

**PHOTOCATALYTIC OXIDATION OF CYCLOHEXENE
ON TITANIUM(IV) OXIDE**Jana KLISÁKOVÁ^{1,+}, Petr KLUSON^{2,*} and Libor ČERVENÝ³*Department of Organic Technology, Institute of Chemical Technology, Prague, Technická 5,**166 28 Prague 6, Czech Republic; e-mail: ¹ jana.klisakova@jh-inst.cas.cz,**² p.kluson@seznam.cz, ³ cervenyl@vscht.cz*Received June 9, 2003
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Photocatalytic oxidation of cyclohexene was carried out over a series of titanium(IV) oxide catalysts. These species acting together with molecular oxygen significantly differed in their surface and structural properties. Attention was paid to elimination of the total decomposition of the alkene molecules to water and carbon dioxide and to favour formation of reaction intermediates, comprising epoxide units. Experiments were performed in liquid phase at atmospheric pressure, room temperature and under UV illumination. A quartz reactor was used and the reaction mixture was agitated by oxygen. Significant variations in the reaction selectivity were detected as a function of catalyst structural properties.

Keywords: Photochemical oxidation; Titania; Partial oxidation; Cyclohexene; Alkenes; Epoxidation; Heterogeneous catalysis.

Oxidation processes play an important role in the production of a wide range of chemicals. Many of them, such as ketones, aldehydes, epoxides, *etc.*, are typical precursors for drugs, vitamins, fragrances and they are also important intermediates for many complex syntheses^{1,2}. However, not many industrial oxidation processes could be referred to as green technologies^{1,3,4}. Traditional oxidants, such as mineral acids, chromates, manganese complexes, permanganates, hydrogen peroxide, organic peroxides, *etc.*, are rather questionable in the context of their toxicity, corrosiveness and necessary stringent reaction conditions. Unlike these, molecular oxygen represents¹⁻⁵ a highly reactive agent, which in cooperation with a suitably chosen heterogeneous catalytic system (supported noble metals, metal oxides) could be expected to meet required environmental standards.

+ Present address: J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic; Dolejškova 3, 18223 Prague 8, Czech Republic.

Photocatalytic oxidation with titanium(IV) oxide (titania) acting together with molecular oxygen as the photoactive species is an option. It has been reported that active species, which may include hydroxyl radical (OH^\bullet), superoxide anion ($\text{O}_2^{\bullet-}$), hydrogen peroxide (H_2O_2) or singlet oxygen (O_2), are generated on the TiO_2 surface. Their existence results from the semiconducting nature of titania, its very strong surface hydroxylation and the presence of oxygen and UV light. Active oxygen species may diffuse to the titania surface and act there as surface sites. These effects have been discussed elsewhere in detail⁶⁻¹³. Photocatalytic oxidation with titania has been extensively used in environmental^{6,11,13-20} photochemistry for complete degradation of various pollutants either in liquid or gas phase.

Typical processes of this kind are water decontamination from phenol, chlorinated phenols, chlorinated hydrocarbons, urea and triazine derivatives, various aromatic compounds, aromatic amines, carboxylic acids or many VOC decomposition reactions using titania thin films.

On the other hand, available information on photooxidation with TiO_2 for synthetic purposes is rather limited. Nonetheless, this generally omitted reaction (partial photooxidation) has a potential to provide a wide range of valuable intermediates for fine chemistry. Epoxidation of olefins, including cyclic alkenes, is an important transformation in synthetic chemistry and the photooxidation complies ideally with the general economy/ecology requirements.

In this paper we report on partial oxidation^{1,3,4} of pure cyclohexene²¹⁻²⁶ (not solved in a solvent, initially the system also does not contain any water) on various types of titania photoactive species. The process selectivity and the product distribution profiles have been discussed together in terms of the structural properties of the used catalysts. It seems that the performance of titania as a photocatalyst strongly depends on the surface and structural properties which are often functions of the preparation method. Thus the major aim of this study was to determine conditions under which complete decomposition of the initial alkene compound was limited and the formation of oxygen intermediates favoured. Commercially available catalysts were compared with those produced by the sol-gel method. These were generated by using a standard sol-gel route and also within templates of assemblies of reverse micelles of the non-ionic surfactant to obtain high-surface-area uniform particles²⁷.

