

# Partial photocatalytic oxidation of cyclopentene over titanium(IV) oxide

Petr Kluson<sup>a,\*</sup>, Hana Luskova<sup>a</sup>, Libor Cerveny<sup>a</sup>, Jana Klisakova<sup>b</sup>, Tomas Cajthaml<sup>c</sup>

<sup>a</sup> Faculty of Chemical Technology, Institute of Chemical Technology—ICT Prague, Technicka 5, 166 28 Prague 6, Czech Republic

<sup>b</sup> J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 182 33 Prague 8, Czech Republic

<sup>c</sup> Institute of Microbiology, Academy of Sciences of the Czech Republic, Videnska 1083, 142 20 Prague 4, Czech Republic

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## Abstract

Photocatalytic oxidation of cyclopentene was performed over a series of structure different titanium(IV) oxide catalysts. The reaction was carried out with a special attention to limit the extent of the cyclic alkene total decomposition to water and carbon dioxide. It was shown that variable surface catalytic structures of titania acting together with active surface species (e.g., surface hydrogen peroxide, hydroxyl radicals, singlet oxygen) may significantly affect the course of the partial photooxidation. Reactions were carried out in liquid phase, isothermally and at atmospheric pressure with oxygen in the quartz reactor fitted with a source of UV. The catalysts' structure dependent selectivity profiles were compared with similar kinetic data obtained previously in partial photocatalytic oxidation of cyclohexene.

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## 1. Introduction

Environmentally attractive and practically feasible photooxidations of water or air pollutants over titanium(IV) oxide catalysts (titania, TiO<sub>2</sub>) have been applied in many green technologies (e.g., [1–14]). TiO<sub>2</sub> due to the presence of lattice point defects reveals properties of a typical semiconductor. Width of its forbidden band is 3.2 eV for anatase and 3.0 eV for rutile (two major allotropies of titania). Due to these relatively high values, its photoexcitation requires highly energetic photon flux with a corresponding wavelength in the UV region (<390 nm). Oxidation potential of the photo generated holes in the valence band of anatase attains a value of +2.9 V (versus SHE/pH 0) which is enough for oxidative decomposition of most of the organic molecules to carbon dioxide and water (e.g., [14,15]). Additionally anatase modification profits of its strongly hydrophilic surface that enables reactions of the generated holes with adsorbed molecules of

water, and thus, to form hydroxyl radicals—strong oxidants [16–18]. On the other hand, utilisation of this type of reactions for synthetic purposes has been reported only rarely [19–26]. If the extent of the photooxidation is intentionally limited valuable intermediates for fine chemistry might be obtained relatively simply comparing with traditional approaches of the organic synthesis. Additionally it benefits of being an environmental friendly method. Photoactive titania is non-toxic, non-carcinogenic and it also does not present any significant fire hazards and environmental risks.

Titania photo induced surface electron vacancies and the adsorbed water molecules act together with molecular oxygen under formation of various active species (e.g., [27]). The most common are hydroxyl radicals (OH•), superoxide anion (O<sub>2</sub><sup>•-</sup>), surface hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or singlet oxygen (O<sub>2</sub>). Their existence obviously results from the general semiconductor nature of titania; however, their abundance differs for variously structured TiO<sub>2</sub>. This fact could be macroscopically manifested, e.g., by variations in reaction selectivities toward different intermediates or partial photooxidation products [27].

\* Corresponding author. Tel.: +420 220 44 4158; fax: +420 224 31 1968.  
E-mail address: P.Kluson@seznam.cz (P. Kluson).

In this paper, we report on partial photooxidation of cyclic alkene—cyclopentene over a series of titania photocatalysts with variable structural properties. Among them commercial products as well as purpose made photocatalysts could be identified. The process selectivity and the product distribution profiles are discussed in terms of the structural properties of the employed photocatalysts. Structure effects of the reacting molecules are also briefly commented in terms of the previous findings on the partial photooxidation of cyclohexene [27].

