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Oxidation of Cyclohexene with Hydrogen Peroxide Using Zirconia–Silica Mixed Oxides: Control of the Surface Hydrophilicity and Influence on the Activity of the Catalyst and Hydrogen Peroxide Efficiency

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Zirconia–silica mixed oxides can be prepared by sol–gel under basic conditions to yield mesoporous solids. Surface modification with methyl groups is possible by addition of methyltriethoxysilane to the preparation mixture in an amount up to 80% of the silane precursor. The extent of methylation controls the surface area, the porosity, and the catalytic activity of the solids in the oxidation of cyclohexene with hydrogen peroxide to yield cyclohexandiol as the major product. An increase in surface methylation results in a fourfold increase in the specific activity and in up to 85% efficiency in the use of hydrogen peroxide. Use of *tert*-butylhydroperoxide as the oxidant is not viable, as catalysts lose almost completely their oxidation activity and it results in the almost complete decomposition of the oxidant. © 2002 Elsevier Science (USA)

Key Words: **zirconia–silica; sol–gel; oxidation; hydrogen peroxide; cyclohexene; surface hydrophilicity.**

INTRODUCTION

Amorphous mixed oxides made by sol–gel based on silica and containing transition metal oxides are becoming increasingly popular in heterogeneously catalyzed oxygen transfer reactions in the liquid phase using hydroperoxides (1–6). The demand for more environmentally acceptable methods in fine chemistry that allow elimination of common but otherwise hazardous or costly oxidants, such as organic peroxyacids, is pushing forward the use of cleaner oxidants like hydroperoxides (particularly hydrogen peroxide) under catalytic conditions (7–10). This in turn requires the development of new insoluble catalysts. With respect to crystalline materials such as TS-1, amorphous mixed oxides offer the advantage of better flexibility in terms of (i) composition, (ii) possible transition metals to be included, (iii) surface area and porosity, and (iv) the possibility of modulating their surface hydrophilicity. To date, TiO_2–SiO_2 has been the system that has been more successful and more widely investigated (11). One of the problems when dealing with mixed oxides in the liquid phase is their generally high hydrophilicity, which hampers the diffusion of organics inside the pores of the solid. This becomes a major hurdle that prevents the practical use of aqueous oxidants like hydrogen peroxide. Indeed, even with TiO_2–SiO_2, alkylhydroperoxides have been almost exclusively used as the oxidants at variance with TS-1.

The key issues for successful use of H_2O_2 with TS-1 (12) are (i) site isolation, (ii) low surface acidity, and (iii) hydrophobicity. With amorphous mixed oxides the first point can be adequately addressed using sol–gel synthetic techniques and keeping the transition metal content sufficiently low (13–15). The second and the third point may somehow be influenced by surface modification of the oxide through the use of organic groups. Some years ago Klein and Maier reported (14) that the reactivity of some microporous TiO_2–SiO_2 amorphous samples could be suitably controlled through appropriate methylation of the surface. This allowed the use of H_2O_2 for the epoxidation of olefins, and according to the authors (14), the surface polarity affected the reaction rate, the conversion, the selectivity, and the catalyst lifetime. Other efforts to explore different surface modifiers on TiO_2–SiO_2 were subsequently carried out by Mallat and Baiker and co-workers (16–18), and more recently by Deng and Maier (19), who thoroughly investigated the effect of methylation on activity and selectivity. Unfortunately, all studies dealt mainly with *t*-butylhydroperoxide as the oxidant, probably because the activity originally observed with H_2O_2 was rather modest (14).

We have recently reported (13) that some ZrO_2–SiO_2 mixed oxides made by sol–gel have been successfully employed for the oxidation of a variety of olefins with hydrogen peroxide to yield diols as the main product. Zr as the active site has been far less investigated with respect to Ti, probably because zirconium complexes are much less efficient than the corresponding titanium species in the oxidation of organic compounds with hydroperoxides as oxidants (20). On the other hand Zr(IV) is far less reducible than Ti(IV), a factor that should limit the decomposition of the oxidant. A major limitation with the above

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materials was found in their microporosity, which limited strongly both their activity and their efficiency in hydrogen peroxide consumption (13). In this work we wish to report a thorough study of the catalytic behavior of a new series of mesoporous samples, in which the effect of the surface hydrophilicity properties has been explored over a wide range by suitably changing the degree of surface methylation.

