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Microporous Zirconia–Silica Mixed Oxides Made by Sol–Gel as Catalysts for the Liquid-Phase Oxidation of Olefins with Hydrogen Peroxide

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The preparation of a series of microporous zirconia–silica mixed oxides by sol–gel is reported. These have been characterized by BET methods, thermogravimetric analysis, X-ray diffraction analysis, UV–vis spectroscopy, and TPD of ammonia. The materials have high surface areas; they are amorphous and possess only mild surface acidity. They have been tested in the oxidation of different substrates with hydrogen peroxide, particularly the oxidation of cyclohexene. The catalysts are moderately active and produce mainly products arising from oxirane ring opening, particularly when the reactions are carried out in the absence of solvent. The use of a less hydrophilic reaction medium and/or the partial methylation of the silica surface tend to increase the reaction productivity and reduce hydrogen peroxide consumption. © 2000 Academic Press

Key Words: **zirconia–silica; mixed oxides; oxidation; hydrogen peroxide.**

INTRODUCTION

The use of hydrogen peroxide in the oxidation of organic molecules is a major goal, both in academia and in industry, because of the environmental acceptability of this oxidant, which depends mainly on the nature of its by-product, water. To date, liquid-phase oxidation with hydrogen peroxide catalyzed by transition metals has been largely dominated by the use of complexes in solution (1). These have been able to perform a wide variety of oxidation reactions (epoxidation and ketonization of olefins, oxidation of alcohols, hydroxylation of aromatics, Baeyer–Villiger oxidation of ketones, etc.) with unsurpassed activity and selectivity (even enantioselectivity). However, while these systems may be suitable for the preparation of fine chemicals or pharmaceuticals, the obvious problem of the catalyst separation and recovery has so far hampered their use in larger scale operations. The major breakthrough in the use of the highly desirable H_2O_2 oxidant in industry has been the discovery some 15 years ago of titanium silicalite TS-1 (2). Other interesting results have been more recently obtained also with Ti, V, Cr, and Sn containing zeolites or aluminophosphates (3–6). However, the major limitation of these crystalline materials rests in the limited number of heteroelements that can be incorporated into the structure. This difficulty seems to have been overcome by the recent discovery that amorphous titania–silica aerogels can exhibit superior epoxidation activity using alkylhydroperoxides as oxidants (7), indicating that a regular crystal structure is not a necessary condition (8).

An important condition for the achievement of catalysts capable of activating hydrogen peroxide is site isolation (2) to avoid extensive H_2O_2 radical decomposition that is easily triggered by the presence of M–O–M (M transition metal) moieties. Site isolation can be easily controlled in crystalline mixed metal oxides, but much less so in the case of amorphous solids made by sol–gel. Moreover, the most extensively studied titania-based amorphous solids activate organic hydroperoxides but in general fail to promote oxidations with hydrogen peroxide because of their surface hydrophilicity properties compared to the hydrophobic silicalites. This important point has been clearly demonstrated by the recent work of Klein and Maier (9) who achieved interesting results with hydrogen peroxide as the oxidant by using sol–gel-prepared TiO_2–SiO_2 amorphous solids in which the surface polarity was modified by partial methylation of the surface of silica through the use of $Si(OMe)_3Me$ precursor. Similar results were observed also by Neumann and Levin-Elad with Ti, Mo, and W silicate xerogels (10) using $MCl_2(OR)_x$-type alkoxides ($M = $ Ti, Mo, W) where the surface polarity was probably locally modified by the presence of covalent chloride ligands. Klein and Meier documented also that the surface polarity can affect not only the reaction rate and the selectivity but also the overall conversion and catalyst lifetime (9). It seems therefore that this surface property may be as important as the presence of catalytically active sites, as a wrong surface polarity may mask otherwise evident catalytic events.

Zirconium–containing mixed oxides have been far less considered as potential catalysts for oxidations with

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hydrogen peroxide. The reason probably relies on the fact that zirconium complexes are much less efficient than the corresponding titanium species in the oxidation of organic compounds with hydroperoxides as oxidants (11). Control of site isolation has been recently achieved by Quignard *et al.* by grafting the transition metal on the silica surface through the use of tetraneopentylzirconium followed by hydrolysis of the residual organic ligands (12). On the other hand, sol–gel methods have been employed by Tuel and coworkers for the preparation of zirconium-containing mesoporous silicas (13). Both types of catalysts have proved capable of epoxidizing cyclohexene. In this work we wish to report our efforts to prepare in a controlled manner microporous zirconia–silica mixed oxides by sol–gel and their reactivity in the oxidation of a variety of organic substrates including olefins.

