

Ring opening, dimerisation and oligomerisation reactions of methyloxirane on solid acid and base catalysts

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Abstract

The reactions of methyloxirane were studied in a pulse microreactor over Nafion-H, K10 montmorillonite, Mg–Al L(ayered) D(ouble) H(ydroxide) and NaN₃-loaded SiMCM-41, to cover a wide acid–base range. The first two solid substances that are acidic, produced appreciable conversion at 363 K, while the latter two that are basic, were hardly active at this temperature. At higher temperature (393 K), however, they displayed fair activity. The nearly superacidic Nafion-H was the most active and transformed the reactant in various ways: single ring opening producing exclusively propionaldehyde, cyclic dimerisation giving five- and six-membered ring compounds, di- and trimerisation producing linear oligomers all occurred. Over the less acidic K10 montmorillonite neither cyclic nor linear oligomer was observed. The NaN₃-loaded SiMCM-41 preferred cyclic dimerisation to single ring opening, while the behaviour of the Mg–Al LDH was the opposite. © 2003 Elsevier B.V. All rights reserved.

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1. 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 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 favors deoxygenation, and the sterically less hindered C–O

bond tends to be ruptured on solids of higher acidity. On porous materials dimerisation is the preferred transformation pathway [8–12] and for this reaction there exists an optimal pore size. In this contribution experimental findings concerning the transformations of methyloxirane over a series of solid substances with wide-ranging acid–base character are communicated.

2. Experimental

2.1. Materials

The reactions of methyloxirane were studied in a pulse reactor over Nafion-H, K10 montmorillonite, Mg–Al L(ayered) D(ouble) H(ydroxide) or NaN₃-loaded SiMCM-41. The first two substances are acidic, while the last two materials are of basic character.

Nafion is the registered trademark of the DuPont company and commercially available. The active H-form was generated from the potassium salt (Nafion 501) by treatment with 25% nitric acid then washing it with water and drying at 378 K for 24 h. Characteristic data are in Table 1, entry

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Table 1
Characteristic data on the catalysts

Catalysts	BET surface area (m ² /g)	Pore diameter (nm)	B/L ^a	Other acid–base characteristics
Nafion-H	~0.2	~0.3–0.5 ^b	–	$H_0 = -12^d$
K10 montmorillonite	229	5.6 ^c	0.88	$H_0 = -8^d$
Mg–Al LDH	360	0.76	–	2.8 ^e
SiMCM-41	1169	4.0	0.03	–

^a Brønsted to Lewis acid sites determined by pyridine adsorption followed by IR spectroscopy.

^b In swollen state, otherwise the acid sites are hardly accessible.

^c Acid treatment largely destroyed the pore structure.

^d Hammett acidity.

^e *cis*-2-Butene/*trans*-2-butene in 1-butene isomerisation.

1. BET surface area is after heat treatment at 573 K for 1 h; pore diameter is of the swollen material.

K10 montmorillonite is an acid-treated clay (Süd Chemie) with large specific surface area. Acid treatment largely destroys its pore structure, but enhances its acidity (for characterisation data [15], please see Table 1, entry 2). BET surface area is after heat treatment at 573 K for 1 h; pore diameter is of the air-dried material.

The preparation of Mg–Al LDH (Mg:Al = 3:1) was based on the recipe of Corma et al. [16]. A solution containing 0.02 mol of Al(NO₃)₂·9H₂O and 0.06 mol of Mg(NO₃)₂·6H₂O in 100 cm³ water was prepared (solution A). Solution B contained 0.8 mol Na₂CO₃ and 1.6 mol NaOH in 1 dm³ water. Solutions A and B were added simultaneously to 200 cm³ water dropwise under vigorous stirring at room temperature. The addition of solution B was to keep the pH between 8.0 and 9.0. The gel formed was autoclaved at 458 K for 18 h in a Teflon-coated container. Characteristic data are to be seen in Table 1, entry 3. BET surface area is after heat treatment at 723 K for 3 h; pore diameter is of the air-dried material.