EXPERIMENTAL

Catalysts and Chemicals

Commercial catalysts used in this work were P-25, D-7701, D-7702 obtained from Degussa and S-7001 supplied by Eurosupport. Catalysts SG1, SG2 and SG3 were prepared for this study by the sol-gel process from titanium tetraisopropoxide (TIOP) (Aldrich, 99.99%). The first two (SG1 and SG2) were obtained by following a standard sol-gel route, with acetic acid and ammonia as reaction media. SG1 preparation conditions differed from those for SG2 in pH values during the hydrolysis and condensation steps (pH 3 and 6). The process was started by mixing TIOP and acetic acid, followed by addition of water dropwise for 1 h. The mixture was vigorously agitated with bubbles of nitrogen and kept at $T = 343$ K. The pH value was adjusted by addition of ammonia. The volumetric ratio for the components was TIOP:acetic acid:water = 1:2:6. The evolved gel was subjected to the aging for 40 h, then dried under vacuum (373 K) and finally calcined at 493 K for 2 h.

SG3 was generated in reverse micelles of a non-ionic surfactant $C_{33}H_{60}O_{10.5}$ (Triton X-100, Aldrich, 99.99%) 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^{-1} . The organic content in a raw gel was significantly reduced by supercritical fluid extraction with carbon dioxide and then the material was thermally treated to adjust its crystallographic phase structure. This method and characteristic features of the obtained catalyst were described previously²⁷.

Other used chemicals were cyclohexene (Sigma Aldrich, 99%) as a substrate and 7-oxabicyclo[4.1.0]heptane (Sigma Aldrich, 96%), cyclohexanol, cyclohexanone (Penta, 99.9%), cyclohex-2-en-1-one, cyclohex-2-en-1-ol (both Sigma Aldrich, 98%) as chromatographic standards.

Typical Experiment

Reactions were conducted at 293 K (isothermally) and atmospheric pressure in liquid phase using a cooling-jacket quartz photoreactor (300 ml) fitted with a vacuum Hg lamp (400 W, $\lambda_{\text{max}} = 320\text{--}390$ nm). The source of the UV light used was not polychromatic and it consisted of several single irradiation wavelengths, which is a typical feature of this kind of a lamp. The reactor was equipped with a condenser, a column with concentrated sulfuric acid (water trap) and a trap composed of a Dewar flask filled with a mixture of acetone and solid carbon dioxide ($T = 238$ K). Finally, in some experiments, the effluent stream was vented through a cartridge with ascarite (Aldrich) for gravimetric evaluation of the amount of carbon dioxide evolved. Oxygen, also used for an effective agitation of the reaction mixture, entered the reactor unit at the bottom by means of a ceramic distributor. It was pre-saturated with cyclohexene at 293 K and the flow rate was digitally adjusted in the range $100\text{--}1200 \text{ ml min}^{-1}$. Separately it was proved that the upper limit value was necessary to carry out the experiments without the effect of the external mass transfer. Catalysts were used as very fine powders to limit internal mass transport effects. The withdrawn samples were analysed on a gas spectrometer HP 5890 with a HP10M column ($50 \text{ m} \times 0.5 \text{ mm} \times 0.5 \mu\text{m}$). Molecular structures of some reaction intermediates were determined with GC-MS Saturn 2000 (Varian) analytical system using an ion trap mass analyser.

Characterisation Methods

Specific surface areas (S_{BET}) of the catalytic samples were determined on a Pulse Chemisorb 2700 apparatus (Micromeritics) using a BET method with nitrogen at 77 K. The cross-sectional area 0.162 nm^2 for a molecule of nitrogen was considered.