EXPERIMENTALS AND METHODS

Materials

The following metal alkoxides were used: zirconium propoxide (Fluka), tetramethoxysilane (TMOS), and methyltriethoxysilane (both from Aldrich). Oxidants were 35% hydrogen peroxide (Fluka) and *t*-BuOOH, 5.5 M, in decane (Fluka). Substrates were purchased from Fluka. All chemicals were purum or puriss grade and used without further treatment.

Methods

BET surface areas and pore size were determined with N_2 at −196°C on a Micromeritics ASAP 2000 apparatus.

X-ray powder diffraction analysis was performed using a Philips X'Pert diffractomer. Cu $K\alpha$ Ni-filtered radiation, a graphite monochromator, and a proportional counter with a pulse height discriminator were used. The diffraction patterns were measured step by step (0.05° in 2θ).

GC–MS measurements were performed on a Hewlett–Packard 5971 mass selective detector connected to a Hewlett–Packard 5890 II gas chromatograph.

Catalyst Preparation

The following general preparation procedure was used in most cases. Minor changes will be mentioned in the next section. To a 250-ml beaker were added TMOS, $MeSi(OEt)_3$ (when necessary), and $Zr(OPr)_4$ in the amounts necessary to achieve the appropriate compositions (Table 1). The precursors were dissolved in EtOH in order to achieve a solution corresponding to 100 g SiO_2/L and the mixture was stirred at room temperature. After 20 min a 30% ammonia solution was added so that the milliliters of NH_3 per mole $ZrO_2 + SiO_2$ ratio was 10/1. Then water was added in a H_2O/Si ratio = 6/1. With methylated samples a H_2O/Si ratio = 1/1 was sufficient to induce gelation, which in all cases occurred within 15–30 min. Gels were normally transparent and were aged for 96 h at room temperature. The different samples were dried at 110°C for 18 h. Where necessary the samples were calcined at 250 and 550°C in air for 2 h: gas flow, 30 ml/min; heating ramp, 5°C/min. A summary of the preparation parameters is shown in Table 1.

TABLE 1

Preparation Conditions of the Different Samples

Sample	Zr (wt%)	% Methylation[a]	Hydrolysis ratio	Heating temp. (°C)
ZrO_2–SiO_2	1	0	6/1	110
ZrO_2–$SiO_2$250	1	0	6/1	250
ZrO_2–$SiO_2$550	1	0	6/1	550
ZrO_2–SiO_2Me5	1	5	1/1	110
ZrO_2–SiO_2Me10	1	10	1/1	110
ZrO_2–SiO_2Me18	1	18	1/1	110
ZrO_2–SiO_2Me25	1	25	1/1	110
ZrO_2–SiO_2Me40	1	40	1/1	110
ZrO_2–SiO_2Me60	1	60	1/1	110
ZrO_2–SiO_2Me80	1	80	1/1	110
Zr2	2	0	6/1	250
Zr5	5	0	6/1	250
Zr10	10	0	6/1	250

[a] The percentage methylation is defined as the molar percentage (in moles) of $MeSi(OEt)_3$ with respect to the total Si precursor introduced.

Catalytic Oxidation Procedures

Catalytic reactions were performed in 10-ml glass vials. The catalyst (20 mg), cyclohexene (2 mmol), and 35% H_2O_2 (4 mmol) were placed in the vial under N_2 flow. The reaction vessel was sealed and placed in an oil bath at constant temperature, while agitation was ensured by an external magnetic stirrer. At the end of the reaction, the mixtures were cooled to room temperature and diluted with EtOH (20 ml), an internal standard was added (1.5 mmol dioxane), and they were analyzed by GC. The reaction products were identified by comparison with authentic samples and by GC–MS analysis. Residual H_2O_2 was determined by iodometric analysis.

No leaching of Zr was observed in randomly selected catalytic runs by analyzing the reaction solution with ICP mass spectrometry.

