance of Brønsted acid sites may also help to increase the proportion of the dimerised product. It is thought that this reaction mainly proceeds over Brønsted-Brønsted acid site pairs over HY and the combination of Brønsted-Lewis acid site pairs over HZSM-5 and AlMCM-41 high-silica aluminosilicates but it is slow or does not even occur over a catalyst containing exclusively Lewis acid sites (see, the product distribution over CuZSM-5 in Table 3). One may argue for an Eley-Rideal-like mechanism when the second epoxide reacts upon the arrival from the gas phase with the already adsorbed and somewhat transformed epoxide molecule. In our view this mechanism should not be predominant since (i) the catalysts were overloaded with the reactant increasing the possibility of adsorption, (ii) we see no driving force for the ring distortion of the incoming second molecule necessary for the reaction to occur and (iii) in the dimerisation of methyloxirane (a directly related molecule) *d*₂-dimerised products were found to be abundant over DY [11]. On the basis of the above points dimerisation is thought to take place *via* a Langmuir-Hinshelwood-like mechanism mainly over Brønsted-Brønsted and Brønsted-Lewis acid site pairs over the HY and the other aluminosilicates, respectively. A viable mechanism is offered in the following scheme (Figure 3).

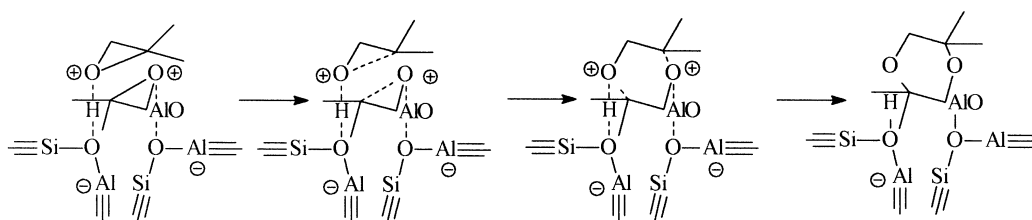


Figure 3. The suggested mechanism of dimerisation proceeding on a Brønsted-Lewis acid site pair.

CONCLUSIONS

The selectivity of the possible transformations of 2,2-dimethyloxirane could be tuned by altering the structural features of the molecular sieves as well as by altering the reaction parameters. Nearly completely selective aldehyde formation could be achieved on AIMCM-41 at small pulse size. To achieve higher dimerisation selectivity it was required to increase residence time and facilitate optimally constrained environment. The reactions were acid-catalysed and could proceed on both Brønsted and Lewis sites, however, for dimerisation the presence of Brønsted sites was helpful.

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