High-resolution adsorption isotherms of nitrogen were measured at 77 K up to a relative pressure of $P/P_0 = 1$. The volumetric measurements were carried out in a static regime on Omnisorp 100 (Coulter). Adsorption experiments with carbon dioxide (for SG3) at 298 K were performed using a Sorptomatic 1800 (Carlo Erba).

Powder X-ray diffraction (XRD) was used to evaluate crystallographic phase structures of TiO_2 samples on RS XRD equipment (R. Seifert Co.) using Bragg-Brentan focusing geometry, $\text{CoK}\alpha$ radiation and a graphite monochromator. Particle size was estimated from the Scherrer equation.

Surface images of the used materials were taken on SEM microscope S-520 (Hitachi). Samples were first sputtered with gold in plasma.

Some of the catalysts were, after the reaction, studied by IR spectroscopy on a Nicolet 740 spectrometer (Nicolet). The same catalysts were also studied on a thermogravimetric apparatus TGA 750 (Stanton & Redcroft) at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ in air (10 ml min^{-1}) with samples in a platinum holder.

RESULTS AND DISCUSSION

Catalysts

A good starting point for the discussion on characteristic features of the used catalysts is Table I. It reflects basic differences between the various TiO_2 in this group. The three commercial products supplied by Degussa (D-7701, D-7702, P-25) could be classified as low-surface-area samples obviously of macroporous nature. Variations in S_{BET} values are not too signifi-

TABLE I
Characteristic features of the used catalysts

Catalyst	$S_{\text{BET}}, \text{ m}^2 \text{ g}^{-1}$	Crystallographic phase structure	Particle size, nm
D-7701	25 ± 2	63% anatase 37% rutile	30–50
D-7702	44 ± 3	40% anatase 60% rutile	30–50
P-25	50 ± 3	80% anatase 20% rutile	30–50
S-7001	209 ± 5	98% anatase	10–20
SG1	350 ± 7	>99% anatase	9.5
SG2	400 ± 7	>99% anatase	8.5
SG3	780 ± 9	>99% anatase	3.8

cant (from 25 to 50 m² g⁻¹), despite the value for P-25 is twice as high as for D-7701. Surface areas of the catalysts S-7001, SG1 and SG2 are higher of the order of magnitude, likely reflecting a contribution of the mesoporous region. The exceptional S_{BET} of nearly 800 m² g⁻¹ was found for the SG3, generated in the reverse micelle environment.

Full adsorption isotherms of nitrogen at 77 K were also measured for the used TiO₂ samples. A typical adsorption curve well representing the group of the Degussa catalysts is given in Fig. 1 for P-25. Even at very low relative pressures, no significant disorders in surface-energetic homogeneity were observed.

Mesopore size distributions of the S-7001, SG1 and SG2 catalysts were evaluated from the desorption branch of the nitrogen isotherm and calculated from the modified Kelvin equation (BJH method). The distribution curves were similar and covered the range from ≈ 1.8 to 12 nm, peaking at $r = 4.1\text{--}4.8$ nm. The mesopore size distribution pattern of SG3 (again the BJH method) is shown in Fig. 2. Unimodal distribution covers the area from 1.3 up to 14.3 nm peaking at $r \approx 3.8$ nm. Owing to the steep initial increase in the dV/dr value, the most significant interval is located between $r \approx 1.5$ and 4 nm. Whereas S-7001, SG1 and SG2 were typically mesoporous, SG3 structure accounts also for a significant contribution of micropores. The contribution of the microporous region to the overall volume was determined from the CO₂ isotherm by the DR (DRS) method (also Fig. 2). The distribution curve starts just below $r \approx 0.6$ nm, showing quite a sharp maximum at $r \approx 0.8$ nm and then decaying with the increasing pore size.

