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# Epoxide Rearrangements on Mineral and Silica-Alumina Surfaces

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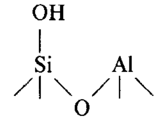
A study has been made of the transformation of epoxystyrene into phenylacetaldehyde catalyzed by a series of natural silicates such as sepiolite and by amorphous silica–alumina. The surface group



acts as an active center and the reaction is almost quantitative even under mild experimental conditions. The number of active centers on sepiolite and on a commercial silica–alumina catalyst has been determined by poisoning with pyridine, thereby enabling the turnover number for the reaction to be obtained. A three-step mechanism for the molecular rearrangement has been proposed. © 1985 Academic Press, Inc.

## INTRODUCTION

Some natural silicates, especially clay minerals, have been used as catalysts for the transformation of organic compounds containing different functional groups. The catalytic conversion of nitriles into amides (*1*), aliphatic amines into hydrocarbons (*2*), and olefins into secondary ethers (*3*) has been reported. The catalytic activity of smectites has been accounted for by their Brønsted and Lewis surface acidity. The Brønsted acidity has been partially attributed to the high degree of dissociation of water molecules in contact with the mineral surfaces (*4*).

In the case of kaolinite, Lewis acidity has been assigned to sites located at the edges of the microcrystals (*5*). Natural microfibrous clay minerals such as palygorskite and sepiolite can also act as catalysts (*5, 6*).

This work aims to study the role of the sepiolite surface in the transformation of 1,2-epoxides into carbonyl compounds, and to compare its activity with those obtained from other natural silicates and synthetic oxides.

## EXPERIMENTAL

*Materials.* Sepiolite, a hydrated magnesium silicate with a microfibrous morphology, has the following ideal half-cell formula: $Si_{12}Mg_8O_{30}(OH)_4\,(H_2O)_4 \cdot 8H_2O$ (*7*). Some of the $Si^{4+}$ in the tetrahedral sheets, or $Mg^{2+}$ in the octahedral sheets can be replaced by other cations ($Al^{3+}$, $Fe^{3+}$, etc.).

The surface is covered with Si–OH groups at the edges of the crystals. These silanol groups are located along the fiber axis, and are the active centers for adsorption and for chemical reactions with organic substances (*8–10*).

The sepiolite mineral used in this work originates from Yunclillos (Toledo, Spain) and contains very little substitution. Its chemical composition is $SiO_2$ 54.29%; $Al_2O_3$ 1.62%; MgO 22.4%; $Fe_2O_3$ 0.47%; CaO 0.40%; $K_2O$ 0.32%; $Na_2O$ 0.21%; $Mn_2O_3$ 0.03%; $H_2O$ (<110°C, zeolitic and physically adsorbed water) 11.9%; $H_2O$

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(>110°C, coordinated water and hydroxyls) 8.3%. The specific surface area is 340 $m^2/g$ (BET, $N_2$, after outgassing overnight at 100°C). The particle size fraction used in this work is smaller than 200 mesh.

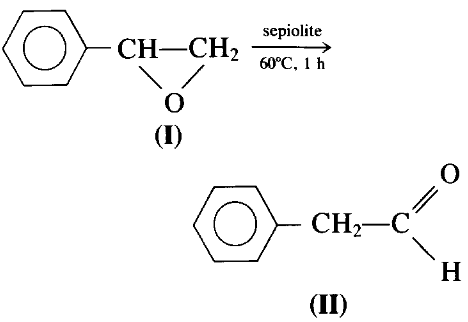
Other natural silicates such as kaolinite (Liria, Valencia, Spain), halloysite (Eureka, Utah), pyrophillite (N.C.), montmorillonite (Upton, Wy.), palygorskite (Serradilla, Caceres, Spain), talc (Puebla de Lillo, León, Spain) have been also studied. They were identified by X-ray diffraction and ir spectroscopy. They exhibit a high degree of purity.