RESULTS AND DISCUSSION

Preparation and Characterization

All samples were prepared via sol–gel method under basic conditions. With respect to previously reported catalysts of the same family (13) that were prepared under acidic conditions, this choice allows a drastic shortening of the gelation times. Under the preparation conditions reported in Experimentals and Methods, gelation times for the individual oxides are 15–30 min for SiO_2 and 1–2 min for ZrO_2 (starting from pure $MeSi(OEt)_3$, gelation never occurs (*vide infra*)). In the case of mixed oxides, ZrO_2 is just a few percentage of the total mixture; therefore, it can be assumed that extensive condensation of ZrOH will take longer, since the precursor is more diluted. This is an important point, as it allows much better matching of the hydrolysis and condensation rates between SiO_2 and ZrO_2,

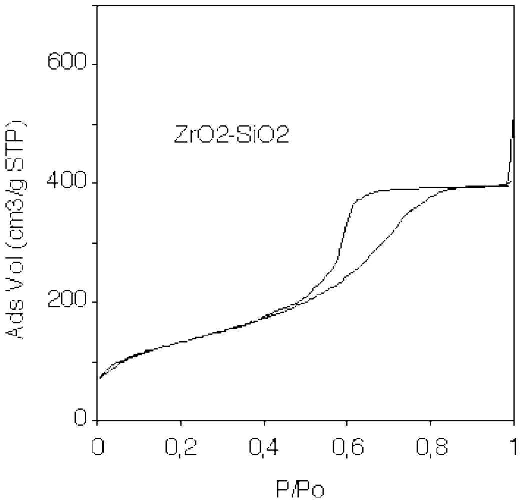


FIG. 1. A typical adsorption isotherm for zirconia–silica mixed oxides (ZrO_2–SiO_2 sample) showing the hysteresis loop typical of mesoporous materials.

a factor that controls the homogeneity of the final mixed oxide gel, and regular dilution of Zr centers within the silica matrix, avoiding the formation of large zirconia domains. The preparation parameters shown in Table 1 allow preparation of highly viscous and transparent gels, with the exception of ZrO_2–SiO_2Me80 and the samples containing more than 1% Zr (Zr2, Zr5, Zr10), where the gel is opaque, indicating a probably lower homogeneity.

All samples were aged in the air for 96 h to yield vitreous xerogels. They were subsequently dried in the oven at 110°C for 18 h to eliminate most of the water. The nonmodified samples were calcined also at 250 and 550°C.

X-ray powder diffraction analysis indicated that all samples were completely amorphous, even those calcined at 250 and 550°C, a feature that is a reasonable indication that ZrO_2 is well dispersed in the silica matrix (13).

Surface area and pore size distribution were determined from N_2 adsorption isotherms and a typical one, which applies to most cases, is reported in Fig. 1. As shown, they are type IV isotherms according to IUPAC classification (21) and they show a hysteresis loop typical of mesoporous solids.

We shall now distinguish between the methylated and nonmethylated samples. The BET (22) surface areas of the latter, along with their average pore diameter calculated according to Barrett *et al.* (23), are reported in Table 2. Figure 2 shows a typical pore size distribution for 1% Zr-containing samples. This is always rather narrow and falls into the range typical of mesopores. It is interesting that all samples having a Zr content higher than 1% are essentially microporous.

In the case of the methylated samples, the adsorption isotherm and the pore size distribution have the same features, as shown in Figs. 1 and 2. Their surface area and average pore size are shown in Fig. 3. As can be seen, with

TABLE 2

Morphological Features of the Nonmethylated Samples

Sample	Heating temp. (°C)	BET surface area (m^2/g)	BJH average pore diameter (Å)
ZrO_2–SiO_2	110	492	75
ZrO_2–$SiO_2$250	250	668	60
ZrO_2–SiO_2	500	510	75
Zr2	250	628	Microporous
Zr5	250	614	Microporous
Zr10	250	541	Microporous

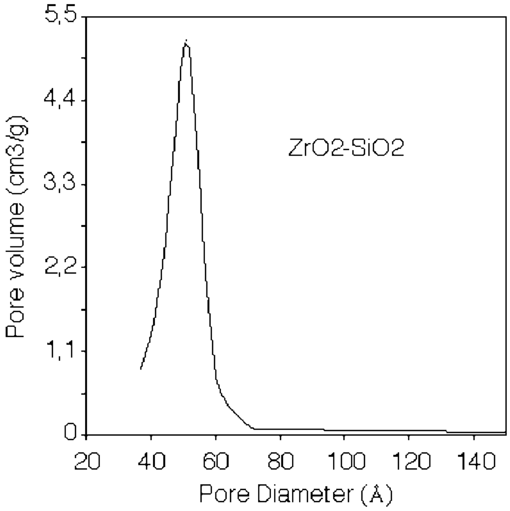


FIG. 2. A typical pore size distribution for zirconia–silica mixed oxides (ZrO_2–SiO_2 sample) calculated from Fig. 1 according to the BJH method.