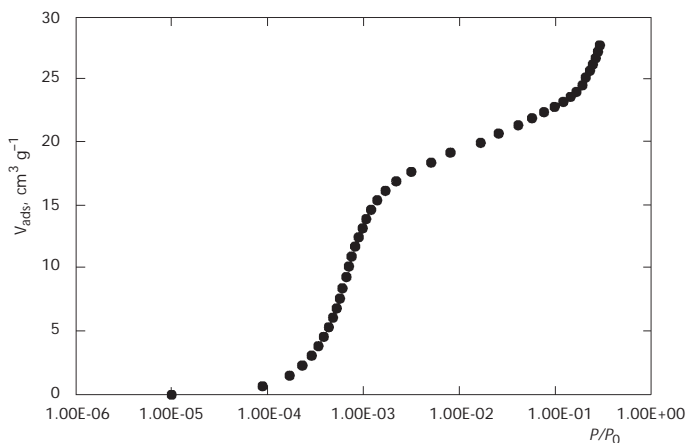


FIG. 1
Adsorption isotherm of nitrogen at 77 K on the surface of P-25

Photoactivity of titania significantly differs with its crystallographic phase structure. Rutile is, unlike anatase, usually referred to as the low-active form. XRD revealed sharp diffraction lines of major planes of rutile and anatase for all the Degussa samples. P-25 is mostly anatase-type titania with 80% of this structure. Compositions of D-7701 and D-7702 are nearly opposite with prevailing anatase for the former (Table I). From the width of the diffraction peaks and the Scherrer equation the particle size was evaluated. For P-25, D-7701 and D-7702 sharp bands corresponded to the calculated particle size of 30–50 nm. This interval is consistent with the appearance of spherical clusters (30–60 nm) observed on SEM images of these commercial catalysts. A typical picture of such a surface (P-25) is given in Fig. 3.

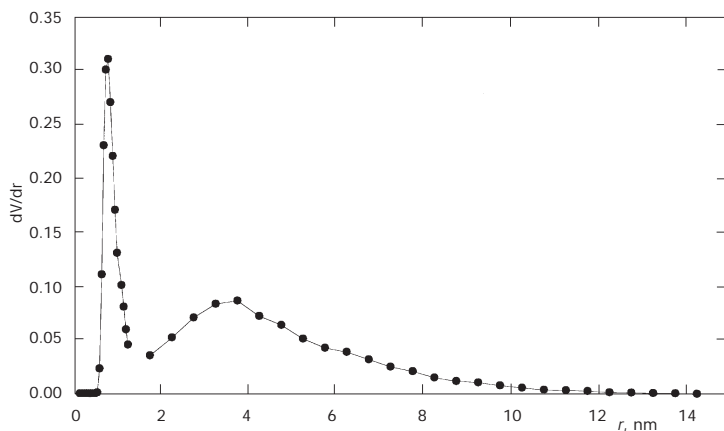


FIG. 2
Pore size distribution patterns of SG3

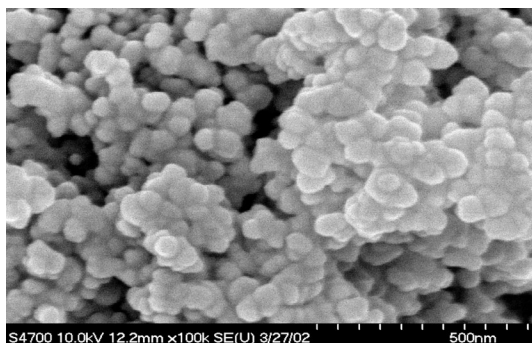


FIG. 3
SEM image of the P-25 surface

The remaining four catalysts (S-7001, SG1, SG2, SG3) were pure anatase samples. Particle size analysis of SG1 and SG2 (XRD) revealed crystallites just below 10 nm, for S-7001 about 16 nm. The value calculated for S-7001 is in a good agreement with the size of well visible particles incorporated in a flat homogeneous surface observable on an image of this material (Fig. 4). Notable properties of SG3 involved small crystallites for which $D \approx 3.8$ nm was calculated.

