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Shape Selective Epoxidation of Alkenes Catalyzed by Polyoxometalate-Intercalated Hydrotalcite

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Hydrotalcite pillared by polyoxometalates of Mo and W catalyzed epoxidation of alkenes with H_2O_2 with significant shape selectivity; epoxidation of 2-hexene was favored than that of cyclohexene. The subsequent hydrolysis of epoxides to form diols was retarded compared to hydrotalcite-free catalysts.

Recently developed methods for pillaring clays have provided a new class of molecular sieves which are structurally different from zeolites.1) However, their application has been rather limited to acid catalysis by pillared cationic clays. There are a family of their mirror-image, anionic clays which have positively charged metal oxide/hydroxide layers with anions located interstitially.2) However, they are less common and their use as catalysts has not been well developed.3,4) Polyoxometalate anions are known to act as versatile oxidation catalysts and it occurred to us that oxidation catalyzed by polyoxometalates incorporated into the gallery region of anionic clays5-7) can be constrained in a shape-selective environment. Here we report a novel heterogeneous polyoxometalate-pillared hydrotalcite catalyst system for the shape selective epoxidation of alkenes.

Polyoxomolybdate pillared-hydrotalcite (Mg^{2+}/Al^{3+} molar ratio = 1.8) was prepared by a procedure described in a literature6) and found to contain 3.1 mmol-Mo/g-catalyst. Polyoxotungstate-pillared hydrotalcite was prepared in a similar manner. To a 200 g portion of a terephthalate-dianion-pillared hydrotalcite slurry containing 7.9 wt% clay was added a solution consisting of 27.7 g $Na_2WO_4 \cdot 2H_2O$ in 36 cm^3 deionized water. After the mixture was stirred for 15 min, 4 M HNO_3 was slowly added to the mixture with vigorous stirring, resulting in a pH drop from 12 to 4.4. After 10 min of additional stirring, the product was filtered, washed, and dried at 120 °C overnight. The yield of white chunks of clay was 24 g. The analytical data were consistent with the molar ratio expected for $Mg_{23.3}Al_{10}(OH)_{66.6}(W_{12}O_{41})$. The *d* spacings of the molybdate- and tungstate-pillared hydrotalcite were found to be 0.99 and 1.22 nm, respectively.

Oxidation reactions of alkenes were carried out in a 100 cm^3 flask containing catalyst (1 mmol of Mo or W), alkene (100 mmol) and 10 wt% H_2O_2 (100 mmol) solution in tributyl phosphate, at 70 °C for 3 h. The solution of H_2O_2 in tributyl phosphate was prepared by adding aqueous H_2O_2 to tributyl phosphate, followed by evaporation of water under reduced pressure at 60 °C. For control reactions support-free 0.143 mmol $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1 mmol of Mo) or 0.083 mmol $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (1 mmol of W) was used.

Table 1 compares the results of epoxidation of 2-hexene (*cis*/*trans* = 0.70) and cyclohexene. In the oxidation of 2-hexene the hydrotalcites pillared by polyoxometalates of Mo or W gave higher turnover numbers, the moles of epoxidation products (epoxides and their hydrolysis products diols) per mole of Mo or W, than the unsupported system, indicating that these polyoxometalate intercalates are effective catalysts for the epoxidation of 2-hexene. In contrast hydrotalcite-free polyoxometalates were more active in the epoxidation of cyclohexene than their intercalates.

In other words, with the molybdate-pillared hydrotalcite, the epoxidation of 2-hexene proceeded faster than that of cyclohexene, whereas cyclohexene was epoxidized faster than 2-hexene with hydrotalcite-free heptamolybdate. The latter seems to be generally the case in the absence of control by the structure of the solid framework. Thus the relative rate r(cyclohexene, **2**)/r(2-hexene, **1**) is usually much larger than unity. The cross sections of 2-hexene and cyclohexene are estimated to be 0.39 nm x 0.47 nm and 0.47 nm x 0.62 nm, respectively. The *d* spacing of the molybdate-pillared hydrotalcite corresponds to a gallery height of 0.51 nm and it would be reasonable to attribute the slower oxidation of cyclohexene (r(**2**)/r(**1**) less than unity) with the molybdate-pillared hydrotalcite to its hampered accessibility to the interlamellar catalytic sites.