Other inorganic materials such as silica–alumina (Azko Chemie, Ketjen Catalysts, grade LA-3P; $Al_2O_3$ = 13.8%; specific surface area: 410 $m^2/g$), silica (Aerosil 200, from Degussa), $\alpha$-$Al_2O_3$ (Fisher), $\gamma$-$Al_2O_3$ (Akzo Chemie), $\alpha$-$Fe_2O_3$ (Merck, p.a.), have been used for comparison. The organic reagents were epoxystyrene (1,2-epoxyethylbenzene) from Merck (>98%); benzene, $CCl_4$, and other solvents were supplied by Merck (p.a.) and used after drying over a 4-Å molecular sieve.

*Methods.* A solution of epoxystyrene (3.0 ml) in anhydrous $C_6H_6$ or $CCl_4$ (250 ml) was refluxed for 1 h in the presence of 0.5 g of finely divided and previously dried (110°C for 24 h) powder. After reaction the solid was recovered by centrifugation and the supernatant liquid was distilled at reduced pressure until total removal of the solvent. The epoxyde/aldehyde ratio was determined by GC and ir techniques.

## RESULTS AND DISCUSSION

In a previous study (*11, 12*) concerned with the grafting of 1,2-epoxides on Si–OH surface groups of amorphous silica and sepiolite, secondary products containing carbonyl groups were detected. When sepiolite was the starting mineral, the yield of these secondary products was enhanced, especially if a 1,2 epoxide with a phenyl substituent in the $\alpha$-position (i.e., epoxystyrene) was employed. Epoxides with alkyl substituents need more drastic experimental conditions to produce carbonyl compounds. The catalytic conversion of epoxystyrene (**I**) into phenylacetaldehyde (**II**) by sepiolite is almost quantitative, even under mild experimental conditions:

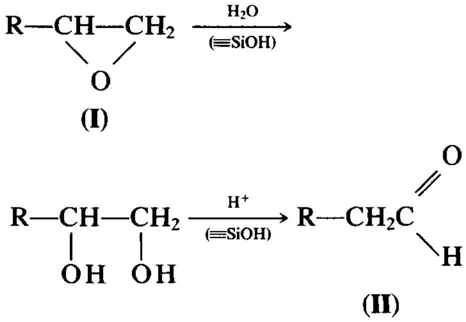


(1)

Phenylacetaldehyde (**II**) was the only product isolated from this reaction; it was identified by ir spectroscopy (characteristic $\nu_{CH}$ bands at 2830 and 2720 $cm^{-1}$ and $\nu_{C=O}$ at 1725 $cm^{-1}$) and by mass spectrometry. In addition, the corresponding hydrazone derivative was obtained after reaction with, 2,4-dinitrophenylhydrazine.

Figure 1 shows the change of the yield as a function of the amount of sepiolite after 1 h reaction. The critical concentration in the solid required to induce the catalytic reaction is about 0.15 g/ml of epoxystyrene. It may be that this value would be different if the yields were determined after longer times of reaction.

A possible mechanism for this reaction is that a pinacol rearrangement is occurring, wherein the Si–OH surface groups and the hydration–dehydration properties of the mineral are involved. In this hypothesis, a two-step mechanism would be required, as represented by Reaction (*2*).



(2)

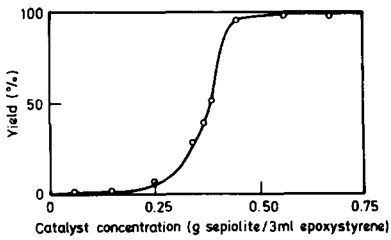
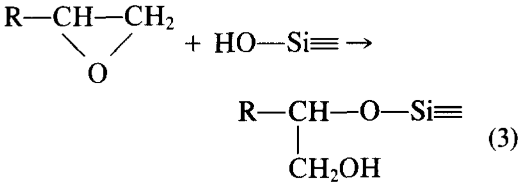


FIG. 1. Dependence of the degree of transformation of epoxystyrene into phenylacetaldehyde on the catalyst concentration. The reaction was carried out by refluxing a benzene solution onto the solid.

However, this mechanism can be rejected because (i) when (**I**) was replaced by the intermediate 1-phenyl-1,2-ethanediol, no carbonyl compound (**II**) was detected, even after more than 72 h, and (ii) replacement of sepiolite by silica (containing also silanol groups) gave very small yields in (**II**). In that case, the resulting product was an organic derivative of the mineral surface which is formed according to Reaction (3).