## 2. Experimental part

### 2.1. Titania based photocatalysts

A series of eight titania photocatalysts is given in Table 1. The first subgroup of four contains only commercial samples (D-7701, D-7702, P-25 Degussa; S-7001 Eurosupport). All the Degussa catalysts could be referred to as low surface area titania with a variable ratio of anatase to rutile. S-7001 TiO<sub>2</sub> is a typical mesoporous solid composed mostly of anatase (98%).

The second subgroup, also of four, involved catalytic samples that had been prepared intentionally for this study by a sol–gel process from liquid precursors. The SG1 and SG2 catalysts were obtained by a standard sol–gel route with hydrochloric acid (1 M HCl/TIOP=0.7) or ammonia (4 M NH<sub>4</sub>OH/TIOP=1). SG1 preparation conditions differed from those for SG2 in pH (pH 3 and 9.5) during the hydrolysis of the initial metal alkoxide (titanium(IV) isopropoxide, TIOP, Aldrich, 99.9%) and condensation of the reaction intermediates (supplied by partial hydrolysis of TIOP). The preparation was started up by mixing TIOP and hydrochloric acid (or ammonia). Then, water (180 ml) was slowly added (1 h). The evolved gels were allowed to stay for 40 h then dried under vacuum at 373 K and finally calcined at 493 K for 3 h to obtain well developed anatase structure, however, still with relatively low extent of particles crystallinity.

The SG3 and SG4 samples were obtained [28,29] within templates of micelles of non-ionic surfactant C<sub>33</sub>H<sub>60</sub>O<sub>10.5</sub> (Triton X-100, Aldrich, 99.99%) from titanium(IV) isopropoxide in cyclohexane (Aldrich, HPLC grade, water content less than 0.01%). The molar ratio of water to surfactant

was kept at  $R=1$  and the ratio of TX-100 to cyclohexane was 0.85 mol kg<sup>-1</sup>. The organic content was then reduced by extraction with supercritical carbon dioxide (SFE) at 45.6 MPa and 373 K for 180 min using methanol as a restrictor. Precursor of the SG3 photocatalyst was treated thermally at 773 K for 3 h to destroy the remaining ~10 wt% of organic matter. The final form was completely free of any organics (elemental analysis, XPS) and could also be referred to as pure anatase with very small particle size. Up to the point of the thermal treatment at 773 K, the process providing SG4 was analogous to that for SG3. In this case, the last step was substituted with an intentional UV illumination (Hg lamp, 125 W,  $\lambda_{\max}=320\text{--}390$  nm) of the titania precursor (~10 wt% of organic carbon) dispersed in water (250 ml, kept at 303 K, agitated with oxygen-flow rate 950 ml min<sup>-1</sup>). The obtained final form (SG4) still retained a certain amount of organic carbon (~2 wt%, elemental analysis) encapsulated within its structure. SG4 revealed the surface area comparable with that of SG3 and also showed some indication of the anatase crystallinity (XPS). Specific surface areas ( $S_{\text{BET}}$ ) of titania based photocatalysts were determined (Pulse Chemisorb 2700, Micromeritics) by using the BET method with nitrogen as an adsorbate at 77 K (cross sectional area of N<sub>2</sub> 0.162 nm<sup>2</sup>). Powder X-ray diffractions (XRD) were measured with the Co K $\alpha$  radiation source and Bragg–Brentan focusing geometry (RS 3000, Rich. Seifert Co.). Particle size was estimated from Scherrer equation. Surface images of samples sputtered with gold in plasma were taken on SEM microscopic apparatus (Hitachi S-520). Extent of surface hydroxylation was assessed by infrared spectroscopy using Nicolet 740 IR spectrometer. Full adsorption isotherms were measured with N<sub>2</sub> at 77 K in a volumetric mode and static regime on Omnisorp 100 (Coulter).

