Journal of Catalysis **203,** 516–524 (2001)
doi:10.1006/jcat.2001.3365, available online at http://www.idealibrary.com on IDEAL®

Flame Made Titania/Silica Epoxidation Catalysts

Wendelin J. Stark,*,† Sotiris E. Pratsinis,* and Alfons Baiker†,[1]

**Laboratory of Process Engineering, ETH Zentrum, CH-8092 Zurich, Switzerland; and †Laboratory of Technical Chemistry, ETH Hönggerberg–HCI, CH-8093 Zurich, Switzerland*

Received May 30, 2001; revised July 23, 2001; accepted July 23, 2001

Flame aerosol technology has been used to prepare titania/silica mixed oxide nanoparticles. A stream of argon containing evaporated hexamethyldisiloxane and titanium-tetraisopropoxide was brought into a methane–oxygen diffusion flame. Upon condensation, nanoparticles of titania/silica with high titania dispersion were formed. The powders were characterized using transmission electron microscopy, nitrogen adsorption, pore size analysis, laser-assisted ion-coupled plasma mass spectroscopy, UV–VIS spectroscopy, and diffuse reflectance IR spectroscopy. The powders consisted of agglomerates of primary particles from 10 to 20 nm in diameter at high oxygen-to-methane ratios in the flame. The morphology changed to larger, spherical particles when low oxygen-to-methane ratios were used. The catalytic materials were tested for the epoxidation of 2-cyclohexenol by *tert*.-butylhydroperoxide at 90°C. The activity and selectivity were investigated as a function of flame parameters used for catalyst preparation. The flame made catalysts showed better selectivity for the epoxidation than corresponding aerogels, but at lower activity. Epoxidation selectivity referred to TBHP reached 93%, whereas olefin selectivity was 83% at 80% conversion. The best catalytic performance was obtained with nanoparticles containing 1 to 3.2 wt% titania. The rate and selectivity achieved with the flame made catalysts were independent of the oxygen-to-methane ratio in the flame at high oxygen flow rate, whereas at low oxygen flow rate the activity and selectivity decreased considerably.

Key Words: **flame aerosol synthesis; titania; silica; nanoparticles; epoxidation; 2-cyclohexenol; *tert*.-butylhydroperoxide.**

1. INTRODUCTION

Since the development of the first heterogeneous titania/silica catalyst for the epoxidation of olefins by Shell in 1971 (1, 2), a series of new preparation methods were developed to synthesize materials containing highly dispersed titanium centers in a silica matrix. However, the use of the most prominent representative, titanosilicalite (TS-1) (3), is limited by inherently small pore size and only relatively few substrates can be oxidized readily. The search for alternative systems with larger pores such as zeolite beta or MCM type silicalites (4, 5) is therefore of great technical importance. Deposition or anchoring of Ti sites on silica circumvents the steric problem by avoiding narrow channels. Catalysts prepared by sol-gel (6–8) or grafting methods (9) contain accessible immobilized Ti within the silica framework. Since high specific surface area is obtained and the resulting porous structure is very open, larger substrates can access the active sites. Better accessibility, however, may be obtained by using small spheres having the active component on the surface. In this arrangement, the pore diffusion is limited to interparticle diffusion and no size selection takes place. In search of a preparation method that would produce this geometric arrangement and a high surface concentration of the active site, i.e., isolated Ti within a silica environment, we investigated the preparation of titania/silica catalysts by flame aerosol synthesis.

In general, flame aerosol synthesis is a cost-effective and versatile process for the controlled production of ceramic nanoparticles (10, 11). In flame reactors, the energy of a flame is used to drive chemical reactions of precursor compounds that result in the formation of clusters which further grow by coagulation and sintering in the hot flame environment to nanometer-sized product particles (11). Silica, titania, and carbon black nanoparticles are commercially produced in aerosol flame reactors at rates of several hundred metric tons per day (11). Ulrich (12) suggested the use of aerosols for catalytic applications in 1984, but to our best knowledge, no research was undertaken yet to test the catalytic potential of flame made titania/silica nanoparticles for selective catalytic oxidation. We recently reported the flame synthesis of vanadia/titania nanoparticles and found excellent activity for the SCR of NO by ammonia (13).

A pronounced mixing gap in the phase diagram of titania/silica (14) shows that titania barely enters the silica phase. This indicates the possibility to cover silica by single titania clusters using a gas phase process. In this work, we achieved this by bringing volatile silicon and titanium containing precursors into a methane–oxygen flame. Flame aerosol synthesis is shown to be excellently suited for the preparation of liquid phase epoxidation catalysts.

---

[1] To whom correspondence should be addressed. E-mail: baiker@tech.chem.ethz.ch. Fax: +411 632 11 63.

0021-9517/01 $35.00

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

A coflow-diffusion burner is used for aerosol synthesis of titania/silica nanoparticles. The experimental setup is shown in Fig. 1. It is similar to the setup used for the preparation of vanadia/titania, reported recently (13). The reactor consisted of three concentric stainless steel tubes with inner diameters of 2.5, 4.0, and 5.5 mm and a wall thickness of 0.3 mm. An argon stream of 1 L/min carrying the precursor vapor was introduced through the center tube; methane flowed through the inner annulus at a rate of 0.5 L/min, while oxygen was provided through the outer annulus, resulting in a simple diffusion flame (15). Experiments were performed with oxygen flow rates of 2 to 10 L/min. All gases (Pan Gas, purity >99.999%) were delivered from cylinders with the flow rates being monitored by calibrated mass flow controllers (Bronkhorst EL-Flow F201). Mixtures of titanium-tetraisopropoxide (TTIP, Aldrich, >97%, distilled under vacuum prior to use) and hexamethyldisiloxane (Fluka, purum, >99%, distilled over liquid sodium prior to use) were prepared and stored under argon. The mixture was fed to an evaporator (Bronkhorst CEM 100W) at a flow rate of 13 g/h controlled by a liquid mass flow meter (Bronkhorst Liqui-Flow L1) and vaporized into the argon stream. Evaporator, precursor delivery tubes, and the burner were heated to 150°C to prevent condensation of the precursor vapor. The flame was surrounded by a quartz chimney (glass cylinder, i.d. = 140 mm) to achieve a stable flame. A stainless steel filterholder with a glass fiber filter (Whatman GF/A) was mounted on top of the cylinder. Product particles were collected on the filter with the aid of a vacuum pump (Vacuubrand RE 5). Nanoparticles were produced in runs of 5 min, each yielding around 500 mg of powder. Each experiment was reproduced at least twice. The different materials are designated as *x*Ti*z*, where *x* denotes the weight fraction of titania and *z* is the oxygen flow rate applied in L/min.