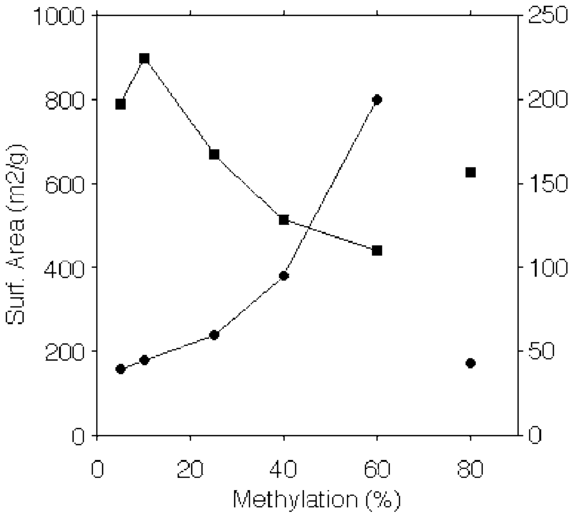


FIG. 3. Dependence of surface area and average pore diameter of surface methylated samples on the extent of methylation.

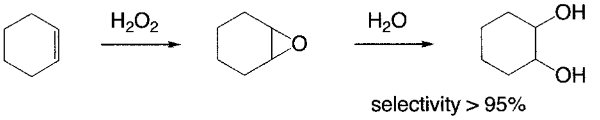
respect to the corresponding nonmethylated sample, the presence of only 5% methylation increases greatly the surface area (789 vs 492 m^2/g) while at the same time decreasing the average pore diameter (<40 vs 75 Å). This is probably due to the different hydrolysis ratio, a factor that can change drastically the morphological properties of xerogels (24). As is clear from Fig. 3 an increase in methylation percentage causes a regular increase in the average pore diameter (from <40 to 200 Å). This may be due to the fact that as the number of methyl groups on the surface increases, the condensation of surface –OH groups is more and more hindered. As a consequence the surface area of the solids decreases also regularly, down to 440 m^2/g (Fig. 3).

In this general trend the behavior of ZrO_2–SiO_2Me80 is odd. This sample has an average mesopore diameter of 43 Å (and a surface area of 628 m^2/g) and is extensively microporous. These irregular characteristics are reflected also during the preparation. At variance with the other samples for which gelation occurs within 15–30 min, in this case about 2 days were necessary; additionally the gel was opaque. All together these observations seem to indicate that the condensation process is made more difficult by the large number of methyl groups. This trend was confirmed by an attempt to synthesize a sample containing only $MeSi(OEt)_3$ as the precursor. Even after 3 weeks no gelation was observed and this seems to confirm that over a certain amount of methylation, the precursors do not polymerize homogeneously, making the resulting solid devoid of the morphological characteristics typical of the other samples.

One point that should be considered is whether there is any surface enrichment of one of the components of the system. In fact, in principle, it is possible, for example, that methyl groups are more concentrated on the surface than in the bulk. Having no experimental indication, in dealing with catalysis data a regular distribution will be assumed.

Oxidation of Cyclohexene

The oxidation of cyclohexene with 35% hydrogen peroxide was chosen as the test reaction to compare the behavior of the different catalysts. In all cases the reaction was carried out in the absence of solvent (i.e., in neat cyclohexene), a condition that may be of interest with respect to environmental issues, and leads to the formation of 1,2-diols (see Eq. 1)



(1)

as the main products (5). A typical reaction profile reporting the formation of cyclohexandiol and the decay of hydrogen peroxide is shown in Fig. 4. The features of this graph are quite general and apply to all catalytic tests here reported. It must be pointed out that the intermediacy of cyclohexene in the reaction, as foreseen by Eq. 1, is confirmed by the buildup of a small amount (~1%) of epoxide during the reaction. The selectivity to cyclohexandiol is always very high (>95%). Minor heavy unidentified products are also present in the reaction mixture.