### 2.2. Experimental arrangement

Photocatalytic reactions with cyclopentene (Aldrich, 99.9%) were conducted in a quartz reactor (300 ml) isothermally at 293 K and atmospheric pressure fitted with a vacuum Hg lamp (250 W). The reaction system also involved a condenser, a column with concentrated sulphuric acid (water trap) and a trap composed of a Dewar flask filled with a mixture of acetone and solid carbon dioxide. In some experiments, the effluent stream was vented through a cartridge with ascarite (silicate support with NaOH on its surface, Aldrich) as a selective trap for carbon dioxide evolved during the reaction. This experimental setup allowed the mass balance calculations. Oxygen used also for agitation of the reaction mixture entered the reactor at its bottom by means of a ceramic distributor. The oxygen stream was presaturated with cyclopentene at 293 K and the flow rate was adjusted to 950 ml min<sup>-1</sup>. All experiments were performed in kinetic regime without the external and internal mass transfer effects. Typically 1 g of the photocatalyst was used. Progress of cyclopentene photooxidation was followed by gas chromatography (HP 5890) with HP10M capillary column (50 m  $\times$  0.5 mm  $\times$  0.5  $\mu$ m).

Table 1  
The photocatalysts

Catalyst	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	Crystallographic phase structure	Particle size (nm)
S-7001	210	Anatase	10–20
P-25	50	80% Anatase 20% rutile	30–50
D-7701	25	63% Anatase 37% rutile	30–50
D-7702	44	40% Anatase 60% rutile	30–50
SG1	350	Anatase	9.5
SG2	400	Anatase	8.5
SG3	780	Anatase	3.8
SG4	700	Amorphous/(anatase)	/

Intermediates' structures were determined on GC-MS analytical system (Varian Saturn 2000) using an ion trap mass analyser.

Some effort has also been spent to describe the progress of the reaction without any catalyst, only with oxygen, UV and the initial cyclic alkene. It must be noted that cyclopentene was not found completely photo-inactive, however, its attained conversion did not exceed 6%. On the other hand, the indispensable role of UV was proofed by excluding this energy source in reactions involving catalysts and oxygen. In all these experiments virtually no transformation of cyclopentene was detected.

### 3. Results and discussion

Data collected in Table 1 reflect basic differences between the catalysts used for photooxidation of cyclopentene. Four commercial titania samples are listed here according to their decreasing content of anatase—the crystallographic phase which is primarily considered responsible for the increased photoactivity. The three products of Degussa (P-25, D-7701, D-7702) could all be referred to as low surface area macroporous/(mesoporous) solids with mixed anatase–rutile phases (as it was evident from their diffraction patterns). In this series, only S-7001 represents a typical mesoporous  $\text{TiO}_2$  anatase with well developed individual particles observable even on its SEM image (Fig. 1) ranging from 10 to 20 nm. These samples were tested on the presence (abundance) of surface hydroxylation by infrared spectroscopy. Significant extent of surface hydroxylation was a common feature of these catalysts (S-7001 dominated). The existence of a characteristic bending mode of water at  $1648\text{ cm}^{-1}$  together with the increased intensity of the OH group at high wave numbers from occluded surface water molecules and Ti–OH groups bear upon a high degree of surface hydroxylation for this particular material (Fig. 2). The broad absorbance at low wave

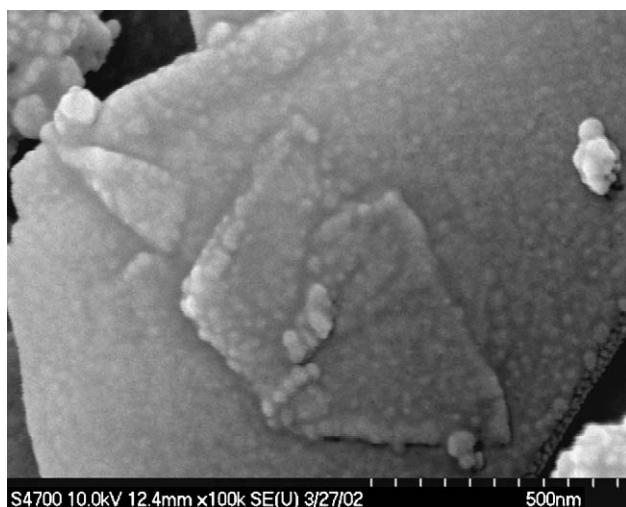


Fig. 1. SEM image of the surface of S-7001.

