Shape-selective Oxidation of Alkanes with H_2O_2 catalysed by Titanosilicate

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Shape-selective oxidation of alkanes with H_2O_2 is catalysed by pentasil zeolite titanosilicate; the rates for oxidation of linear alkanes are much higher than those of branched and cyclic alkanes.

Zeolites consist of channels and cages which are only accessible to those molecules with the correct shape and dimensions. Incorporating catalytic sites within such a structure provides the basis of molecular shape-selective catalysts and shape-selective effects have been frequently observed with reactions catalysed by inherent acidic sites, e.g., hydrocarbon cracking and alcohol dehydration.[1] The use of zeolites as shape-selective oxidation catalysts, however, has not been well developed. The parallels between zeolite chemistry and biological oxidation systems have been demonstrated by the pioneering work of Herron et al.[2,3] Recently, titanosilicate exhibiting a pentasil structure[4] has been found to catalyse the oxidation of a variety of substrates, such as aromatic hydrocarbons, alkenes, and alcohols, with an aqueous solution of H_2O_2.[5] Since this material contains the active Ti atoms in a zeolite framework, oxidation can be constrained in such a shape-selective environment. We now wish to report that titanosilicate effects partial oxidation of unactivated alkanes under very mild conditions, with outstanding substrate shape selectivity, probably resulting from the zeolite interior structure.

Titanosilicates with Si/Ti = 60 were prepared from $Ti(OC_2H_5)_4$, $Si(OC_2H_5)_4$, and $(C_3H_7)_4NOH$ according to a method in a patent.[6] A typical oxidation run used 0.05—1.0 g of a catalyst in 10 cm³ of alkanes in a round-bottom flask, to which was added a 30% aqueous solution of H_2O_2 (10 cm³). The resulting mixture was stirred for 3 h at 323 K. Catalysts were filtered off and both the resultant organic and aqueous phases were subjected to gas chromatographic analysis.

Table 1 compares the results of oxidation of C_6 saturated hydrocarbons. The oxidation turnover of hexane was seventeen times as high as that of cyclohexane. A competitive oxidation of hexane and cyclohexane led to a more pronounced substrate selectivity of hexane/cyclohexane of 41. Rates for oxidation of branched alkanes such as 2-methylpentane and 3-methylpentane were also negligible and no oxidized compound was produced from 2,2-dimethylbutane. Thus this catalyst system may distinguish the linear alkane from the branched and cyclic ones. Such substrate selectivity presumably arises from the molecular sieving action of

titanosilicate, which was revealed by elution chromatography[7] performed at 150 °C and monitored with a flame ionization detector. Cyclohexane (b.p. 80.7 °C) was eluted from titanosilicate much faster than hexane (b.p. 69 °C), suggesting the diffusion and sorption of cyclohexane was restricted because of its molecular dimensions, which are estimated at 0.47 × 0.62 × 0.69 nm from Courtald space-filling models. It has been found that the rate of uptake of cyclohexane by ZSM-5, of which the pore dimensions are 0.54 × 0.56 nm for the sinusoid channel and 0.52 × 0.58 nm for the straight channel, is significantly smaller than that of hexane.[8] The presence of water in the reaction will reduce the internal pore dimensions and must also be considered. A control reaction using an amorphous TiO_2–SiO_2 resulted in oxidation of neither hexane nor cyclohexane irrespective of whether t-butyl hydroperoxide or H_2O_2 was used as the oxidant.

As is also shown in Table 2, addition of a small amount of methanol led to a large increase in the oxidation products, giving up to 35 catalytic turnovers, corresponding to hexane conversion of 0.60%. Without addition of methanol, no product was found in the water phase. With increasing added amount of methanol, however, the portion of the products present in the water/methanol phase greatly increased. Addition of the excess amount of methanol resulted in a decrease in the turnover.

Table 1 also compares the oxidation conversion of the linear alkanes hexane, heptane, octane, and nonane by such a zeolite system. These rates decreased in the order hexane > heptane > octane > nonane. This order is consistent with the observed large decrease in diffusivity in zeolites with increasing chain length,[9] demonstrating transport restrictions preclude oxidation of molecules of sizes hindered from passing through the crystalline channels. In the oxidation of these alkanes regioselectivity was absent; oxidation at the secondary carbon atoms occurred statistically.

Investigation of the time-course of the oxidation of hexane revealed that the ratio of ketone to alcohol increased with time. This suggests that the ketones were secondarily formed from the alcohols. Formation of the product alcohols and ketones was levelled off 4—5 h after the start of the run. The

Table 1. Oxidation of alkanes[a] with H_2O_2 catalysed by titanosilicate.

Substrate	Turnover[b] (mol/mol-Ti)	Selectivity (%)							
		2-ol	3-ol	4-ol	5-ol	2-one	3-one	4-one	5-one
Hexane	7.0	17	39	—	—	34	10	—	—
Cyclohexane	0.37	ol 50				one 50			
2-Methylpentane	0.24	0	0	0	—	—	0	100	—
3-Methylpentane	0.26	0	0	—	—	100	—	—	—
2,2-Dimethylbutane	0	—	—	—	—	—	—	—	—
Heptane[c]	4.5	16	47	17	—	10	8.0	2.0	—
Octane[c]	0.50	28	34	22	—	9.0	4.0	3.0	—
Nonane[c]	0.10	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]

[a] *Conditions*: titanosilicate (Si/Ti = 60) 0.05 g, H_2O_2 (30%) 10 cm³, substrate 10 cm³, 323 K, 3 h. [b] Mol-products (alcohol + ketone)/mol-Ti. [c] Titanosilicate 1.0 g. [d] Not determined.

Table 2. Effect of addition of methanol on hexane oxidation.[a]

MeOH (ml)	Turnover (mol/mol)[b]	W/(O + W) (%)[c]
0	7	0
0.5	23	17
1.0	35	18
5.0	24	58
10	13	75
20	9	89

[a] *Conditions:* titanosilicate 0.05 g, H_2O_2 (30%) 10 cm^3, hexane 10 cm^3, 323 K, 3 h. [b] Mol-products (C_6 alcohol + C_6 ketone)/mol-Ti. [c] Portion of products present in the water/methanol phase.

recovered, dried, and calcined (at 550 °C) catalyst, however, exhibited its initial activity. Hence we believe the levelling-off of turnover is not due to catalyst destruction but due to a pore blocking mechanism; organic oxidation products fill the zeolite interior and eventually stop access of further hydrocarbon substrate to the internal active sites. However, as is distinct from metalloporphyrin based catalysts for biomimetic oxidation of unactivated alkanes,[10] this complete inorganic system seems to be free from the degradation under strongly oxidizing conditions.

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