The SiMCM-41 molecular sieve was synthesized in our laboratory following recipes published in the literature [17–20]. Sodium silicate was the silica source and hexadecyltrimethylammonium bromide was the surfactant. NaOH and sulfuric acid solutions were used for adjusting the pH. The resulting gel was crystallized for 6 days under autogenous conditions at 373 K. Then, it was 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 characteristic data, please see Table 1, entry 4. NaN₃ was loaded into SiMCM-41 (5 wt.%) in methanolic solution. After drying the azide at 523 K it was decomposed by heat treatment (slow heating by 3 °C/min up to 653 K [21] under nitrogen atmosphere). This cautious heating procedure facilitates the transformation of maximum amount of NaN₃ into sodium metal clusters [21] and keeping the integrity of the host material. The obtained material was basic giving *cis*-2-butene to *trans*-2-butene ratio of 3.8 in the double-bond isomerisation of 1-butene. It was stored in a vacuum desiccator before use.

Methyloxirane (**1**, for the structure, please see Scheme 1) was a commercially (Fluka) available compound (racemic

mixture was purchased) and was used as received. Hydrogen was produced in a Matheson generator. The high purity nitrogen contained less than 0.0001% contamination.

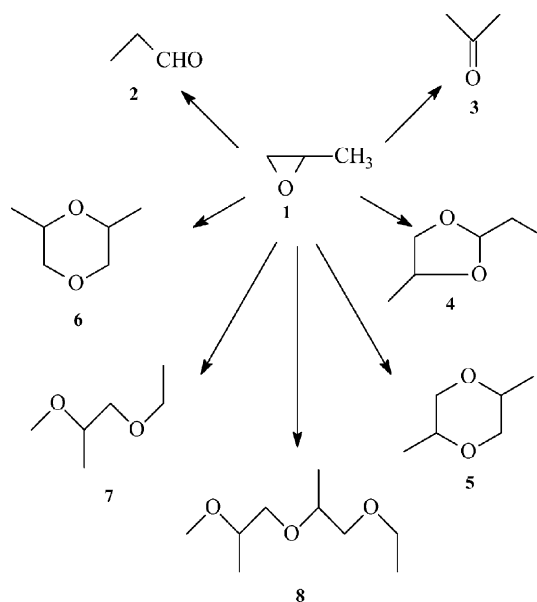
2.2. Characterisation

The samples were characterized by powder X-ray diffraction, BET surface area measurements, pyridine adsorption followed by FT-IR spectroscopy and the double-bond isomerisation reaction of 1-butene.

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 in various ways: 723 K for 3 h for Mg–Al LDH, 573 K for 1 h for Nafion-H, K10 montmorillonite and SiMCM-41.

The acid–base properties were studied by pyridine adsorption followed by IR spectroscopy (Mattson Genesis I



Scheme 1. Viable transformation pathways of methyloxirane over acid–base catalysts

FT-IR spectrometer, 128 scans for one spectrum, WIN-IR software package). Self-supported wafers (10 mg/cm² thickness) were pressed from the montmorillonite and the zeotype 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 and 1450 cm⁻¹ were used for calculating Brønsted and Lewis acidities, respectively.

For testing the base character of the calcined Mg–Al LDH the double-bond isomerisation reaction of 1-butene was used. For the run, a tank reactor with constant material content was used. Hundred milligrams of catalysts was placed into the reactor and activated at 723 K for 3 h. After cooling to the reaction temperature (373 K), 26.7 kPa of 1-butene was introduced into the system ($V = 76.6 \text{ cm}^3$). Samples withdrawn were analysed with a Hewlett-Packard 5710 A gas chromatograph, using a 4.5 m long column packed with 30% DMS on acid washed Chromosorb W at 293 K. The initial *cis/trans* ratio was calculated.