Reaction

Partial oxidation of cyclohexene over titania photoactive species yielded an impressive collection of intermediates under standard reaction conditions ($m_{\text{cat}} = 1$ g, 200 ml of cyclohexene, oxygen flow rate 1200 ml min^{-1}). The distribution of intermediates could be assumed as a sensitive indicator of the existence of various sites on catalyst surfaces (structural variations) which can catalyse oxidation and epoxidation. We considered formation of cyclohexenylhydroperoxide as a common initial intermediate even without a catalyst, only in the presence of oxygen, accelerated by UV light. Typically, five intermediates were repeatedly proved in reaction mixtures. Their distribution was a function of the catalyst used. Due to their interesting structures, attention was primarily paid to molecules bearing an epoxide grouping. These were 7-oxabicyclo[4.1.0]heptane, 7-oxabicyclo[4.1.0]heptan-2-one and 7-oxabicyclo[4.1.0]heptan-2-ol. Two other major products were cyclohex-2-en-1-one and cyclohex-2-en-1-ol. We may hypothetically consider many formal reaction schemes involving relations of the individual components of a reaction mixture. Experimentally there has been some evidence for the preferential initial formation of 7-oxabicyclo-

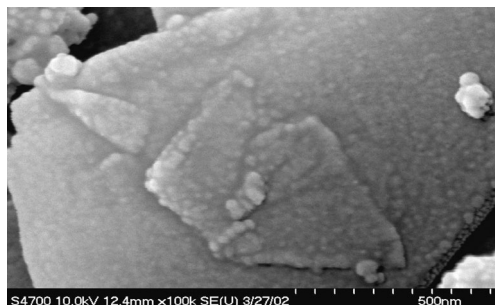


FIG. 4
SEM image of the S-7001 surface

[4.1.0]heptane and cyclohex-2-en-1-one. These compounds were further transformed.

Kinetic Parameters

The kinetic parameters used for the discussion of the course of the photo-oxidation on different types of titania catalysts are given in Table II. Besides the conversion of cyclohexene (x , conversion achieved) and the initial reaction rate r_0 , two types of selectivities and yields were introduced. S_e^1 and S_e^2 were defined at $x = 50\%$ as the amount of cyclohex-2-en-1-one relative to the overall amount of other intermediates and that of 7-oxabicyclo[4.1.0]heptane also relative to the total amount of other intermediates, respectively. Yields Y^1 and Y^2 reflect the final composition when the reaction was terminated (zero reaction rate, typically at $t = 400$ min) for the same compounds. This time, however, all products were included (reaction intermediates, carbon dioxide and water). The unreacted cyclohexene was not included to the calculation of these parameters.

From the series of the tested catalysts, only SG3 afforded to achieve a total conversion of cyclohexene. Other catalysts were deactivated, which is discussed later. Initial activity (r_0 values) of all the catalysts prepared by the sol-gel process was generally very high (SG1, SG2, SG3). In contrast, the Degussa catalysts (P-25, D-7701, D-7702) were, not surprisingly, due to their low surface area, much less active. Particularly in this group, it is evi-

TABLE II
Kinetic parameters

Catalyst	x %	S_e^1 wt.% ^a	S_e^2 wt.% ^b	Y^1 wt.% ^a	Y^2 wt.% ^b	r_0 mmol g _{cat} ⁻¹ min ⁻¹
D-7701	74	37	13	26	10	2.3
D-7702	70	39	22	28	19	1.7
P-25	24	–	–	10	9	2.9
S-7001	60	42	13	32	7	1.6
SG1	72	22	33	14	24	14.2
SG2	83	17	45	12	34	19.9
SG3	99	12	59	9	45	32.8

^a Superscript 1 for cyclohex-2-en-1-one. ^b Superscript 2 for 7-oxabicyclo[4.1.0]heptane.

dent that the photoactivity may also depend on the content of the anatase form. The two anatase-rich samples (P-25, D-7701) were more active than D-7702 with 60% of rutile. A typical course of the reaction is demonstrated in Fig. 5 for D-7702. The catalyst S-7001 did not follow this trend. Amazingly, this anatase-rich sample (S-7001), with a relatively high surface area, was the least active catalyst. On the other hand, all the SG catalysts (also pure anatase forms) revealed a notable photoactivity.