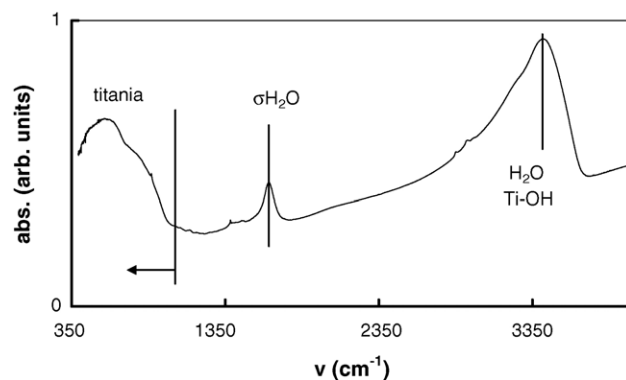


Fig. 2. IR spectrum of S-7001.

numbers (below  $900\text{ cm}^{-1}$ ) is generally characteristic for the Ti–O linkage.

The four sol–gel catalysts were not in principal too different from those of the commercial series (Table 1). However, their adsorption properties (reflected here in  $S_{\text{BET}}$  values) pointed out on contribution of microporous regions. A typical adsorption isotherm of nitrogen at 77 K is shown in Fig. 3 for SG4. With exception of mostly amorphous SG4 these catalysts involved only anatase with relatively small and uniform particles. High degree of internal organisation and particle uniformity of SG3 resulted from its preparation route [28]. It involved the non-ionic surfactant templates inducing formation of spherical particles. The SG4 catalyst could not be assessed in a standard way due to its non-standard preparation method (activation by UV illumination, experimental part). However, since the precursors of SG3 and SG4 were identical most of the discussion was also applicable to SG4. Surfaces of the sol–gel samples showed an increased affinity to molecules of water. Extent of surface hydroxylation of SG3 and SG4, as revealed by IR, was weaker than observed, e.g., for the commercial S-7001 catalyst. An interpretation might be sought in terms of the preparation method [28,29] using a limited (low) number of water molecules entrapped within the structure of the template, and thus, preventing to constitute the strong and irreversible forms of the surface hydroxylation.

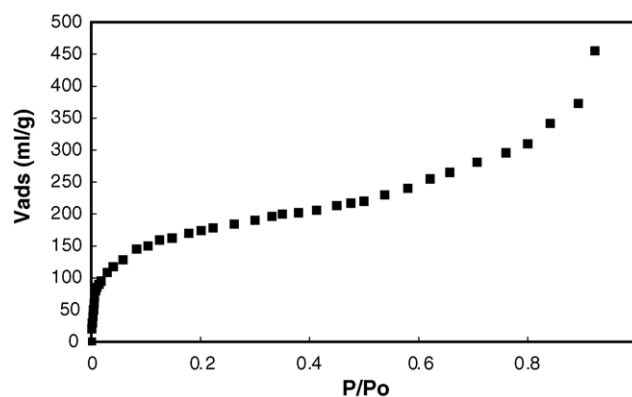


Fig. 3. Full adsorption isotherm of nitrogen at 77 K onto the surface of SG-4.

At this point, basic findings of our recent work [27] on the transformation of cyclohexene should be reminded. Tested catalysts, reaction conditions and the experimental arrangement were analogous. The reaction yielded generally two major groups of intermediates: first, products of oxidation—among them cyclohex-2-en-1-one dominated (preferred on commercial catalysts including the mesoporous hydrophilic pure anatase S-7001); second, products of epoxidation with 7-oxabicyclo[4.1.0]heptane as the principal reaction product. Infrared spectroscopy of the used catalytic samples supported the notion that cyclohex-2-en-1-one was strongly adsorbed on the catalytic surface, and thus, it was responsible for the catalysts' activity decline. The later group of compounds (epoxides) was selectively formed on sol-gel catalysts, especially on SG3. The yield of 7-oxabicyclo[4.1.0]heptane was defined as the amount of this most abundant intermediate relative to the total amount of other intermediates and reaction products including carbon dioxide and water (evaluated from mass balance calculations). When the reaction terminated (zero reaction rate) the yield parameter attained an impressive value of 45% (on SG3).