EXPERIMENTAL

Materials

The following metal alcoxides were used: tetramethoxysilane, TMOS (Aldrich); tetraethoxysilane, TEOS (Fluka); methyltriethoxysilane (Aldrich); zirconium propoxide (Fluka). The oxidant used was 35% hydrogen peroxide (Fluka). Substrates were purchased from Fluka. All chemicals were purum or puriss grade and used without further treatment.

Methods

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

Differential thermal analysis (DTA) was performed using a Netzsch apparatus with calcined alumina as the reference material. The following experimental conditions were set: heating rate, 10°C/min; sensitivity, 0.1 mV for a full-scale expansion; sample weight, 160 mg.

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).

TPD of ammonia was performed according to the following procedure: the sample was previously heated at 550°C *in vacuo* (10^{-2} Torr) for 1 h. Then, it was cooled down to 90°C, saturated with pure NH_3 for 15 min, and finally cooled down to room temperature under a NH_3 atmosphere. After physisorbed ammonia was removed by flowing He (30 ml/min) at room temperature for 2 h, the TPD run was performed with a heating ramp of 10°C/min up to 550°C.

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. TMOS (32 mmol) is dissolved in MeOH (11.36 ml) followed by the addition of water (192 mmol) and 65% HNO_3 (4.98 mmol) and the solution is stirred at room temperature for 5 h. Zirconium propoxide (0.19 mmol) diluted in MeOH (0.9 ml) is then added dropwise. After about 2 h, gelation is evident and the sample is put aside to age for 18 h. The transparent xerogel is dried *in vacuo* (10^{-2} Torr) and then heated at 110°C for 18 h.

Where necessary, the samples were calcined at 550 and 850°C in air for 3 h: gas flow, 75 ml/min; heating ramp, 10°C/min.

In the preparation of partially methylated samples, the procedure was the same but appropriate amounts of TEOS and methyltriethoxysilane were used instead of TMOS.

Catalytic Oxidation Procedures

Catalytic reactions were performed in 10-ml glass vials. The catalyst (40 mg), MeOH as the solvent (4 ml), the substrate (4 mmol), and 35% H_2O_2 (8 mmol) were placed in a 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. Reaction mixtures were analyzed by GC and 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 when the reaction solution was analyzed with ICP mass spectrometry.

RESULTS AND DISCUSSION

Preparation of the Microporous Mixed Oxides

One of the major problems to be circumvented in the preparation of zirconia–silica mixed oxides by sol–gel is the markedly different gelation times of the individual oxides (14). This is especially important in the present case where the zirconia sites should in principle be molecularly dispersed within the silica matrix to attain the required site isolation. For this reason a prehydrolysis of silica was performed prior to zirconium propoxide addition. The major parameters influencing the prehydrolysis reaction are the pH and concentration of the alcoxysilane solution and, mostly, the H_2O/alcoxysilane molar ratio, the so-called prehydrolysis ratio (15, 16). After optimizing the synthetic procedure, we found that concentrations in the range 50–100 g of SiO_2/L and a $H_2O/Si(OMe)_4$ 6/1 molar ratio allowed us to reduce the prehydrolysis time to about 5–10 h. Similarly, a decrease of the concentration of the zirconium alcoxide solution slows down the corresponding hydrolysis so that

TABLE 1

Preparation Conditions and Morphological Properties of 1% ZrO_2/SiO_2 Mixed Oxide Samples

Sample no.	Prehydrolysis conditions	pH	Conc. SiO_2 (g/L)	Heating conditions	BET (m^2/g)
ZS4	8 h, 25°C	0.8	50	110°C, 18 h	494
ZS5	24 h, 60°C	0.8	50	110°C, 18 h	406
ZS6	5 h, 25°C	0.5	100	110°C, 18 h	430
ZS5C550	24 h, 60°C	0.8	50	550°C, 3 h	374
ZS5C850	24 h, 60°C	0.8	50	850°C, 3 h	190
ZS6Me25[a]	2.5 h, 25°C	0.5	100	110°C, 18 h	809
ZS6Me40[b]	2.5 h, 25°C	0.5	100	110°C, 18 h	712

Note. All samples contain 1% ZrO_2 and were prepared using a H_2O/TMOS ratio, 6/1, and a H^+/Si ratio, 0.16.

[a] Sample prepared by mixing 25% $MeSi(OEt)_3 + 75\%$ $Si(OEt)_4$ instead of TMOS.