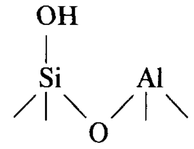
$$\underset{O}{R-CH-CH_2} + HO-Si\equiv \rightarrow \underset{CH_2OH}{R-CH-O-Si\equiv} \qquad (3)$$

For these reasons, a pinacol rearrangement involving only SiOH groups as active centers can be discarded.

Other silicates and oxides were also tested and the results, given in Table 1, show that (i) talc, a very pure magnesium silicate, as well as magnesia and iron oxides produce only small amounts of phenylacetaldehyde, whereas (ii) palygorskite (a natural fibrous silicate similar to sepiolite but richer in Al), kaolinite, halloysite, and pyrophyllite (Al containing silicates) are good catalysts for this reaction.

From the marked enhancement of the catalytic role observed for the minerals containing structural aluminium it may be inferred that Al is involved in the reaction mechanism. However, when the reaction is carried out in the homogeneous phase in the presence of anhydrous $AlCl_3$, the yield is much lower than with aluminosilicates. $\alpha$-$Al_2O_3$ and $\gamma$-$Al_2O_3$ also give low yields whereas the transformation of (**I**) into (**II**) is quantitative over amorphous silica-alumina.

Therefore it seems logical to conclude that surface groups such as



are the active centers on sepiolite as well as on amorphous silica–alumina, halloysite, kaolinite, pyrophyllite, and palygorskite. On most of these silicates, these functional groups would be located on the edges of the microcrystals.

The high activity of sepiolite, which has a relatively low content in aluminium (0.8% in our sample) is surprising. It would indicate that due to its high specific surface

TABLE 1

Yields of the Catalytic Conversion of Epoxystyrene (**I**) to Phenylacetaldehyde (**II**)[a]

| | $Al^{3+}$ (%) | Yield (%) | |
|---|---|---|---|
| | | 1 hr | 6 hr |
| (A) Silicates | | | |
| Sepiolite | 0.85 | 100 | 100 |
| Palygorskite | 6.65 | 100 | 100 |
| Montmorillonite | 11.5 | 26 | 88 |
| Talc | Traces | 3 | 14 |
| Kaolinite | 20.1 | 64 | 100 |
| Halloysite | 18.9 | 100 | 100 |
| Pyrophyllite | 14.2 | 19 | 100 |
| (B) Oxides | | | |
| MgO | — | 0 | 0.5 |
| $Mg(OH)_2$ | — | 3 | 5 |
| $\alpha$-$Fe_2O_3$ | — | 0 | 0.5 |
| $\alpha$-$Al_2O_3$ | 52.9 | 2 | 4 |
| $\gamma$-$Al_2O_3$ | 52.9 | 7 | 10 |
| Silica | — | 2 | 8 |
| Silica-alumina | 6.9 | 100 | 100 |

[a] Experiments carried out in boiling benzene with different kinds of inorganic materials.

area all the active centers are accessible to the reactant.

The epoxide rearrangement can be suppressed by adding pyridine to the solids before reaction. The $Al^{3+}$ centers are blocked by coordination with the pyridine molecules. In the case of sepiolite, the number of the active sites is too low to be even detected by ir spectroscopy. However, it can be determined from the quantity of added pyridine necessary to suppress the transformation. In Fig. 2, the rate of conversion is plotted against the amount of pyridine added to sepiolite and silica-alumina before the reaction. For sepiolite, about $10^{-4}$ mole of pyridine per gram of solid is sufficient to poison the active centers, whereas for the commercial silica–alumina, this quantity is approximately four times larger.

Theoretical calculations of "external" $Al^{3+}$ cations present at the surface of sepiolite can be made from the total $Al^{3+}$ content (0.85%, i.e., $3.1 \times 10^{-4}$ eq/g) and the ratio between the external surface (270 $m^2/g$) determined by pyridine adsorption (unpublished data from the authors) and the total surface area (850 $m^2/g$) (*8*, *13*). The ratio of the number of active Al centers is indeed of the order of $10^{-4}$ eq/g sepiolite.

This agreement with the experimental value may be only fortuitous, but if not, it would indicate that $Al^{3+}$ cations are homogeneously distributed within the structure of sepiolite.