Basic molecular structure differences of cyclohexene and cyclopentene could be simply assessed by molecular mechanics—the approach which applies laws of classical physics to molecular nuclei without explicit consideration of electrons. For this particular job, the MM2 method was used [30,31]. Thermodynamically the most stable conformation of cyclohexene at conditions of the current experiment is the “half-chair” isomer ( $17.5 \text{ kJ mol}^{-1}$ ). Comparing it with

the corresponding C6 cyclic alkane—cyclohexane, due to the presence of the alkenic double bond, the length of the C–C is reduced of 0.0187 nm and the valence angle C–C–C is increased of  $12.5^\circ$ . Unlike cyclohexene, cyclopentene is under same conditions nearly planar and it is thermodynamically more stable ( $12.4 \text{ kJ mol}^{-1}$ ). The C–C bond is shorter of 0.0186 nm and the C–C–C angle increases of 9.2 in comparison with C5 cyclic alkane—cyclopentane.

Partial photooxidation of cyclopentene yielded an impressive list of products. Cyclopentenylhydroperoxide (A) was assumed formally as a common initial intermediate for all reaction pathways. In analogy with cyclohexene a group of oxidation products appeared mainly including cyclopent-2-en-1-one (B) and in much lower quantities also cyclopent-2-en-1-ol. The epoxide fraction involved mostly 6-oxabicyclo[3.1.0]hexane (C), appearance of other products of this type was marginal. The third group was characteristic by aliphatic compounds such as penta-1,4-diene-3-ol, 3-methylbutane-1-ol and mainly penta-1,5-dial (glutaraldehyde, D). It should be noted that the aliphatic product fraction did not exceed 9 wt% on any of the sol-gel catalysts; commercial catalysts were virtually inactive in this respect. It seemed plausible that aliphatics were yielded only by reactions of/from epoxides. Also very low concentrations of aliphatic products were detected in reactions with cyclohexene. Molecular mechanics indicated much lower stability of the cyclopentene-structure based epoxide 6-oxabicyclo[3.1.0]hexane in comparison with 7-oxabicyclo[4.1.0]heptane. Due to such speculative interpretations of the reaction mechanism only a formal reaction scheme is presented in Fig. 4.

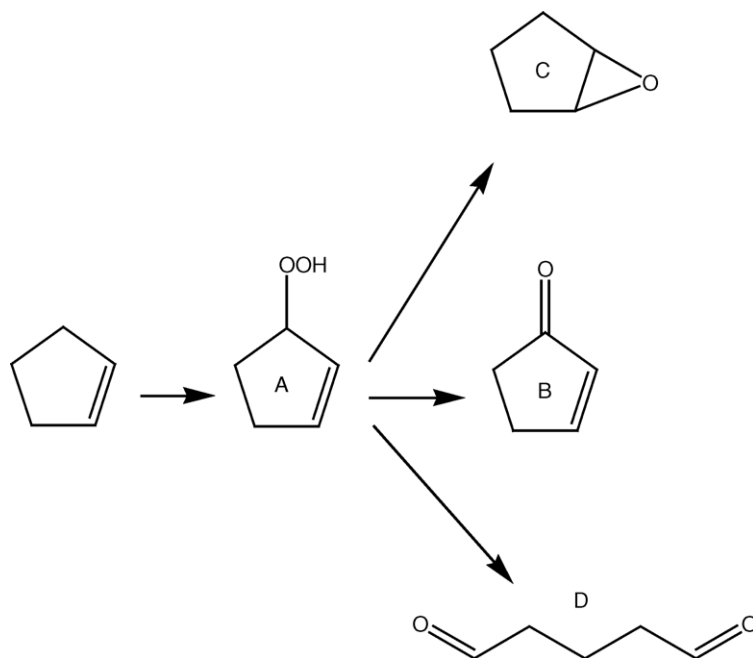


Fig. 4. Formal reaction scheme of partial photooxidation of cyclopentene.