[b] Sample prepared by mixing 40% $MeSi(OEt)_3 + 60\%$ $Si(OEt)_4$ instead of TMOS.

the two processes (hydrolysis of the zirconia and silica precursors and subsequent condensation) can be reasonably matched and lead to the formation of a perfectly transparent gel. The same method was used for the preparation of the partially methylated samples, although in this case a shorter prehydrolysis time seemed more appropriate. A summary of the preparation parameters for the different samples is reported in Table 1.

Characterization

The surface area and porosity of the materials were characterized by nitrogen adsorption/desorption isotherms. All samples show type I isotherms (17) characteristic of purely microporous materials (Fig. 1). The BET surface area of the samples are reported in Table 1. As can be seen, the surface areas of samples ZS4, ZS5, and ZS6 fall in the range 430–500 m^2/g. During the optimization of the synthesis procedure, we also found in other samples not reported in Table 1 that a higher pH of the medium in which gelation is performed (pH 2–4) strongly decreases the surface area of the samples. In this respect, it is known that in zirconia–silica mixed oxides containing a few percent zirconia the surface area of samples prepared under acidic conditions is generally 1 order of magnitude higher than that of samples prepared under basic conditions (18). Calcination at temperatures >500°C (samples ZS5C550 and ZS5C850) results, as expected, in a decrease of the surface area of the samples. Interestingly, partially methylated materials (samples ZS6Me25 and ZS6Me40), prepared under conditions very similar to those of the other samples, show a much higher surface area.

DTA/TGA analyses of the dry xerogel samples are quite similar. A typical example is reported in Fig. 2. They all show an endothermic peak at ~150°C, corresponding to the weight loss of adsorbed water. A second minor weight loss is evident around 320°C, corresponding to possible further loss of water, probably arising from condensation of surface hydroxyls and/or some trace organics still chemically bound to the surface. No peak is evident in the DTA up to 1000°C that can be associated to phase transitions of zirconia. This observation is per se not sufficient evidence to exclude nucleation of zirconia in the samples as the zirconia content is quite low (1%). Indeed, also a mechanical mixture containing 1% uncalcined, amorphous ZrO_2 mixed with silica gel did not show any evidence of phase transition upon DTA analysis, indicating that in this range of concentration the sensitivity of the instrument is probably insufficient.

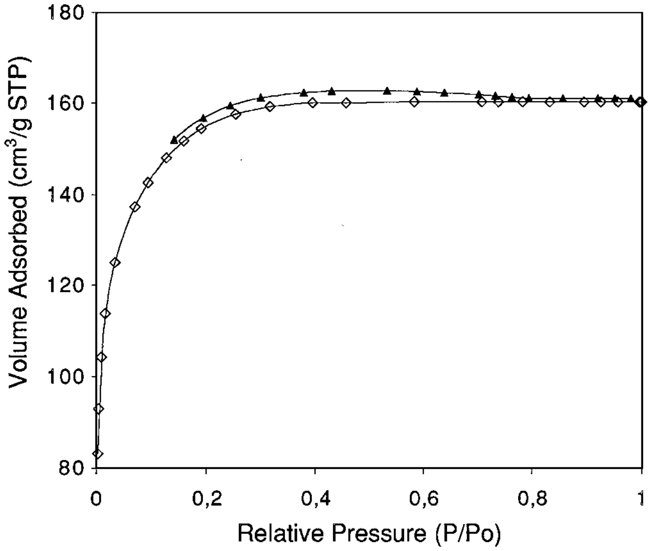


FIG. 1. Typical (sample ZS5) N_2 adsorption isotherm for 1% ZrO_2–SiO_2 sol–gel mixed oxides.

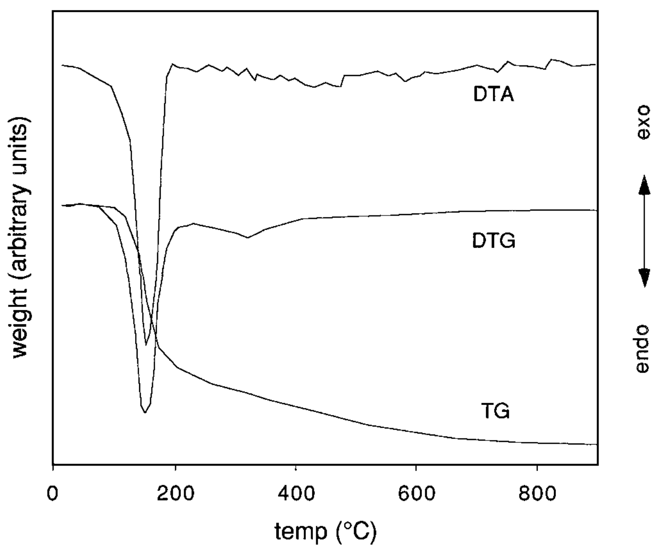


FIG. 2. Typical (sample ZS6) DTA/TGA analysis for 1% ZrO_2–SiO_2 sol–gel mixed oxides.