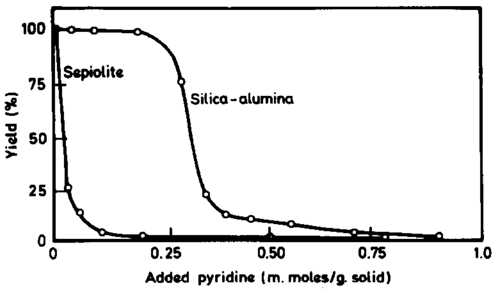


FIG. 2. Transformation of epoxystyrene into phenylacetaldehyde: number of active sites in sepiolite and silica–alumina obtained by poisoning the reaction with pyridine.

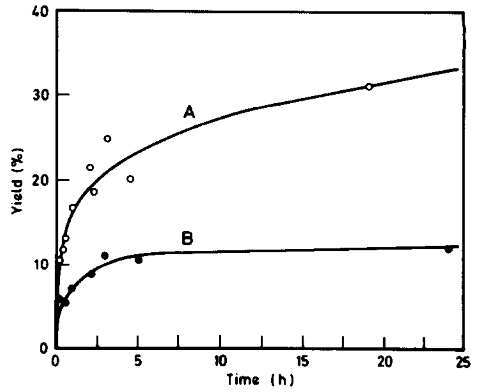


FIG. 3. An example of the kinetics of the transformation of epoxystyrene into phenylacetaldehyde carried out at 35 ± 0.3°C in a benzene solution containing an amount of silica–alumina (A) or of sepiolite (B) with an identical number of active sites in both solids.

Hence, the numbers of active centers are 0.2 and 0.9/$nm^2$ for sepiolite and amorphous silica–alumina, respectively.

The catalytic activity of sepiolite and silica-alumina for the conversion of epoxystyrene into phenylacetaldehyde may be determined from the kinetic data (Fig. 3) obtained at 35 ± 0.3°C. The turnover numbers are $1.3 \times 10^{-2}$ $s^{-1}$ and $6.0 \times 10^{-2}$ $s^{-1}$ for sepiolite and silica-alumina, respectively, showing that the activity of the commercial catalyst is about four times greater than for sepiolite.

The proposed elementary reaction steps, schematized in Fig. 4, are as follows:

(1) The epoxystyrene is adsorbed on the active centers; silanol groups open the epoxide ring and lead to a subsequent "grafting" reaction onto the mineral surface, as evidenced by ir spectroscopy in a previous work (*11*, *12*). It must be recalled that this reaction also occurs (i) when amorphous silica replaces sepiolite (i.e., when only Si–OH groups are present), and (ii) with an epoxide with an alkyl chain (for instance, epoxybutane in place of epoxystyrene). By adding pyridine the process is blocked at this stage.

(2) In the second step, a carbonium ion is formed by transferring two electrons of the oxygen atom to the aluminium center. This

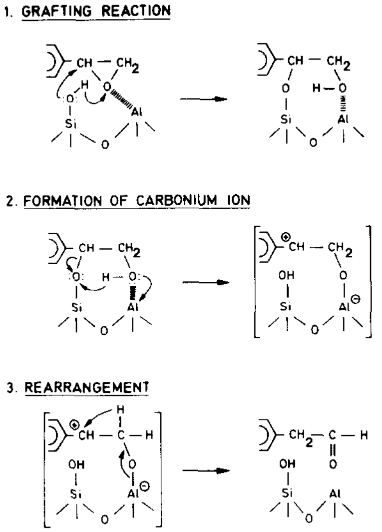


FIG. 4. Mechanism of the catalyzed molecular rearrangement proposed for the transformation of epoxystyrene into phenylacetaldehyde.

carbonium intermediate is probably stabilized by the proximity of the aromatic ring and by the negative charge brought about by the Al tetrahedron; when 1,2-epoxides with an alkyl substituent (epoxybutane) are reacted, the rate of conversion is very low.

(3) The last step consists in the rearrangement reaction, where the aldehyde is formed. At the same time, the catalytic centers are regenerated.

An interesting outcome of this work is that the epoxide rearrangement of epoxystyrene into phenylacetaldehyde could be a very simple test to detect the surface active centers of silica-alumina.

## ACKNOWLEDGMENTS

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