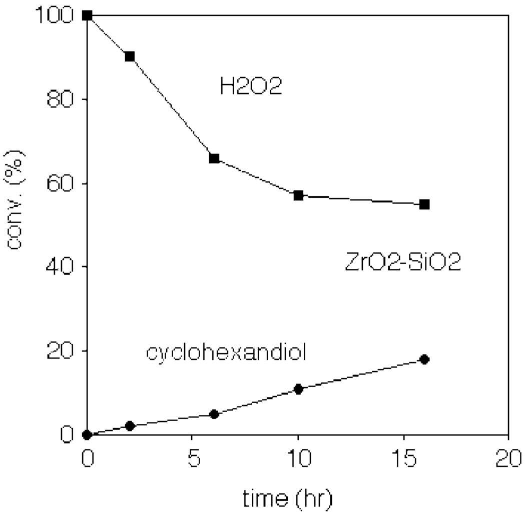


FIG. 4. A typical cyclohexanediol formation and hydrogen peroxide decay in the oxidation of cyclohexene catalyzed by zirconia–silica mixed oxides (ZrO_2–SiO_2 sample) at 90°C.

Initial tests were carried out on the nonmethylated samples at 70°C. The catalysts heated at the different temperatures were tested and in Table 3 their conversions after 16 h, the specific conversions normalized per square meter of surface, their hydrogen peroxide consumption, and the hydrogen peroxide efficiency expressed as in Eq. 2

$$\text{efficiency} = \frac{\text{mmol } H_2O_2 \text{ convtd into products}}{\text{mmol } H_2O_2 \text{ consumed}} \ \% \qquad (2)$$

are reported. As can be seen, the conversion and, more evidently, the specific conversion increase with the heating/calcination temperature, while the hydrogen peroxide consumption decreases and the hydrogen peroxide efficiency increases, although it remains rather low. At variance with the previously reported microporous samples (13), these observations seem to suggest that there exists a correlation between the activity and the efficiency (with

TABLE 3

Catalytic Performance at 70°C of the Nonmethylated Samples

Sample	Conversion (%)	Spec. conv. (%/m^2)	H_2O_2 consumption (%)	H_2O_2 eff. (%)
ZrO_2–SiO_2	20	2.0	49	10
ZrO_2–$SiO_2$250	26	1.9	60	13
ZrO_2–$SiO_2$550	35	3.4	34	18

Note. Reaction conditions: catalyst, 20 mg; cyclohexene, 2 mmol; 35% H_2O_2, 4 mmol; N_2, 1 atm; *T*, 70°C.

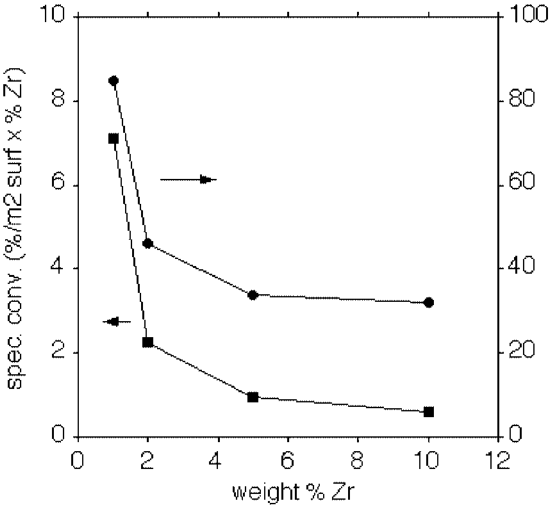


FIG. 5. Dependence of the specific conversion and the hydrogen peroxide efficiency on the zirconium content in different nonmethylated zirconia–silica mixed oxides.

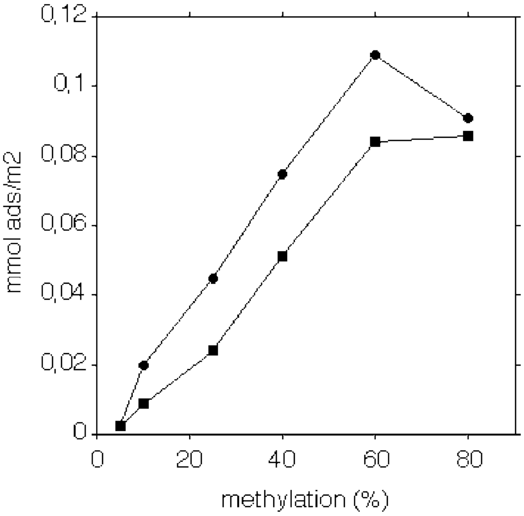


FIG. 6. Dependence of the adsorption of cyclohexene on the extent of methylation in surface methylated samples: (circles) in pure cyclohexene; (squares) in cyclohexene/water mixture.

respect to H_2O_2) of the catalyst and the amount of residual surface –OH groups. In other words activity and efficiency seem to depend on the hydrophobicity of the surface. This point will be reconsidered below when the methylated samples are analyzed.