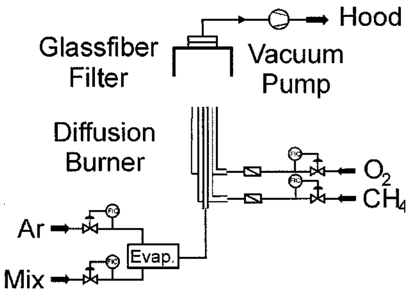

FIG. 1. Experimental setup of the flame aerosol synthesis unit. A precursor mix is brought into an evaporator (bottom) and fed into the center of a methane–oxygen flame. Product particles are collected on top of a glass fiber filter.

2.2. *Catalyst Characterization*

Specific surface area and isotherms. The specific surface of the collected powders was analyzed by nitrogen adsorption at 77 K using the BET method (Micrometrics GEMINI 2360). The results were cross-checked by recording a full adsorption isotherm (Micrometrics ASAP 2010 Multigas system).

Transmission electron microscopy (TEM). The TEM investigations were performed with a CM30ST microscope (Philips; LaB_6 cathode, operated at 300 kV, point resolution ~2Å). Particles were deposited onto a carbon foil supported on a copper grid.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). LA-ICP-MS was used to determine the elemental composition of a representative sample of several catalyst. A 193-nm Excimer laser system (GeoLas, MicroLas, Göttingen, Germany) coupled to a ICP-MS (ELAN 6100, Perkin Elmer, Norwalk, MA), extensively described in (16), has been used in standard mode to determine the Ti and Fe concentrations. The samples were ablated under helium atmosphere using a 60-μm crater diameter at a repetition rate of 10 Hz. External calibration was carried out using the reference glass 612 from NIST and Si was used as internal standard for quantification.

UV–VIS spectroscopy. UV–VIS diffuse reflectance spectra measurements were performed on a Perkin Elmer Lambda 16 spectrophotometer equipped with a 76-mm integrating sphere using $BaSO_4$ as a reference. The samples were analyzed under ambient conditions or preheated to 600 K for 1 h, sealed, and cooled down to room temperature. The reflection in percentage was measured and presented by the Kubelka–Munk function.

Diffuse reflectance IR Fourier transform spectroscopy (DRIFTS). The Ti-O-Si groups of dehydrated titania/silica powders were monitored by DRIFTS under argon. Spectra were recorded on an FTIR instrument (Perkin Elmer, Model 2000) containing a diffuse reflectance unit and a controlled environmental chamber equipped with two ZnS windows. The powdered sample was mounted on a ceramic frit (alumina) which could be heated to elevated temperature (here 573 K) via a PID controller (Tecon 501). Prior to measurements, the powders were outgassed in an Ar stream (Pangas, 99.999%; 5 ml/min) for 1 h at room temperature. Dehydration was performed under flowing argon at 573 K for 1 h. After the samples cooled, measurements were made by collecting 500 scans at a resolution of 4 cm^{-1}.

2.3. *Catalytic Studies*

The epoxidation reactions were carried out batchwise in a mechanically stirred, 50-ml thermostated glass reactor equipped with a thermometer, reflux condenser, and a septum for withdrawing samples. All reactions were performed

TABLE 1

Preparation Conditions, Specific Surface Areas, and Catalytic Performance in the Epoxidation of 2-cyclohexenol by TBHP

Sample	O_2 flow/ L min-1	Ti content wt%	S_{BET}[c]/ $m^2\ g^{-1}$	Initial rate[d]/ mmol $g^{-1}\ h^{-1}$	Rate (1 h)[e]/ mmol $g^{-1}\ h^{-1}$	S_{Peroxide}[f]/ %	S_{Chxol}[f]/ %
no cat				0	0	—	—
0Ti10	10	0[a]	293	0	0	—	—
0.5Ti10	10	0.35[a]	266	—	2.3	80	37
0.5Ti6	6	0.5[b]	180	—	0.5	—	—
1.2Ti10	10	0.83[a]	305	36	9.3	97	91
1.2Ti8	8	1.2[b]	193	27	8.5	97	87
1.4Ti10	10	1.19[a]	251	33	12.3	94	90
1.4Ti6	6	1.4[b]	226	30	12.9	97	90
1.6Ti10	10	1.31[a]	245	39	12.5	94	88
1.6Ti8	8	1.6[b]	195	38	11.9	92	90
1.6Ti6	6	1.6[b]	165	30	11.7	94	89
1.6Ti4.5	4.5	1.6[b]	175	34	10.8	88	91
1.6Ti3	3	1.6[b]	108	24	9.2	95	85
1.6Ti2	2	1.6[b]	67	24	5.5	81	82
1.1Ti10	10	1.07[a]	303	33	11.6	95	68
1.1Ti6	6	1.1[b]	184	30	8.9	97	60
100Ti6	6	100[b]	50	6	0.34	15	10
0.8Ti6	6	0.8[b]	105	18	5.1	70	79
0.8Ti10	10	0.8[b]	269	21	8.1	90	86
3.2Ti10	10	3.17[a]	239	100	14	96	90
10Ti10	10	10[b]	231	—	—	—	—
2Ti10	10	2[b]	308	30	12.1	94	86
1.6Ti10z[g]	10	1.35[a]	245	42	14.8	83	80

[a] Measured by LA-ICP-MS.
[b] Nominal content.
[c] Error ± 3%.
[d] Determined after 2 min reaction time, error ± 5%.
[e] Average rate after 1 h, error ± 2%.
[f] Selectivities at 50% conversion, error ± 3%.
[g] Zeolithe 4A is added to the reaction mixture.