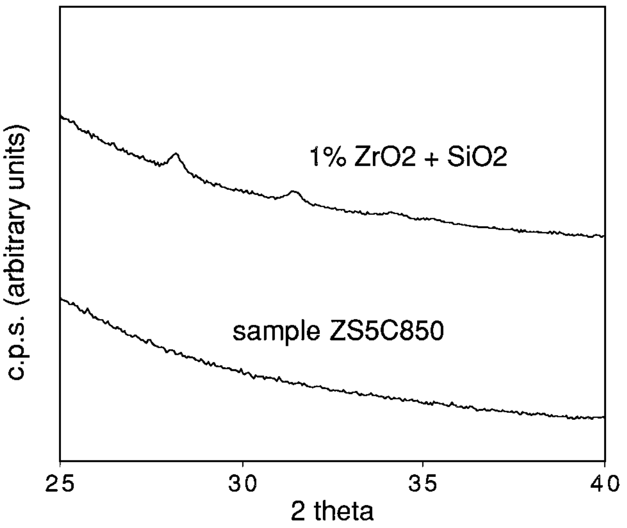


FIG. 3. Powder X-ray diffraction profile for sample ZS5C850 (bottom line) and for a 1% monoclinic zirconia + 99% silica mechanical mixture.

Similarly, powder X-ray diffraction analysis indicated that all samples are completely amorphous, including those calcined at high temperature in which crystallization of possible ZrO_2 aggregates could occur. In this case, to test the sensitivity of the method, the analysis of a mechanical mixture of 1% monoclinic zirconia in silica indicated that the former can be easily detected, even if the mixture is very diluted (Fig. 3).

To confirm the presence of Zr centers very well dispersed within the silica matrix, some UV measurements have been carried out. This technique has been used to identify the nature and coordination of Ti species in zeolites (19) and has provided evidence to the fact that when Ti centers are isolated in a silica matrix a broad band at ∼230 nm appears, significantly shifted to lower wavelengths with respect to Ti oxide species. Similarly, it is known (13b) that zirconia shows an absorbance maximum at 240 nm, whereas a maximum at lower wavelengths (205 nm) was observed in materials in which the possible presence of isolated Zr centers was inferred. All samples reported in Table 1 show a maximum at 203–205 nm, indicative of possible site isolation and in agreement with the findings of Gontier and Tuel (13b), although the absence of systematic UV–vis data on zirconium-containing molecular sieves suggests taking this conclusion cautiously.

In summary, although the X-ray and UV data are indicative of a good dispersion of Zr centers within the silica matrix, conclusive evidence for site isolation cannot be safely drawn.

TPD of ammonia was used to test the presence of possible acid centers (13b). Experiments were performed on sample ZS5C850, i.e., the only one thermally treated at a temperature (calcined at 850°C) higher than the maximum temperature reached during the TPD experiment (550°C). As can be seen from Table 1, sample ZS5C850 has a much lower surface area with respect to most of the other samples; however, its catalytic activity is very similar. Because of the microporous nature of these materials, ammonia adsorption was performed under static conditions at 90°C, following extensive outgassing at high temperature (550°C). The TPD profile of sample ZS5C850 is shown in Fig. 4. As can be seen, no desorption peaks other than the one (150°C) associated with ammonia adsorbed on the surface hydroxyls of silica can be observed. These results are in contrast to previous findings by Gontier and Tuel on mesoporous materials of a similar type (13b).

Catalytic Activity

Prior to testing the catalytic activity of these materials in the oxidation of organic compounds, their reactivity toward hydrogen peroxide decomposition was analyzed. In these experiments a series of samples (all made by sol–gel) were considered in which the ZrO_2 content was the following:

$$100\%, 20\%, 5\%, 2\%, 1\%$$

Of these, only the samples containing 1% ZrO_2 are reported in Table 1. Contact of these solids with H_2O_2 resulted in effervescence (massive oxygen evolution) for ZrO_2 contents >2%. Conversely, 2% and 1% ZrO_2-containing samples revealed upon analysis 28% and 25% decomposition of hydrogen peroxide, respectively, over a contact period of 24 h. These preliminary experiments demonstrate that, similar to Ti-containing materials, the presence of extended Zr–O–Zr entities is primarily responsible for hydrogen peroxide decomposition with these materials and allows one to identify the proper catalyst composition range.