The crystallographically mixed samples (rutile/anatase) were more selective for cyclohex-2-en-1-one. In this context the highest yield was achieved on the rutile-richest catalyst D-7702 for the group of Degussa TiO_2 . S_e values were not evaluated for the P-25 catalyst since $x = 50\%$ was not achieved. It was that one suffering most seriously from the deactivation. An extraordinary position for the low-active, pure-anatase S-7001 appeared again. It was identified as the most selective catalyst for this intermediate ever observed (cyclohex-2-en-1-one). The selectivity S_e^1 of 42% was recorded, despite its low activity. The SGs were not too selective for this intermediate. On the other hand, a significantly preferential formation of 7-oxabicyclo[4.1.0]heptane was apparent on all of them. The S_e^2 value for SG3 was nearly 60% and the corresponding yield 45%. Also the two remaining SGs could be referred to as catalysts directing the partial oxidation reaction through the initial epoxide stage.

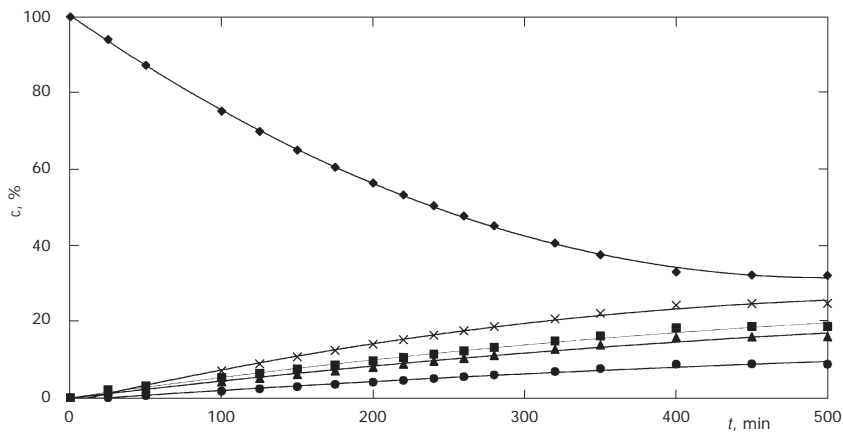


FIG. 5

Partial photooxidation of cyclohexene on D-7702. ♦ Cyclohexene, × cyclohex-2-en-1-one, ■ 7-oxabicyclo[4.1.0]heptan-2-one, ▲ 7-oxabicyclo[4.1.0]heptane, ● 7-oxabicyclo[4.1.0]heptan-2-ol

Deactivation

As mentioned, all catalysts, except SG3, suffered from deactivation. Elimination of this phenomenon, causing termination of the reaction, was rather complicated and sustained even a doubled load of a catalyst (Fig. 6). Infrared spectroscopy revealed a strong and increasing surface hydroxylation of titania withdrawn from the reaction. This is characteristic feature of anatase, which is, to a certain extent, also responsible for its enhanced photoactivity. Nevertheless, the surface water over-saturation could manifest a completely opposite effect – deactivation. Water molecules formed as products of the total oxidation are selectively trapped on the anatase surface, due to its strong affinity to water, and then act there in active species blocking. The anatase-richest P-25 from the group of low-surface-area catalysts was affected most seriously. IR spectra also supported the notion that cyclohex-2-en-1-one is a very strongly adsorbed surface species and thus also potentially responsible for the loose of activity. As seen in Table II, all reactions selective for this intermediate suffer more from the deactivation.