under nitrogen (99.999%) to avoid the presence of oxygen or moisture. In a standard procedure, 100 mg of nanoparticles were predried *in situ* in the reactor under flowing nitrogen for 15 min at 423 K. After the samples cooled, 8.05 ml of toluene (Fluka, 99.8%, stored over molecular sieve 4A) as solvent and 0.5 ml dodecane (Fluka, 99%) as internal standard were added. The mixture was heated to 363 K and 1 ml of 2-cyclohexenol (Fluka, 99%) was injected. The reaction was started by introducing 0.45 ml *tert.*-butylhydroperoxide (TBHP, Fluka, 5.4 M in decane, stored over molecular sieve 4A). The total reaction volume was 10 ml. For leaching experiments, 2 ml of the reaction mixture were filtered hot through a dry, preheated membrane filter (pore diameter 0.2 μm). The filtrate without catalyst was kept at 90°C and the concentrations of all species were monitored as for normal runs. Tests for Ti leaching were carried out for reaction mixtures after 50 and 70% peroxide conversion. The mixtures were analyzed using a HP 6890 gas chromatograph equipped with a cool on-column inlet and a HP-FFAP capillary column. Products were identified by GC-MS and by comparison with authentic samples. In all runs, the internal standard method was used to quantitatively analyze all components. The TBHP conversion was monitored by GC and iodometric titration using a Metrohm 686 Titroprocessor. The epoxide selectivity, related to the olefin consumed, S_{Chxol}, and the peroxide selectivity, S_{perox}, related to the consumed TBHP are calculated as

$$S_{\mathrm{Chxol}}(\%) = 100\{[\mathrm{Epoxide}]/([\mathrm{Chxol}]_0 - [\mathrm{Chxol}])\},$$
$$S_{\mathrm{perox}}(\%) = 100\{[\mathrm{Epoxide}]/([\mathrm{TBHP}]_0 - [\mathrm{TBHP}])\},$$

where the subscript 0 stands for the initial value and all concentrations are expressed on a molar basis. The rates of epoxide formation and the corresponding selectivity were compared after 2 min and after 1 h (Table 1).

3. RESULTS

Titania/silica nanoparticles with different titania content were produced in methane–oxygen diffusion flames. The influence of the preparation conditions on the material properties was investigated as a function of the oxygen flow rate in the flame. Table 1 gives an overview of the samples produced, listing composition, preparation conditions,

TABLE 2

Major and Trace Element Concentrations Determined by LA-ICP-MS

Sample	TiO_2/wt%	Fe/μg g^{-1}
0Ti10	0.0001[a]	3.1
0.5Ti10	0.35 ± 0.004	3.4
1.2Ti10	0.83 ± 0.01	1.8
1.4Ti10	1.19 ± 0.01	8.5
1.6Ti10	1.31 ± 0.015	2.5
1.1Ti10	1.07 ± 0.02	3.2
3.2Ti10	3.17 ± 0.02	3.9

[a] Limit of detection.

and catalytic data. Powders with no titania (0Ti10) and up to 10 wt% TiO_2 were synthesized using 2 to 10 L O_2/min. Table 2 lists the chemical composition of these materials as determined by LA-ICP-MS. The measured titania content is somewhat below the nominal content given by the composition of the precursor mixture. All powders contained traces of iron. Transient signal data acquisition indicated a homogeneous distribution of Si, Ti within all samples. Depending on the flame structure, powders with different morphology were obtained. Figure 2 shows a transmission electron micrograph of a titania/silica catalyst prepared in an oxygen rich flame (sample 1.3Ti10). The powder consisted of agglomerates of primary particles of 10 to 20 nm in diameter. Figure 3 shows a TEM image of spherical particles of 30 to 80 nm prepared at a low oxygen flow rate (sample 1.0Ti2). No crystalline domains were detectable. The mass flow rate of the precursor was kept constant over all experiments to assure similar enthalpy delivery into the flame, ensuring constant preparation conditions for all samples.

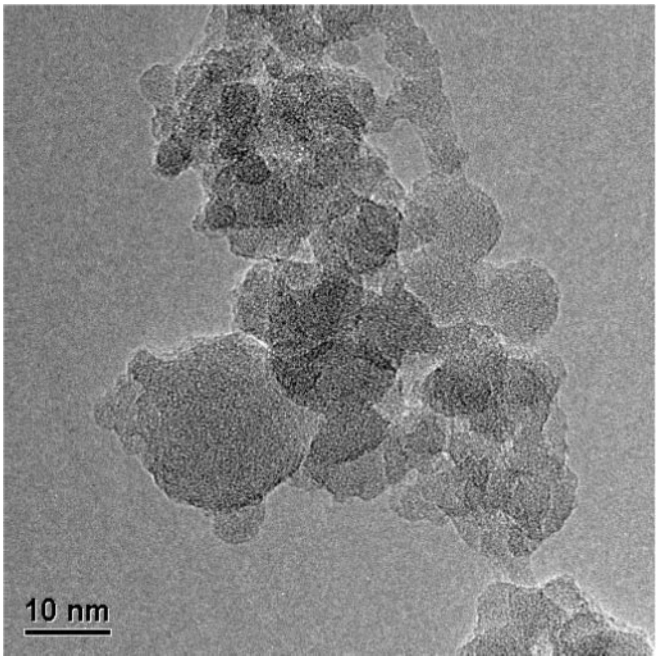

FIG. 2. Transmission electron micrograph of silica with 1.3 wt% titania prepared in a fast, oxygen rich flame (10 L O_2/min). The material consists of irregular agglomerated nanoparticles with no crystalline areas.