2.3. The reaction and the analytical method

The reactions of methyloxirane were studied in a pulse reactor system applying hydrogen as carrier (45 cm³/min gas flow). The reaction temperature was 363 K for the acidic materials throughout the four-pulse sequence, while for the basic substances the first pulse was injected at 363 K and the temperature of the subsequent pulses was 393 K. The size of the pulse was 1 μl and 20 mg of catalyst was used. Sixty minutes were allowed to pass between the pulses.

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.

3. Results

The activities of transforming methyloxirane varied from catalyst to catalyst. Generally, the acidic materials were more active than the basic substances and in particular the nearly superacidic Nafion-H was more active than K10 montmorillonite. Reaction pathways as well as their proportion were also different (for a general picture of the identified products, please see Scheme 1).

In spite of its low surface area, Nafion-H proved to be the most active catalyst. It did produce almost all the products in Scheme 1, except acetone (**3**) (Table 2).

Table 2
Product distribution in the transformations of methyloxirane on Nafion-H

Number of pulses	Compounds (mol%)						
	1 ^a	2	4	5	6	7	8
1	74.8 ^a	5.9	4.7	7.5	4.5	1.4	1.2
2	70.8 ^a	6.6	6.1	7.4	4.3	1.5	3.3
3	70.3 ^a	7.5	6.0	7.2	4.3	1.5	3.2
4	70.3 ^a	7.5	6.0	7.2	4.3	1.5	3.2

Reaction conditions: 363 K, 1 μl pulse size, H₂ as carrier.

^a Reactant.

Single C–O ring opening gave propionaldehyde (**2**) in significant amounts, however, the sum of products from cyclic dimerisation revealed that this latter was the main transformation route. Among the cyclic dimers 1,4-dioxanes are more important than 1,3-dioxolanes. Beside cyclic dimerisation linear oligomerisation (dimerisation and trimerisation) also took place, the linear trimer being the more significant product. After the first pulse a stabilised catalyst was formed: product distribution hardly changed on subsequent pulses.

Over the freshly activated K10 montmorillonite, whose layered structure is largely destroyed by acid treatment, only single ring-opening products were produced (Table 3).

The major product was propionaldehyde (**2**) from the rupture of the sterically more hindered C–O bond, however, acetone was formed as well, though in much smaller amounts. Interesting is the complete lack of desorbed cyclic dimers and linear oligomers. This catalyst displayed smaller activity than Nafion-H, nevertheless, similarly to Nafion-H, product distribution hardly changed after the first pulse.

The first pulse at 363 K produced only isomerisation products over the calcined Mg–Al LDH with propionaldehyde in excess (Table 4).

Since the reactivity was very low, the reaction temperature was raised to 393 K. At this temperature appreciable conversion could be achieved. The second pulse at this temperature produced some linear trimer. Its quantity increased on the subsequent pulse. Cyclic dimers were not identified among the products. The activity of the catalyst slowly increased on subsequent pulses.

The NaN₃-loaded SiMCM-41 also displayed small activity at 363 K, thus, the subsequent pulses were injected at higher temperature, that is at 393 K (Table 5).

Table 3
Product distribution in the transformations of methyloxirane on K10 montmorillonite

Number of pulses	Compounds (mol%)		
	1 ^a	2	3
1	97.2 ^a	2.6	0.2
2	96.1 ^a	3.4	0.5
3	96.0 ^a	3.3	0.7
4	96.0 ^a	3.5	0.5

Reaction conditions: 363 K, 1 μl pulse size, H₂ as carrier.

^a Reactant.

Table 4

Product distribution in the transformations of methyloxirane on calcined Mg–Al LDH

Number of pulses	Compounds (mol%)			
	1 ^a	2	3	8
1	99.6 ^a	0.3	0.1	0
2	97.2 ^a	2.6	0.2	0
3	96.8 ^a	2.7	0.4	0.1
4	94.7 ^a	3.5	1.5	0.3

Reaction conditions: first pulse: 363 K, second to fourth pulses: 393 K, 1 μ l pulse size, H₂ as carrier.

^a Reactant.