Since the activity observed above is in general rather modest, the reaction temperature was increased to 90°C and the effect of a higher amount of Zr on the catalysts was considered. The specific conversions normalized per square meter of surface and percentage Zr and the hydrogen peroxide efficiency as a function of the Zr content of the catalyst are reported in Fig. 5. As shown both parameters decrease sharply with the increase in the Zr content. The overall conversions observed fall in the 60–70% range for all catalysts, which implies that the expected increase in conversion due to the increase in the Zr content is balanced by a lower efficiency of the Zr centers (Fig. 5), probably due to a lower affinity for cyclohexene as a consequence of the microporosity (higher content of surface –OH groups) of the samples with Zr content >1% and also to the formation of more-extended ZrO_2 domains, as seems to be confirmed by the larger decomposition of H_2O_2 testified by Fig. 5.

Effect of Surface Hydrophilicity

In order to shed more light on the role of the surface hydrophilicity/hydrophobicity we analyzed the behavior of the different methylated catalysts in the oxidation of cyclohexene. Preliminarly, the affinity of the different catalysts for cyclohexene was analyzed through the determination of their adsorption properties. This was done with pure cyclohexene and with a mixture of cyclohexene/water using amounts identical to those employed in the oxidation reactions, but using H_2O instead of H_2O_2. Adsorption measurements were carried out at room temperature, leaving the catalyst in contact with the adsorbate for 16 h to reach equilibrium conditions. The results are reported in Fig. 6. As shown, on increase of the methylation degree a huge increase in the adsorption of/affinity for cyclohexene is observed both with and without water present. These results demonstrate that an increase in the methylation degree increases the hydrophobicity of the surface, as expected, thereby favoring the penetration of the porous material by hydrophobic molecules and/or increasing the mobility of water, as observed by Krause *et al.* in microporous TiO_2–SiO_2-type materials (25).

The catalytic oxidation of cyclohexene was carried out at 90°C. The reaction profiles for ZrO_2–SiO_2Me5 and ZrO_2–SiO_2Me80 are reported in Fig. 7 and show that after 8 h

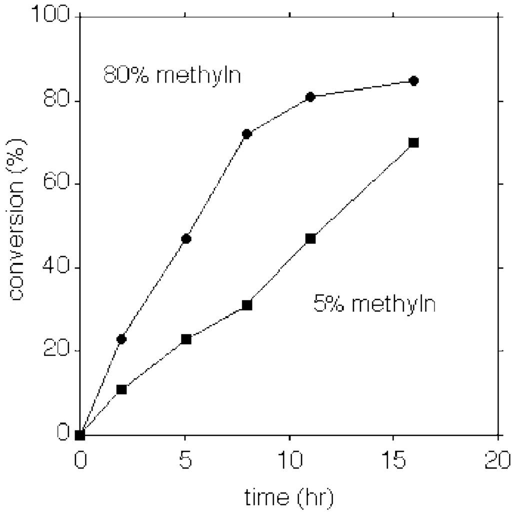


FIG. 7. Cyclohexene conversion vs time for ZrO_2–SiO_2Me5 and ZrO_2–SiO_2Me80. Reaction carried out at 70°C.

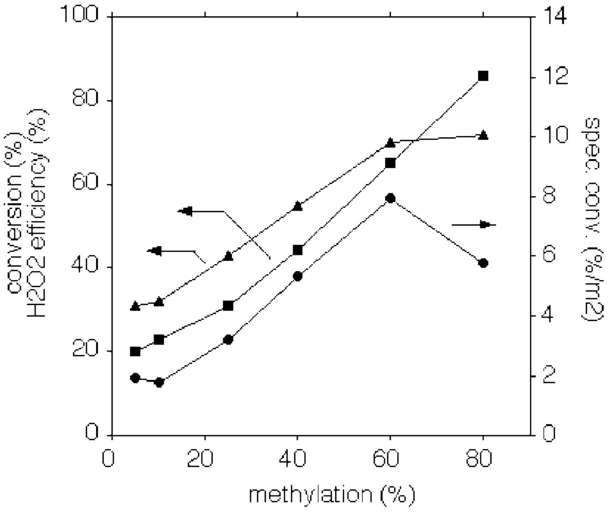


FIG. 8. Dependence of cyclohexene conversion, specific conversion, and hydrogen peroxide efficiency on the extent of methylation for the oxidation of cyclohexene with hydrogen peroxide catalyzed by differently methylated samples at 70°C.

