

Catalytic Oxidation of Cyclohexane into Cyclohexanol and Cyclohexanone over a TiO₂/TS-1 System by Dioxygen under UV Irradiation

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Cyclohexanol and cyclohexanone are obtained with high selectivity by direct oxidation with molecular oxygen catalysed by a TiO₂/TS-1 system under UV irradiation and mild conditions.

C–H bond activation leading to catalytic oxidation of hydrocarbons is one of the most challenging chemical problems, in addition to being of great practical importance. In terms of oxidant, dioxygen (O₂) is clearly the most desirable due to its ready availability and high reduction potential. There has been much progress in the area of oxidation of alkanes under mild conditions by molecular oxygen.^{1–6} However, we are not aware of any reports of highly selective catalytic systems for the direct oxidation of cyclohexane into cyclohexanol by molecular oxygen under mild conditions in the absence of a coreductant such as CO or H₂. Herein, we describe a system which achieves this goal with cyclohexanol selectivity of nearly 50%. The system involves a photocatalyst TiO₂, titanium silicalite-1 (TS-1) and UV irradiation. The photocatalyst TiO₂, serves as a catalyst for the formation of active oxygen species from oxygen uptake under UV irradiation, and the TS-1 serves as a selective oxidation catalyst for the oxidation of cyclohexane into cyclohexanol.

Anatase TiO₂ and Degussa P25 TiO₂ (70% anatase) were used as obtained. TS-1 was synthesized according to published procedures^{7,8} (Si:Ti = 30:1). The TS-1 zeolite product was confirmed by XRD, IR and TEM methods. It was freed of sodium ions by ion exchange prior to use. The catalytic runs were carried out in a quartz reactor fitted with a gas inlet and outlet (50 ml capacity) at room temperature. Illumination was provided by a 250 W mercury lamp. The irradiated cross-section was ca. 6 cm². Catalysts (30–130 mg), cyclohexane (10 ml), acetonitrile (10 ml) or other solvents were placed in the reactor and stirred with a magnetic stirrer. The oxygen gas was bubbled into the liquid at a flow rate of 20 ml min⁻¹. After 3 h, the catalysts were filtered off, and the liquid phase was subjected to capillary GC analysis and occasionally checked by HPLC (HP1090B). Good agreement was found in all cases. Carbon dioxide was analysed by GC, equipped with a Porapak Q column.

Our results on the selective oxidation of cyclohexane are summarized in Table 1. The anatase TiO₂ shows moderate activity for the oxidation of cyclohexane, with the expected low selectivity for cyclohexanol. These results are almost identical with those of Mu *et al.*⁶ Only high selectivity for cyclohexanone is observed (82.5%), the other products are cyclohexanol (5.0%) and CO₂ (12.5%). We ascribe these results to the photocatalytic oxidation which has occurred at the TiO₂ particles surface. This product distribution is understandable because the oxidation rate of cyclohexanol is ca. 1.3 times greater than that of cyclohexane under TiO₂ conditions.⁶ With the TiO₂/TS-1 system this is not the case: after 3 h reaction, analysis of the organic phase indicates a much higher selectivity for cyclohexanol (49.7%), and lower selectivities for cyclohexanone and CO₂, while the total oxidation products are almost identical with the anatase TiO₂. This indicates that the further oxidation of cyclohexanol into cyclohexanone is dramatically inhibited, which results from the addition of titanium silicalite. Since no oxidation products formed in the experiment using TS-1 alone, we presume that the variation of the product distribution is due to the shape-selective oxidation of TS-1.^{9,10} Further addition of TS-1 results in an increase of oxidation product quantities. The time course results indicate that the reaction is a catalytic process. When the anatase TiO₂ is replaced with P25 TiO₂, the oxidation product quantities are almost the same as those obtained with anatase TiO₂ under the same conditions, but a lower cyclohexanol selectivity is observed. When rutile TiO₂ (anatase TiO₂ calcined at 900 °C for 8 h) was used, a much slower reaction was observed. The experiments above indicate that the crucial step of selective oxidation in that system is the activation of oxygen.

With the addition of a small amount of water to the oxidation medium, we found a significant decrease in the quantity of products obtained, but the product distribution

Table 1 Oxidation of cyclohexane into cyclohexanol and cyclohexanone over TiO₂/TS-1 system by molecular oxygen^a

Entry	Catalyst /mg		Solvent /ml			Cyclohexane /ml	Products /μmol (selectivity%)		
	TiO ₂	TS-1	CH ₃ CN	H ₂ O	Other		cyclohexanol	cyclohexanone	CO ₂
1	30 ^b					10	2.54 (5.0)	42.51 (82.5)	6.45 (12.5)
2	30 ^b	10	10			10	26.64 (49.7)	25.23 (47.03)	1.77 (3.3)
3	30 ^b	50	10			10	11.61 (55.23)	8.90 (42.34)	0.54 (2.6) ^c
4	30 ^b	50	10			10	28.44 (48.3)	28.29 (48.1)	2.14 (3.6) ^f
5	30 ^b	50	10			10	33.44 (45.45)	37.26 (50.63)	2.88 (3.9) ^g
6	30 ^b	100	10			10	58.08 (62.4)	33.24 (35.7)	1.80 (1.9)
7		100	10			10	—	—	—
8	30 ^c	100	10			10	47.88 (46.7)	53.01 (51.8)	1.53 (1.5)
9	30 ^c	100	10	1		10	22.11 (47.3)	21.33 (45.63)	3.30 (7.1)
10	30 ^c	100	10	10		10	6.51 (39.9)	4.80 (29.4)	5.01 (30.7)
11	30 ^d	100	10			10	17.07 (66.1)	8.34 (32.3)	0.42 (1.6)
12	30 ^b	100			10 ^h	10	77.34 (30.9)	169.20 (67.6)	3.66 (1.5)
13	30 ^b	100			10 ⁱ	10	13.38 (94.7)	trace	0.75 (5.3)
14	30 ^b	100			10 ^j	10	30.81 (54.4)	24.12 (42.6)	1.74 (3.1)
15	30 ^b	100			10 ^k	10	—	—	1.05