Table 2  
Kinetic parameters

Catalyst	$x$ (%)	$r_0$ (%) (mmol g <sub>cat</sub> <sup>-1</sup> min <sup>-1</sup> )	$S_{e1}$ (%)	$S_{e2}$ (%)	$Y_1$ (%)	$Y_2$ (%)
S-7001	54	2.3	49	12	36	9
P-25	51	3.0	38	17	21	9
D-7701	57	1.9	40	15	28	6
D-7702	53	1.6	35	12	25	5
SG1	66	8.1	16	26	15	23
SG2	69	9.1	14	31	12	29
SG3	96	18.3	9	49	11	43
SG4	53	7.9	11	38	13	37

Total oxidative decomposition of cyclopentene to carbon dioxide and water was relatively low, 17–27 wt%, depending on a catalyst. This interval was of ~10 wt% lower than observed for cyclohexene. Since the reaction conditions and the used catalysts were identical it could be interpreted by means of the cyclopentene higher thermodynamic stability or by means of the direct deactivation effect of some of the intermediates. Deactivation of commercial catalysts in the reaction was apparent (Table 2).

For the purpose of this study, six kinetic parameters were introduced (Table 2)—conversion of cyclopentene ( $x$ ); initial reaction rate ( $r_0$ ); selectivity ( $S_{e1}$ ) defined at  $x=50\%$  as the amount of cyclopent-2-en-1-one relative to the total amount of other intermediates; selectivity ( $S_{e2}$ ) defined at  $x=50\%$  as the amount of 6-oxabicyclo[3.1.0]hexane relative to the total amount of other intermediates, yields ( $Y_1$ ,  $Y_2$ ) reflected the final composition when the reaction terminated (zero reaction rate) for the same intermediates. Unlike for selectivities, the yield parameters involved all products (reaction intermediates, carbon dioxide and water; unreacted cyclopentene was not included).

As seen in Table 2, a total conversion of cyclopentene was not achieved on any of the catalysts. However, an exceptional position of SG3 with its  $x=96\%$  was apparent. The commercial samples were much more “vulnerable” for losing activity. On all of them conversions above 50% were achieved, however, not a single one overcame the value of 60%. It was likely due to their high selectivity toward intermediates strongly bound to the surface of titania as evidenced by IR spectroscopy of the used catalysts. Initial activities ( $r_0$ ) of the catalysts prepared by sol–gel were generally higher. It was not surprising due to much lower surface areas of commercial samples and their variable content of anatase. Epoxide intermediates were not favoured in reactions with these catalysts and the major product was cyclopent-2-en-1-one (Table 2). In this group of catalysts, a distinctive positions of S-7001 and P-25 were obvious. The former revealed the highest selectivity  $S_{e1}$ , the second was the most active despite its lower content of anatase and lower surface area. High yield of the catalytic surface deactivating molecule (cyclopent-2-en-1-one) could be likely blamed for the lower activity of relatively high surface area mesoporous S-7001. The SGs could be referred to as highly active and as catalysts directing the partial oxidation

through the initial epoxide stage (in analogy with cyclohexane). With exception of SG3 these catalysts also suffered of deactivation (this phenomenon is being currently studied).

There are more possible interpretations of the observed selectivity variations as a function of the catalysts structural (surface) properties. However, with the available knowledge all are rather speculative. One of the possible explanations comprises involvement of two mechanisms involving participation of different surface active species. First mechanism might involve formation of hydroxyl radicals through the contact of positively charged electron vacancies with adsorbed surface water. It could be responsible for oxidative reactions. The second mechanism might involve a series of interlinked transformations started by reaction of oxygen with excited electrons. This reductive mechanism provides a number of active species such as surface hydroperoxide or singlet oxygen and could potential be responsible for epoxidation reactions.

#### 4. Conclusion

Partial photocatalytic oxidation of cyclopentene provided a list of structurally interesting intermediates at ambient conditions with high yields. Some of them may find their utilisation in synthesis of fine chemicals. The extent of the total decomposition to carbon dioxide and water was relatively low. A certain indication of the dependence of the observed selectivity profiles on the surface and structure properties of the used catalysts was presented. Analogies with a similar transformation of cyclohexene discussed recently might support the current findings. More attention will be paid to this topic in near future.

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