there is a sufficient span of conversion among the different catalysts so that this experimental datum can be taken as indicative of their activity in the reaction. Figure 7 shows the profiles up to 17 h. As a matter of fact, when reactions are allowed to proceed, after >24 h almost complete conversion (∼95%) can be observed. A summary of the conversions of the catalysts after 8 h, of their specific conversion, and of the H_2O_2 efficiency is reported in Fig. 8. As shown the activity increases about three times on going from 5 to 80% methylation and the conversion can be driven up to over 80%. This is possibly due to the excess oxidant used in these reactions, a feature that is not very common with TiO_2–SiO_2 catalysts or even with Ti silicalites. Figure 8 shows also that the specific conversion increases about four times, with a maximum for the 60% methylation sample, and the H_2O_2 efficiency increases to 85%. The latter result is of particular interest, as it compares favorably with TiO_2–SiO_2-based systems. In fact, these materials generally require excess olefin in order to minimize H_2O_2 or even *t*-BuOOH decomposition (26–28), thereby preventing the observation of high olefin conversions. On the other hand, high conversions of olefin and high efficiencies in peroxide use are generally achieved only with *t*-BuOOH as the oxidant in the oxidation of allylic alcohols (11) and with a 40% methylated TiO_2–SiO_2 catalyst in the oxidation of a variety of olefins (19).

A comparison between Figs. 6 and 8 indicates, however, that the activity observed with increasing methylation is not merely due to a higher concentration of cyclohexene in proximity of the active sites. Most likely, an increase in the hydrophobicity of the surface, while beneficial to avoid H_2O_2 decomposition, leads also to a lower concentration of this reactant within the pores of the catalyst.

Methylated samples were also calcined at 250°C. Higher temperatures were not considered, to avoid thermal degradation of the organic functional groups (29). These new samples were tested in the oxidation of cyclohexene under the usual conditions and gave essentially the same results (Table 4) observed in Fig. 8 for the samples heated at 110°C.

The possibility of recycling these catalysts was checked in the case of ZrO_2–SiO_2Me40. The catalytic experiments were carried out under the reaction conditions specified in Fig. 8 or Table 4. After each cycle the catalyst was filtered, washed with EtOH, and dried overnight in the oven at 110°C. The conversions observed were the following: initial cycle, 55%; second cycle, 53%; third cycle, 56%; fourth cycle, 52%. Therefore, it can be concluded that no appreciable loss of activity is observed at least for the first four cycles, indicating that the catalysts are quite resistant and stable.

The catalytic data reported above indicate that an increase in the hydrophobicity of the catalyst surface, which can be easily tuned through an appropriate methylation degree, improves the adsorption capacity with respect to cyclohexene, hence the specific activity of the catalyst, and minimizes hydrogen peroxide side reactions, allowing an efficient use in the oxygen transfer reaction. At variance with previously reported TiO_2–SiO_2 catalysts (14), where surface methylation was able to exert a certain control on the product distribution, with the present catalysts no influence was observed. Independent of the hydrophobicity of the surface, only cyclohexandiol is always observed as the reaction product.

Use of t-BuOOH as the Oxidant

In order to determine whether a change in the oxidant was able to switch the selectivity of the catalysts toward the formation of epoxide, *t*-BuOOH was tested as the oxidant in the oxidation of cyclohexene. As stated above, this hydroperoxide is commonly used for the oxidation of olefins with mixed oxides and generally leads to the formation of epoxides. In our experiments, reactions were carried out at 90°C in the absence of solvent. Some selected catalysts

TABLE 4

Catalytic Performance at 90°C of the Methylated Samples Calcined at 250°C

Sample	Conversion (%)	H_2O_2 cons. (%)	H_2O_2 effic. (%)
ZrO_2–SiO_2Me5	38	48	40
ZrO_2–SiO_2Me10	40	45	44
ZrO_2–SiO_2Me25	52	50	52
ZrO_2–SiO_2Me60	70	54	65
ZrO_2–SiO_2Me80	71	50	72

Note. Reaction conditions: catalyst, 20 mg; cyclohexene, 2 mmol; 35% H_2O_2, 4 mmol; N_2, 1 atm; *T*, 90°C.