^a Conditions: room temp. reaction time 3 h. ^b Anatase TiO₂. ^c P25 TiO₂. ^d Anatase TiO₂ after calcination at 900 °C for 5 h. ^e Reaction time 1 h. ^f Reaction time 3 h. ^g Reaction time 4.5 h. ^h Dichloromethane. ⁱ Trichloromethane. ^j Acetone. ^k Methanol.

remains almost the same. When a further 10 ml of water is added, we found that not only do the product quantities decrease, but the product distribution changes (40% cyclohexanol and 29.4% cyclohexanone), while the tested amount of CO₂ increases (30.7%). This decrease in selectivity for cyclohexanol and cyclohexanone and the product quantities represents a change in the reaction mechanism. In the aqueous TiO₂ dispersion, the mechanism for photocatalytic oxidation appears to involve the expected generation of hydroxyl radicals rather than organic peroxide formation. Since the hydroxyl radical is of quite high activity and low selectivity, and is capable of deeper oxidation and of complete mineralization of cyclohexane, the cyclohexane and formed cyclohexanol are inclined to further oxidation into cyclohexanone and other oxidation products such as CO₂ (the photocatalytic mineralization has been used in the decomposition of organic pollutants).^{11,12} In contrast to the aqueous dispersion, the reaction mechanism in dry organic phase appears to involve organic peroxide formation and transfer.¹³ We presume that the molecular oxygen in the dry organic phase is activated by combining an electron from TiO₂ under UV irradiation, and converted into active oxygen species (*e.g.* organic peroxide) with cyclohexane, then this species oxidizes cyclohexane into cyclohexanol and cyclohexanone in the shape-selective environment of TS-1. Although the nature of the actual oxidizing species is unknown, our results do confirm that this selective oxidation can be achieved within a shape-selective environment. We believe the product selectivities in this system are a consequence of shape-selectivity in TS-1, which favours the formation of cyclohexanol. The efficiency of the TiO₂/TS-1 system is dependent on the synergistic effect of TiO₂ and TS-1. The selectivities of products are dependent on the shape-selective titanium silicalite.

The reaction can be also performed in acetone, dichloromethane and trichloromethane, but not in methanol. In dichloromethane, the reaction is the fastest, but lower selectivity of cyclohexanol is observed. We observed slower reaction, the highest selectivity of cyclohexanol and the lowest selectivity of cyclohexanone in trichloromethane.

In conclusion, we have discovered a highly catalytic system P25/TS-1 system for the direct oxidation of cyclohexane into cyclohexanol with high selectivity (*ca.* 50%) by oxygen under mild conditions (room temperature). Although the detailed mechanism must await further studies, the overall oxidation appears to involve molecular oxygen activation by TiO₂ under UV irradiation, oxidizing oxygen species transfer and oxidation of cyclohexane in shape-selective titanium silicalite. Finally, we note the oxidation of aromatic substrate (hydroxylation) into phenol with an identical system. Full details of such investigations will be reported in the future.

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References

- 1 N. Herron and C. A. Tolman, *J. Am. Chem. Soc.*, 1987, **109**, 2837.
- 2 M. Lin and A. Sen, *J. Am. Chem. Soc.*, 1992, **114**, 7307.
- 3 T. Tatsumi, K. Yuasa and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1992, 1446.
- 4 M. Mahroof-Tahir and K. D. Karlin, *J. Am. Chem. Soc.*, 1992, **114**, 7599.
- 5 S.-I. Murahashi, Y. Oda, T. Naota and N. Komiya, *J. Chem. Soc., Chem. Commun.*, 1993, 139; D. H. R. Barton, S. D. Beviere, W. Chavasiri, E. Csuhai and D. Doller, *Tetrahedron*, 1992, **48** (14), 2895.
- 6 W. Mu, J.-M. Herrmann and P. Pichat, *Catal. Lett.*, 1989, **3**, 73.
- 7 A. Thangaraj, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **57**, L1-L3.
- 8 M. Taramasso, G. Perego and B. Notari, *US. Pat.* 2071071, 1981.
- 9 T. Tatsumi, M. Nakamura, S. Negishi and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1990, 476.
- 10 M. G. Clerici, *Appl. Catal.*, 1991, **68**, 249.
- 11 I. Izumi, W. W. Dunn, K. O. Wilbourn, F.-R. F. Fan and A. J. Bard, *J. Phys. Chem.*, 1980, **84**, 3207.
- 12 M. A. Fox, *Chemtech.*, 1992, 680, and references therein.
- 13 C. A. Tolman and N. Herron, *Catal. Today*, 1988, **3**, 235.