Table 5

Product distribution in the transformations of methyloxirane on 5% NaN₃-loaded SiMCM-41

Number of pulses	Compounds (mol%)					
	1 ^a	2	3	4	5	6
1	99.2 ^a	0	0	0.3	0.2	0.3
2	98.9 ^a	0	0	0.4	0.2	0.5
3	96.4 ^a	0.1	0	0.9	1.1	1.5
4	95.0 ^a	0.2	0.1	1.3	1.4	1.7

Reaction conditions: first pulse: 363 K, second to fourth pulses: 393 K, 1 μ l pulse size, H₂ as carrier.

^a Reactant.

Irrespective to the temperature cyclic dimerisation was the main reaction channel. The formation of isomerised product(s) was insignificant if it (they) formed at all. The three cyclic dimers were roughly evenly distributed, which means that the 1,4-dioxanes were more important than 1,3-dioxolane, once again. Linear oligomers could not be identified here. The activity of the catalyst slowly increased on subsequent pulses.

4. Discussion

It is known from any fundamental organic chemistry course that a substituted epoxide, like, e.g. propylene oxide (methyloxirane), 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 S_N1 and S_N2 reactions, while the latter is a typical S_N2 transformation. The S_N1 reaction proceeds via a “free” carbenium ion, while the S_N2 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 S_N1 reaction gives propionaldehyde and that analogous to S_N2 results in acetone. It is also well known that epoxide easily undergoes polymerisation providing polyethers of

various lengths. It is a recent discovery that dimerisation occurs on acidic zeolites and zeotypes producing dioxane and dioxolane derivatives [8,10,12]. It has been established, that for this reaction constrained environment is advantageous.

Keeping all these in mind it is clear that we managed to collect catalysts showing different faces of the viable transformations of this reactant. The close to superacidic Nafion-H with overwhelmingly Brønsted acid sites gives the fullest scale of transformations. Linear oligomerisation, not seen before on zeolitic materials [7–12], also appears. As far as isomerisation is concerned exclusively the sterically more hindered C–O bond cleaves pointing at the formation of carbenium ion, an S_N1-like intermediate. Similar observation was made by Olah and co-workers when the ring opening of styrene oxides was studied over Nafion-H in the liquid phase [23]. The porous structure of the resin provides the necessary constrained environment for cyclic dimerisation. This reaction disappears when the porous structure is lost, e.g. when acid treatment destroys the layered structure like in our K10 montmorillonite. Then, only the usual isomerisation pathway of ring opening remains. The mechanism mixed with both propionaldehyde and acetone are formed, the former is overwhelming, however. (It is to be noted that Nafion-H and activated K10 montmorillonite differs from each other in the composition of acid sites too. While the former has predominantly Brønsted acidity, in the latter Lewis acid sites are more abundant than Brønsted acid sites [24].) If there is porous structure like in NaN₃-loaded SiMCM-41, dimerisation is seen once again. Nevertheless, there is no linear oligomerisation on this catalyst and isomerised products are detected only at higher temperature on the used catalyst and in negligible amounts. Since the SiMCM-41 molecular sieve is completely inactive it is believed that adsorbed ionic species provide the acid–base sites for this low level of isomerisation ring opening over the NaN₃-loaded SiMCM-41. Interestingly, the calcined Mg–Al hydrotalcite (which is basic and earlier was shown to be able to isomerise a related compound, the styrene epoxide [25]), as far as selectivities are concerned, behaved like K10 montmorillonite, although it showed comparable activity to that of K10 montmorillonite only at temperature 30 °C higher.

5. Conclusions

Studying the transformations of methyloxirane on structurally diverse catalysts of different acid–base character, it was found that the isomerisation, the dimerisation and the linear oligomerisation pathway of ring opening can occur simultaneously only on porous catalysts with strong acid sites. Having porous system is a necessity for dimerisation to occur, appreciable linear oligomerisation requires strong acid sites, while the isomerisation type of ring opening requires sites of moderate acidity or basicity.

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