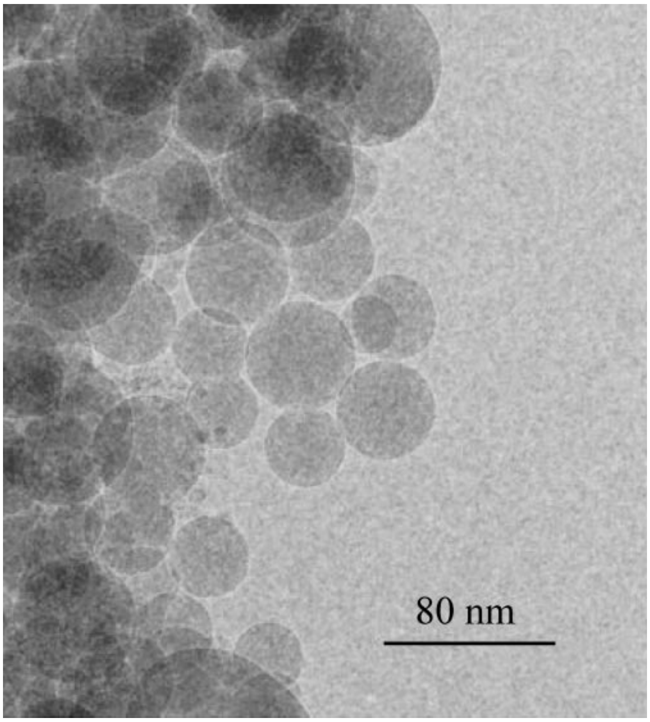

FIG. 3. Transmission electron micrograph of silica with 1.3 wt% titania prepared in a slow, stoichiometric flame (2 L O_2/min). The material consists of regular spherical particles with no crystalline areas.

Figure 4 depicts the isotherm of a typical catalyst (sample 2Ti10). According to IUPAC nomenclature, it may be

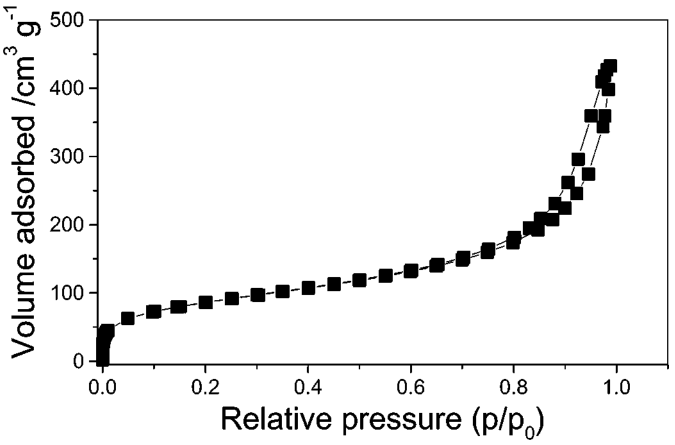

FIG. 4. Isotherm of a typical catalyst (2Ti10). According to IUPAC, it can be classified as a type IV isotherm. The powders are nonporous, the micropore content probably stems from agglomeration.

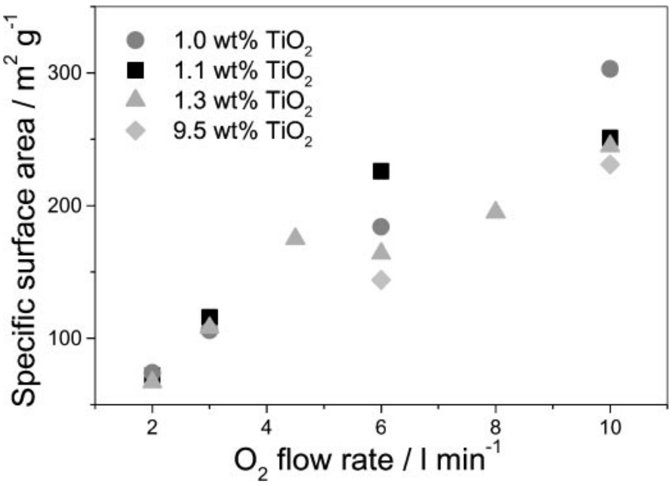

FIG. 5. Specific surface area for silica powders containing different amounts of titania as a function of oxygen flow rate during flame synthesis. Low O_2 flow rates result in long flames and long particle residence times at high temperature. The specific surface is independent of the composition. The latter greatly influenced the specific surface area at high oxygen flow rate that produces short flames and particle residence times.

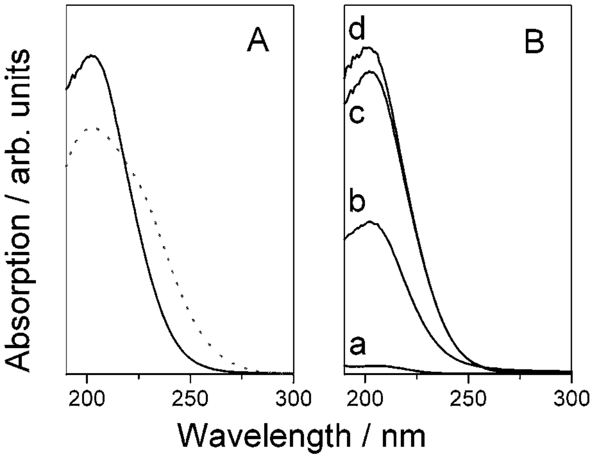

FIG. 6. (A) UV-VIS spectra of 1.1 wt% titania on silica before (dashed) and after dehydration at 300°C (full line). The shift to lower wavelength indicates the loss of OH groups from the Ti center. (B) UV–VIS spectra of dehydrated samples containing increasing amounts of Ti: (a) no Ti, (b) 0.35 wt%, (c) 1.1 wt%, and (d) 1.3 wt% titania on silica, produced at 10 L O_2/min.

classified as a type IV isotherm with a weak hysteresis and indicates only marginal micropore content which may stem from agglomeration. The specific surface area of these mixed oxide nanoparticles strongly depends on the synthesis conditions. Figure 5 shows the BET specific surface area of different powders as a function of the oxygen flow rate used in the preparation. The specific surface in low oxygen flames was independent of the titania content. High oxygen flow rates lead to high specific surface for all powders, but significant differences appeared for changing compositions. Pure silica obtained in a 10-L flame yielded 300 m^2/g, while adding 1.3 wt% titania decreased the specific surface to 250 m^2/g. Pure titania (100Ti6) had a much lower specific surface area, a 6-L flame produced materials with only 50 m^2/g. Pure silica samples showed a specific surface of 180 m^2/g under the same conditions.