The steric constraint factor was estimated by comparing the relative rates on hydrotalcite-free catalysts and hydrotalcite intercalates, being smaller for the tungstate catalysts than for the molybdate catalysts; the decrease in the relative reactivity of cyclohexene was less remarkable for the tungstate pillared hydrotalcite. This is in agreement with the wider basal plane distance for the tungstate pillared hydrotalcite and indicates the possibility of control of shape selectivity by changing the size of gallery species.

Table 1. Epoxidation of 2-Hexene and Cyclohexene[a]

Catalyst	Turnover to epoxide and diol (mol/mol-metal)				Relative rate r(**2**)/r(**1**)	Steric constraint factor[b]
	2-Hexene(**1**)		Cyclohexene(**2**)			
	Epoxide (*cis*/*trans*)	Diol	Epoxide	Diol		
$(NH_4)_6Mo_7O_{24}$	4.4 (1.5)	1.8	8.4	17	4.1	6.2
Molybdate/hydrotalcite	16 (1.9)	trace	6.0	4.5	0.66	
$(NH_4)_{10}W_{12}O_{41}$	1.7 (1.6)	2.3	3.9	20	6.0	4.0
Tungstate/hydrotalcite	14 (1.9)	trace	7.8	14	1.5	

a) Alkene 100 mmol, 10 wt% H_2O_2 (in tributyl phosphate) 100 mmol, catalyst 1 mmol-metal, 70 °C, 3 h.

b) r(**2**)/r(**1**) for unsupported catalysts / r(**2**)/r(**1**) for supported catalysts.

Shape-selective poisoning,[8] using triethylamine and triphenylamine, has been employed in the epoxidation experiments to distinguish between catalysis which occurs on the internal and external surface of the hydrotalcite. Both are known to be capable of poisoning the homogeneous epoxidation reaction.[8] The epoxidation of cyclohexene over the polyoxometalate-pillared hydrotalcites was completely inhibited by triethylamine (2.5 g) which is supposed to be able to enter the interstices, but not affected by triphenylamine (2.5 g), which is too large to enter. Thus it was concluded that the epoxidation reaction occurred at interlamellar active sites, rather than on the active sites on external surfaces. It should be noted that with the polyoxometalate-pillared hydrotalcites shape selectivity was less distinguished than with titanosilicate;[9] no epoxidation of cyclohexene was observed with titanosilcate. Heterogeneity of the size of micropores of the pillared hydrotalcites might lead to the appreciable cyclohexene epoxidation.

Starting with 2-hexene (*cis*/*trans* = 0.70), 2,3-epoxyhexane with *cis*/*trans* = 1.5-1.6 was obtained with hydrotalcite-free polyoxometalates. This is accounted for by preferential epoxidation of *cis*-isomer, as is usually observed with homogeneous catalyst systems.[10] Higher *cis*/*trans* ratio was obtained with the polyoxometalate-pillared hydrotalcites. This enhanced selectivity is inferred to result from constraint imposed by the interstitial environment.

Another effect of intercalation is high selectivity for epoxides. With hydrotalcite-free catalysts, considerable amounts of epoxides were consecutively hydrolyzed to diols owing to the slightly acidic property of polyoxometalates.11) In contrast the formation of diols was slow with the pillared hydrotalcite. This might be related to the basic nature of the brucite layers of the hydrotalcite structure.

References

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11) The pH of 0.01 M aqueous solution of $(NH_4)_6Mo_7O_{24}$ and $(NH_4)_{10}W_{12}O_{41}$ was found to be 5.1 6.0, respectively, at 20 °C.

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