TABLE 5

Oxidation of Cyclohexene with *t*-BuOOH as Oxidant Using Various ZrO_2–SiO_2 Mixed Oxide Catalysts

Catalyst	React. time (h)	React. temp. (°C)	Epoxide (%)	Glycol (%)	Remaining *t*-BuOOH (%)
ZrO_2–$SiO_2$550	16	90	2	7	0
Zr5	16	90	0	0	0
ZrO_2–SiO_2Me40	16	90	0	0	0
ZrO_2–SiO_2Me60, calc. 220	29	90	3	4	0
	102		7	6	0
ZrO_2–SiO_2Me80	16	90	3	0	0
ZrO_2–SiO_2Me40	7	60	<1		77
ZrO_2–SiO_2Me60, calc. 220	7	60	<1		72

were tested in order to have a wide range of different samples, namely (i) a nonmethylated catalyst calcined at high temperature (ZrO_2–$SiO_2$550), (ii) a similar catalyst containig a higher amount of Zr (Zr5), (iii) two methylated catalysts, one with high (ZrO_2–SiO_2Me80) and one with an intermediate (ZrO_2–SiO_2Me40) methylation degree, and (iv) a highly methylated catalyst (ZrO_2–SiO_2Me60) calcined at 220°C. Table 5 summarizes the results obtained. As shown, at 90°C, conversions are very poor for all samples even after long reaction times. Small amounts of cyclohexene oxide and the corresponding diol are observed. The presence of the latter is surprising and is probably due to trace water present in the oxidant and/or to water extracted from the silica matrix. It is in any event an important indication of the acidity of the catalyst. No residual oxidant is observed at the end of the reactions. In order to check whether the poor conversions were due to possible rapid decomposition of the oxidant at high temperature, some test experiments were carried out at 60°C with ZrO_2–SiO_2Me60 and ZrO_2–SiO_2Me80. After 7 h, neglible amounts (<1%) of epoxide were observed as the sole reaction product while, respectively, 77 and 71% decomposition of the oxidant was observed.

CONCLUSIONS

The results reported in this work clearly indicate that sol–gel methods can be a viable way to prepare mesoporous ZrO_2–SiO_2 mixed oxides and these are indeed effective catalysts for the selective oxidation of simple olefins to give glycols. Since the reactions are better carried out in the absence of solvent, this is in principle more environmentally acceptable and potentially attractive for practical use.

Surface methylation is an effective method to control the morphology of the catalysts. In fact, it increases the pore size of the solid, probably by statistically reducing the tetrahedral growth of the Si–O–Si network, and consequently, it decreases the surface area of the solids, at least as long as they remain mesoporous.

An increase in the hydrophobicity of the solids, which can be achieved either by increasing the calcination temperature or (better) by increasing the degree of methylation, allows improvement in the specific activity of the catalysts by three to four times and it allows control of the efficiency with which hydrogen peroxide is consumed in the oxidation reaction. Efficiencies as high as 85% can be observed coupled with high conversion of the olefin. This is uncommon for similar systems based on titanium and may reflect the lower reducibility of Zr^{4+}, which makes less likely the radical decomposition of H_2O_2.

No effect of the hydrophobicity of the surface is observed with respect to the chemoselectivity of the system: glycol (selectivity >95%) is always the reaction product.

At variance with similar Ti-based systems, in the present case *t*-BuOOH is far less effective as oxidant, conversions are very poor, and extensive decomposition of the oxidant occurs. Even the selectivity cannot be adequately switched to epoxide, as the system utilizes even trace water to promote hydrolysis of the oxirane ring.

The catalyst synthetic method here reported seems to be a viable way to tune the affinity of the surface to the properties of the substrate (like adsorbs like) and in principle can be a powerful synthetic tool to use in overcoming mass transport phenomena, which can be particularly especially severe in liquid-phase oxidation reactions, where reactants with different hydrophilicity properties have to be brought together on the catalyst surface.

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