The powders were investigated spectroscopically using UV–VIS and DRIFTS. Figure 6A shows the UV–VIS spectra of a typical flame made titania/silica catalyst before and after dehydration at 300°C in the spectral range from 190 to 300 nm. In Fig. 6B, the UV–VIS spectra of catalysts prepared at 10 L O_2/min are shown for increasing titania contents. Pure silica (a) showed no pronounced absorption between 190 and 300 nm. Addition of 0.35 wt% titania led to a strong absorption signal at 212 nm. Further increasing the titania content resulted in a stronger signal but no shift in wavelength was observed. Pure silica itself does not show any transition between 190 and 400 nm which agrees with its high band gap. The peak at 212 nm was assigned to both isolated [TiO_4] or [$TiO_3(OH)$] tetrahedral units (17, 18). The absence of a signal around 360 nm due to anatase corroborates the findings of the TEM where no traces of anatase were detectable. The band around 240–260 nm, responsible for the appearance of a broad shoulder in Fig. 6A, is generally attributed to Ti(IV) in an octahedral environment (19). The spectra in Fig. 6B measured for samples with increasing titania content corroborate proper incorporation of titania in the materials. Figure 7 shows the DRIFTS spectra of samples with increasing titania content in the range of 800 to 1050 cm^{-1}. Pure silica (Fig. 7A) showed no absorption signal around 960 nm. A sample containing 0.8 wt% titania (Fig. 7B, sample 1.2Ti2) gave rise to a weak signal at 960 nm, indicating the presence of some Ti-O-Si units. The same band appeared more pronounced in catalyst

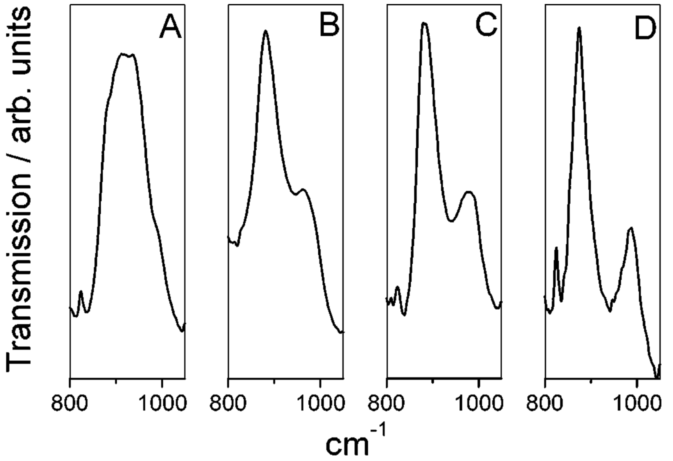

FIG. 7. DRIFT spectra for silica containing no Ti (A), 0.9 wt% TiO_2, slow flame (B), 1.3 wt% TiO_2, fast flame (C), and 3.2 wt% TiO_2 (D). The 960 cm^{-1} absorption (Ti-O-Si) grows for increasing titania contents and correlates qualitatively with catalytic activity.

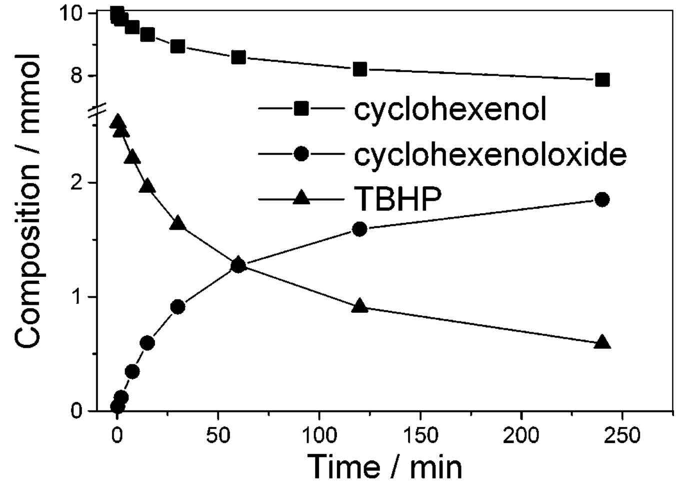

FIG. 8. Composition of the reaction mixture over the course of an epoxidation reaction (catalyst 1.6Ti6). The TBHP is used as a limiting reactant.

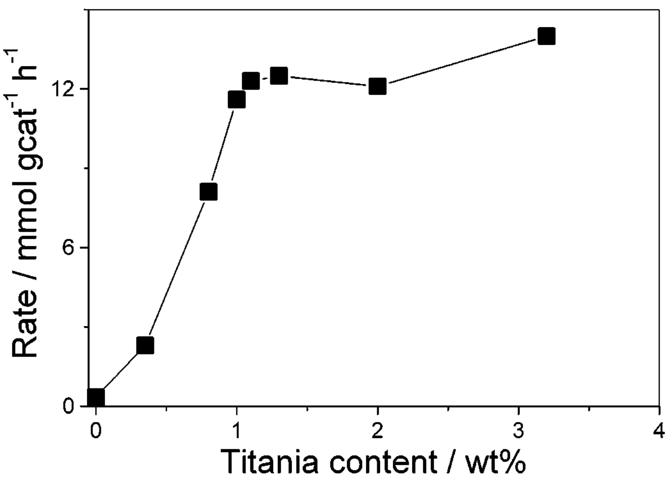

FIG. 9. Epoxidation rate as a function of the composition of materials prepared under constant flame preparation conditions. Samples were prepared with 10 L O_2/min yielding a specific surface from 250 to 300 m^2/g. A sharp drop is visible below 1 wt% titania.

1.6Ti8, containing 1.3 wt% titania (Fig. 7C). Nanoparticles containing 3.2 wt% titania (Fig. 7D, sample 3.2Ti10) produced a broad signal at 960 nm, indicating a high density of Ti-O-Si units in the powder.

The influence of composition and preparation conditions of different titania/silica mixed oxide catalyst on the activity for the demanding epoxidation of 2-cyclohexenol by TBHP (20) was investigated. Table 1 lists the initial epoxidation rate, epoxidation rate after 1 h, epoxide selectivity with respect to TBHP (S_{perox}), and cyclohexenol (S_{Chxol}) of a series of catalysts as a function of composition and oxygen flow rate used in the preparation. Conversion of the reactants, olefin and peroxide, as well as the product, 2,3-epoxy-cyclohexenol, were followed for 4 h. Figure 8 depicts a typical concentration profile over the course of an epoxidation reaction (sample 1.6Ti6). The peroxide is used as a limiting reactant and its initial concentration of 2.5 mmol decreases to less than 0.8 mmol. At the same time, 2-cyclohexenol decreases from 10 to about 8 mmol. The formation of the product epoxide is initially very fast and slows down over the course of the reaction as expected for a first-order reaction with respect to peroxide consumption. Sample withdrawal did not much affect the volume of the batch reactor, since nine samples of 0.1 ml were taken out of 10 ml overall. As a byproduct typically less than 10% of cyclohexenone could be detected. No other volatile compounds were found in significant amounts and the carbon balance can be closed.