Attempts were made to reactivate thermally the used catalysts. TGA curves of two samples of P-25 (fresh and used) evidenced that above the 773 K no thermal desorption appears. Also, an initial “bump” corresponding to the dehydroxylation is well apparent. The used P-25 was treated at 773 K in air for three hours and then used in the standard photooxidation experiment. The achieved conversion of cyclohexene was nearly identical

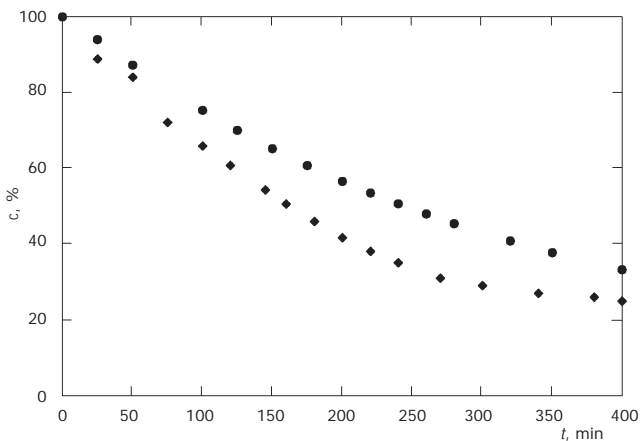


FIG. 6

Effect of the increased loading of a catalyst. ◆ 2 g of D-7702, ● 1 g of D-7702

with that of the fresh catalyst. A little lower initial activity was caused by an insignificant change in the rutile content during the thermal treatment.

Other Factors

For the sake of completeness, the exigency of the presence of oxygen, catalyst and UV light were tested. Standard experiments for the group of Degussa catalysts were carried out first in nitrogen instead of oxygen. A limited formation of some of the oxidation intermediates was found, arising probably from TiO_2 lattice oxygen (O^{2-}). When this source was expended, the reaction stopped. The highest conversion achieved was $x = 9.8\%$ for D-7701. According to very low values of Y and the mass balance calculations, the reaction in such an arrangement proceeded significantly to carbon dioxide and water. It was interesting that among the partially oxidised intermediates those with the epoxide grouping were completely missing.

Some effort has also been spent to describe the progress of the reaction without any catalyst, only with oxygen, UV and cyclic alkene. Cyclohexene was not found completely photo-inactive; however, its attained conversion was only 3%. Besides some water and CO_2 , only 7-oxabicyclo[4.1.0]heptane was formed. Synthetically, there is no practical reason to utilise this arrangement. Due to low temperature of the experiments (293 K) no thermal decomposition of cyclohexene and reaction intermediates was observed.

Finally the UV source was excluded from the system and the experiments were carried out as standard catalytic oxidations (not photooxidation) on P-25 and SG3. Negligible transformation of cyclohexene for both catalysts was observed, obviously suggesting the indispensable role of UV in formation of active surface species on titania.

CONCLUSION

Partial UV photooxidation of cyclohexene under ambient conditions on various types of titania was identified as a suitable system for synthesis of some valuable intermediates. Special attention was paid to cyclohex-2-en-1-one and to 7-oxabicyclo[4.1.0]heptane. Formal reaction schemes were suggested, reflecting different reaction pathways. The reaction selectivity profiles were dependent, to a certain extent, on structural properties of the used catalysts. On the basis of a series of experiments, the existence of surface-active species on titania could be envisaged. Their formation is substantially dependent on the presence of oxygen, UV illumination and also surface hydroxylation. On the other hand, extensive surface coverage with

water and very strong adsorptivity of cyclohex-2-en-1-one may cause the generally observed deactivation. The found differences of the proportion between the yields of photoproducts (cyclohex-2-en-1-one to 7-oxabicyclo[4.1.0.]heptane) ascribed to the different surface properties of particular photocatalysts, could also actually reflect the proportion between reaction rates of two parallel running photoprocesses, *i.e.*, the photocatalytic oxidative degradation (leading to cyclohex-2-en-1-one and other intermediates) and the direct photooxidation (producing mainly 7-oxabicyclo[4.1.0.]heptane).

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