Figure 9 shows the rate of epoxide formation after 1 h as a function of titania content. A pronounced increase in activity was found for powders containing up to 1.1 wt% titania. Further increasing the titania content led to similar activity. At 1 wt% titania content, up to 13 mmol of the epoxide were formed per gram catalyst and hour. Addition of Zeolite 4A to the reaction mixture, which proved to be beneficial in earlier experiments with aerogels (21), did not show a significant improvement with flame made catalysts (Table 1, 1.6Ti10z). This corroborates the dehydrated state of flame made catalysts. For most catalysts containing 1 to 3.2 wt% titania, the selectivity of the reaction with respect to peroxide consumption S_{perox} was above 90%, the selectivity toward cyclohexenol consumption S_{Chxol} was above 85%. In the case of 1.2Ti10, the selectivity increased to $S_{\text{perox}} = 97\% \pm 3\%$ and $S_{\text{Chxol}} = 90\% \pm 2\%$. The leaching behavior of flame made catalyst was tested following a procedure described by Sheldon *et al.* (35). The filtrate of a reaction mixture at 50 or 70% conversion was kept at 90°C, but no more changes in epoxide concentration occurred.

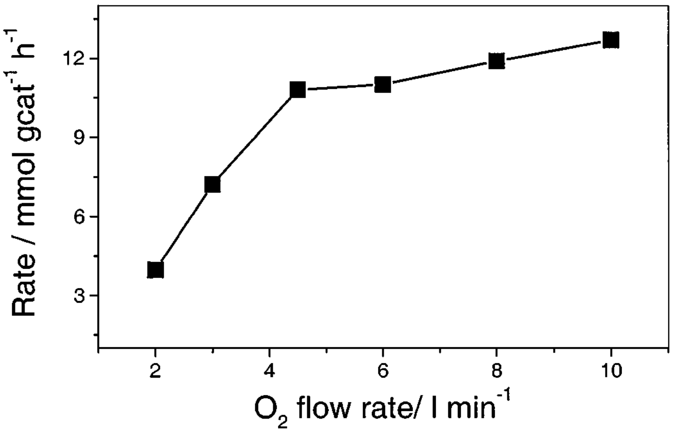

FIG. 10. Epoxidation rate as a function of oxygen flow rate during catalyst preparation for a fixed composition of 1.3 wt% titania. The activity is almost constant at high flow rates but drops for long and hot flames.

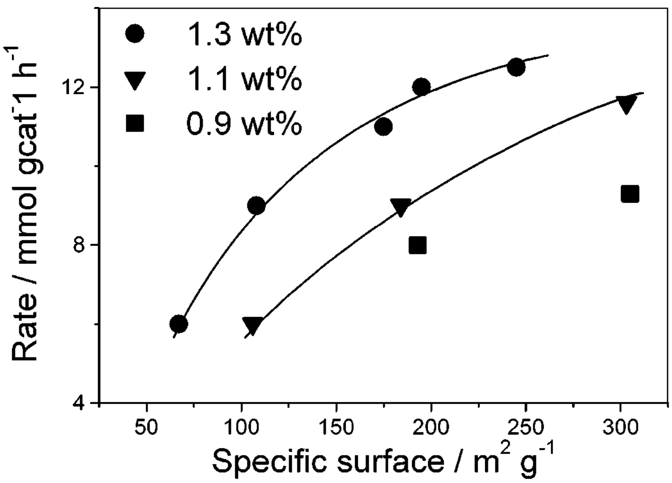

FIG. 11. Epoxidation rate as a function of the BET surface area for different compositions. Increasing the specific surface area leads to enhanced activity. At low Ti content, the rate is limited by the available Ti, and additional surface cannot improve the rate.

Figure 10 depicts the rate of epoxide formation after 1 h for catalysts prepared in different flames. At high oxygen flow rates, above 6 L O_2/min, the reactivity was not much influenced by the flame conditions. A pronounced drop in activity was found when lowering the oxygen flow rate to 2 L/min. Similar activity and selectivity were observed up to a titania content of 3.2 wt%. Figure 11 depicts the rate for samples with different Ti contents as a function of the BET surface area. The changes in rate as a function of surface were more prominent for the sample with 1.3 wt% titania compared to the samples with lower titania contents. This behavior indicates that the high surface area materials prepared by flame aerosol synthesis can host more than 1 wt% titania in the form of active isolated titania species. At higher loading, the formation of titania clusters, exhibiting considerably lower activity, is likely to occur. At high titania content (sample 10Ti10, Table 1), the activity behavior changed drastically. A high dehydration activity was observed at the beginning of the reaction, consuming large amounts of cyclohexenol. The corresponding dienolether, di-(2-cyclohexenyl)ether, formed rapidly. The addition of TBHP reduced the dehydration activity, but epoxide formation rates were much lower.

4. DISCUSSION

The morphology of flame made titania/silica nanoparticles strongly depends on their synthesis conditions. High oxygen flow rates during preparation lead to short flames and low residence time of oxidic constituents. Excess oxygen accelerates the burning process but also cools the flame. The oxide vapor condenses extremely fast resulting in particles in the diameter range from 10 to 20 nm. These primary particles stick together, sinter partially, and form large aggregates (Fig. 2). Low oxygen flow rates lead to long and hot flames. No additional oxygen has to be heated up. The oxidation is slow and controlled by the mixing process in the flame. Particle formation proceeds again as above, but since the flame is long and hot, initially formed particles have time to collide and due to the high temperature, they fully coalesce leading to bigger and spherical particles. This mechanism is active throughout the hot part of the flame and finally leads to particles as large as 80 nm (Fig. 3). The specific surface, determined by the mean size of the nonporous particles, is independent of the composition of the mixed oxide at low oxygen flow rates (Fig. 5). Here, the long collision and sintering process is the dominant factor determining the size. At high oxygen flow rates, the particle formation process is short, no larger particles can be formed. The number of small primary particles depends on the composition of the gas since silica and titania have an individual nucleation behavior. The flame is quickly depleted from oxide vapor and the specific surface is controlled over this complex process in the early stage of the flame. The additional oxygen takes up energy from the combustion and the resulting lower temperature favors agglomerated, irregular particles (Fig. 2) since sintering is too slow to form spherical particles.

Epoxidation activity (Table 1) was observed for silica powders with 0.5 to 3.2 wt% titania, at higher titania content, the formation of di-cyclohexenylether, an unwanted byproduct, is observed. This range of composition has already been found optimal for the Shell catalysts (22). Titanium silicalites such as TS-1 contain similar amounts of titania, typically less than 4 wt% (23). Aerogels can contain more titania and are found very active with up to 20 wt% titania (24). Isolated Ti sites within a silica matrix have been suggested to be the most active component in aerogel epoxidation catalysts (20, 25–28).

The appearance of a strong band at 960 cm^{-1} in the DRIFTS spectra (Fig. 7), the lack of anatase signals in UV–VIS (Fig. 6) and pertinent reflections in XRD, and the homogeneous structure uncovered by TEM (Figs. 2 and 3) are indicative of high Ti dispersion. Crystalline titania domains are well detected in TEM under the measurement conditions and can therefore be excluded (13). The phase diagram of titania/silica shows no mixing gap for bulk mixtures (14). Even though the flame aerosol process entails high temperature, the high surface of the nanoparticles leads to a different behavior: No separate titania crystallites are formed and titania is mainly found at the surface of the particle. The differences in the UV–VIS spectra for samples before and after dehydration (Fig. 6A) suggest that most titania is subject to hydration/dehydration processes and therefore not fully incorporated in the silica matrix. We assume that the predominant species in these powders is $[TiO_3(OH)_x]$ which agrees with the catalytic activity. Only at high titania loading, more acidic species

TABLE 3

Epoxidation of 2-cyclohexenol by TBHP or H_2O_2 with Different Titania/Silica Catalysts

Catalyst[a]	T/K	Conversion	S_{Perox}	S_{Olefin}	Reactivity[b]/ mmol g^{-1} h^{-1}	Ref.
Shell type, TTIP	r. t.	100	0[c]	0	after 24 h	(20, 36)
Shell type, $TiCl_4$	383	84	84	—	after 20 h	(20, 22)
Aerogel[d]	363	85	65	67	61	(37)
TS-1/H_2O_2	330	85	—	80	5.5	(20, 38)
3.2Ti10	363	50	96	88	14	—
		80	93	83		

[a] TBHP as an oxidant if not specified.
[b] After 1 h.
[c] Only ketones are formed.
[d] 20 wt% titania.

form as indicated by decreasing selectivity for low surface powders or significant byproduct formation in the case of a 10-wt% titania sample.

The epoxidation of 2-cyclohexenol forms two products: *cis*- and *trans*-2,3-epoxy-cyclohexenol (20). The ratio of the two diastereomers is a very sensitive tool to investigate the active site. This ratio is constant for most catalysts with 0.5 to 3.2 wt% titania, prepared at high oxygen flow rates. A 10% change is found for powders from hot flames and associated with increased acidity. This indicates that no major change in structure occurs over this range of experimental conditions.

The catalytic performance of several Ti-based materials have been compared in a recent review (20). Some representative epoxidation rates and selectivities are given in Table 3. The epoxidation rate referred to catalyst mass of flame made catalysts is lower than that of aerogels. However, the rate per surface area is similar. This similarity corroborates that the flame aerosol technique produces a surface similar to that in the sol-gel process and one may conclude that the active site is similar in both systems. The epoxidation activity of titania/silica catalysts was found to be sensitive to additives or pretreatment conditions: Klein and Maier (29) pointed out the importance of fine tuning the hydrophobicity of titania/silica catalysts. Tatsumi *et al.* (30) compared Ti-ß catalyst prepared by dry-gel conversion and by a hydrothermal method and attributed the enhanced selectivity of the former to its more hydrophobic character. Kochkar *et al.* (31) and Muller *et al.* (32) synthesized hydrophobic aerogels by introducing phenyl or methyl groups on the surface and observed increased selectivity for the epoxidation of cyclohexene and allyl alcohols. Dusi *et al.* (21) found that careful drying *in situ* prior to reaction significantly increased epoxidation selectivity. They assumed that drying reduced the Brønsted acidity by condensation of surface silanol groups. A different attempt to reduce the influence of acidic sites is the addition of an organic base (31, 33) or the use of weakly basic solvents such as acetonitrile (34). Since flame aerosol derived powders are generated at high temperature, the surface is likely to be poorly hydrated. As-prepared silica is almost inactive for TBHP decomposition as well as pure titania (both less than 5% conversion after 1 h). This is in agreement with the mechanism involving directly Ti-O-Si units. The good selectivity of the flame made powders is attributed to a homogeneous titania distribution on the surface. Low hydration leads to low Brønsted acidity and therefore to reduced peroxide decomposition. The absence of epoxide formation in the reaction mixture after the catalyst is removed by filtration indicates that no significant leaching takes place in these catalysts under reaction conditions and corroborates the stability of the flame made catalysts.

Competing oxidation of the alcoholic OH function of cyclohexenol leads to cyclohexenone, the major byproduct of the reaction. High specific surface area samples such as 1.6Ti10 produce only 6.6% ketone, while the corresponding low surface samples 1.6Ti2 affords 13.4% ketone. That means that the selectivity with respect to C=C bond attack for 1.6Ti10 is above 97%. No dimer formation, resulting from the dehydration of cyclohexenol, can be detected for these catalysts. This further corroborates the low Brønsted acidity of these samples. The activity per mass is a function of the specific surface area (Fig. 11). The surface takes up a certain amount of Ti that is very active, but further increasing the Ti concentration does not change the activity. The additional Ti probably stays rather inactive at the surface in the form of condensed species. As a consequence, the catalytic behavior is not greatly affected by this decrease in surface area.

5. CONCLUSION

The flame aerosol method has been successfully applied for synthesis of titania/silica epoxidation catalysts. Materials with high selectivity for the epoxidation of 2-cyclohexenol by TBHP can be produced easily in oxygen rich methane flames. Powders are made up of agglomerated nonporous nanoparticles from 10- to 20-nm size. High titania dispersion was found for silica containing up to 3.2 wt% titania. Surface chemical properties and the overall catalytic behavior seem to be similar to corresponding sol-gel made materials. However, the flame made titania/silica shows improved efficiency with respect to peroxide and olefin consumption compared to corresponding aerogels. This behavior is traced to a more dehydrated state of the surface of the flame made material, resulting in lower Brønsted acidity and higher hydrophobicity.

ACKNOWLEDGMENTS

We thank Reto Strobel and Carsten Beck for help with the catalytic measurements, Professor Dr. Guenther (ETH) for the LA-ICP-MS and Dr. Frank Krumeich (ETH) for the TEM. Financial support granted by the ETH Gesuch Nr 19/01-1 is kindly acknowledged.

REFERENCES

1. Sheldon, R. A., Van Doorn, J. A., Schram, C. W. A., and De Jong, A. J., *J. Catal.* **31**, 438 (1973).
2. British Patent 1,079, C. A. reference 74, 12981M, 1971.
3. U.S.-Patent, C. A. reference 95, 206272k, 1983.
4. Corma, A., Navarro, M. T., and Pérez-Pariente, J., *J. Chem. Soc.-Chem. Commun.* 147 (1994).
5. Camblor, M. A., Corma, A., Martìnez, A., Pérez-Pariente, J., and Primo, J., *Stud. Surf. Sci. Catal.* **78**, 393 (1993).
6. Neumann, R., Chava, M., and Levin, M., *J. Chem. Soc.-Chem. Commun.* 1685 (1993).
7. Thorimbert, S., Klein, S., and Maier, W. F., *Tetrahedron* **51**, 3787 (1995).
8. Hutter, R., Dutoit, D. C. M., Mallat, T., Schneider, M., and Baiker, A., *J. Chem. Soc.-Chem. Commun.* 163 (1995).
9. Jorda, E., Tuel, A., Teissier, R., and Kervennal, J., *J. Chem. Soc.-Chem. Commun.* 1775 (1995).
10. Wooldridge, M. S., *Prog. Energy Combust. Sci.* **24**, 63 (1998).
11. Pratsinis, S. E., *Prog. Energy Combust. Sci.* **24**, 197 (1998).
12. Ulrich, G. D., *Chem. Eng. News* **62**, 22 (1984).
13. Stark, W. J., Wegner, K., Pratsinis, S. E., and Baiker, A., *J. Catal.* **197**, 182 (2001).
14. De Vries, R. C., Roy, R., and Osborn, E. F., *Trans. Brit. Ceram. Soc.* **53**, 531 (1954).
15. Pratsinis, S. E., Zhu, W. H., and Vemury, S., *Powder Technol.* **86**, 87 (1996).
16. Günther, D., and Heinrich, C. A., *J. Anal. Atom. Spectrom.* **14**, 1363 (1999).
17. Reddy, J. S., and Kumar, R., *J. Catal.* **130**, 440 (1991).
18. Geobbaldo, F., Bordiga, S., Zecchina, A., Giamello, F., Leofanti, G., and Petrini, G., *Catal. Lett.* **16**, 109 (1992).
19. Zecchina, A., Spoto, G., Bordiga, S., Ferrero, A., Petrini, G., Leofanti, G., and Padovan, M., *Stud. Surf. Sci. Catal.* **69**, 251 (1991).
20. Dusi, M., Mallat, T., and Baiker, A., *Catal. Rev-Sci. Eng.* **42**, Nos. (1 & 2), 213 (2000).
21. Dusi, M., Mallat, T., and Baiker, A., *J. Catal.* **173**, 423 (1998).
22. Wattimena, F., and Wulff, H. P., British Patent 1,249,079 (to Shell), 1971.
23. Taramasso, M., Perego, G., and Notari, B., U.S. Patent 4,410,501 (to Enichem), 1983.
24. Hutter, R., Mallat, T., and Baiker, A., *J. Catal.* **153**, 177 (1995).
25. Dutoit, D. C. M., Schneider, M., and Baiker, A., *J. Catal.* **153**, 165 (1995).
26. Klein, S., Weckhuysen, B. M., Martens, J. A., Maier, W. F., and Jacobs, J., *J. Catal.* **163**, 489 (1996).
27. Dutoit, D. C. M., Schneider, M., Hutter, R., and Baiker, A., *J. Catal.* **161**, 651 (1996).
28. Dutoit, D. C. M., Gobel, U., Schneider, M., and Baiker, A., *J. Catal.* **164**, 433 (1996).
29. Klein, S., and Maier, W. F., *Angew. Chem., Int. Ed. Engl.* **35**, 2230 (1996).
30. Tatsumi, T., and Jappar, N., *J. Phys. Chem. B* **102**, 7126 (1998).
31. Kochkar, H., and Figueras, F., *J. Catal.* **171**, 420 (1997).
32. Muller, C. A., Maciejewski, M., Mallat, T., and Baiker, A., *J. Catal.* **184**, 280 (1999).
33. Dusi, M., Mallat, T., and Baiker, A., *J. Catal.* **187**, 191 (1999).
34. Corma, A., Esteve, P., Martìnez, A., and Valencia, S., *J. Catal.* **152**, 18 (1995).
35. Sheldon, R. A., Wallau, M., Arends, I., and Schuchardt, U., *Acc. Chem. Res.* **31**, 485 (1998).
36. Cativiela, C., Fraile, J. M., Garcìa, J. I., and Mayoral, J. A., *J. Mol. Catal. A* **112**, 259 (1996).
37. Dusi, M., Mallat, T., and Baiker, A., *J. Mol. Catal. A* **138**, 15 (1999).
38. Kumar, R., Pais, G. C. G., Pandey, B., and Kumar, P., *J. Chem. Soc.-Chem. Commun.* 1315 (1995).