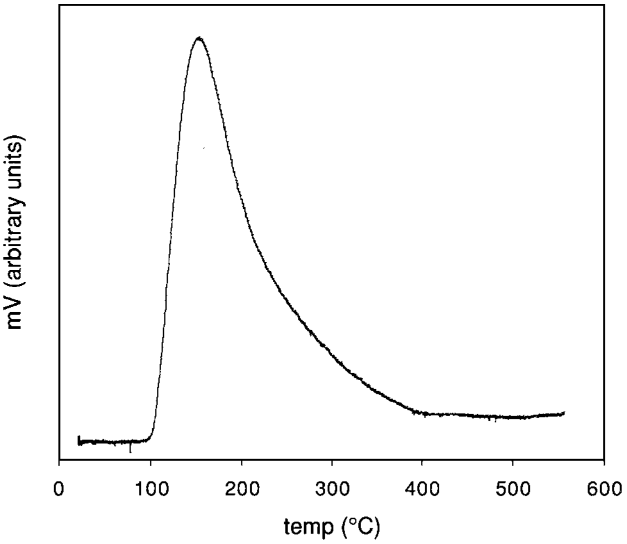
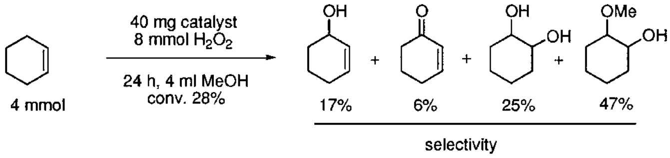


FIG. 4. NH_3 thermal programmed desorption profile for sample ZS5C850.

The catalytic activity of the samples reported in Table 1 was initially tested in the oxidation of cyclohexene. Previous results with ZrO_2/SiO_2 systems have been obtained either in acetone (13) or in acetonitrile (12) as the solvent. The former is intrinsically unsafe because of the detonation properties of some of its mixtures with hydrogen peroxide (20) that are related to its easy addition to the carbonyl group, leading to the formation of organic peroxides (21). Similarly, acetonitrile can add H_2O_2 under basic conditions to form peroxycarboximidic acid, which is capable of converting alkenes into epoxides (22). Although the direct involvement of derivatives of hydrogen peroxide with acetone and acetonitrile in the reaction conditions generally used with silica-supported heterogeneous catalysts seems unlikely, the use of these solvents may generate some ambiguities as to the nature of the actual oxidant involved in the reaction. On the basis of these considerations, methanol was chosen as the solvent for our initial catalytic tests. Methanol is water miscible, is not oxidized by H_2O_2 under these conditions, and has been reported to be the solvent of choice in the case of TS-1 (2).

The reaction was performed at 90°C in sealed vials and the reaction mixture was analyzed after 24 h. A typical profile showing the decays of H_2O_2 and cyclohexene is shown in Fig. 5. In this case the reaction was monitored for about 70 h using sample ZS6 as the catalyst. As can be seen, the consumption of hydrogen peroxide is maximum at the beginning of the reaction and then slows down and runs approximately parallel to the consumption of cyclohexene. The latter follows an approximately zero-order decay. The amount of hydrogen peroxide going into products is about 25% of the amount consumed. An analysis of the reaction composition shows four main products (Scheme 1), which account for about 95% selectivity of the reaction. A minor fraction (~5% of the total product formation) is constituted by two unidentified minor products. As can be seen from Scheme 1, ~20%–25% of the products arise from allylic oxidation, while the remaining 70%–75% is constituted by products derived from cyclohexene oxide, which appears to be the major primary product of the reaction.



SCHEME 1

The catalyst samples reported in Table 1 have been tested in the same reaction under identical conditions. The data corresponding to samples ZS4–ZS5C850 are reported in Table 2. As shown, they all seem to behave in a rather similar manner. With the exception of ZS4, conversions are in the 28%–36% range and hydrogen peroxide consumption is approximately 60% of the amount initially introduced for all samples. Product distribution is also quite similar, again with the exception of ZS4. Apparently, there are no differences between samples dried at 110°C and samples calcined at higher temperatures, despite a decrease in the surface area. In contrast a moderate increase in conversion is apparent, at least for the sample calcined at 550°C (ZS5C550).

The catalytic properties of catalyst ZS6 used as the prototype have been analyzed in the oxidation of a variety of substrates. Results are summarized in Table 3. As can be seen, the catalyst is capable of oxidizing substituted olefins but show no activity toward terminal olefins. It is also moderately active toward alcohols but fails to oxidize phenol. Similarly, no Baeyer–Villiger activity was observed in the oxidation of ketones.

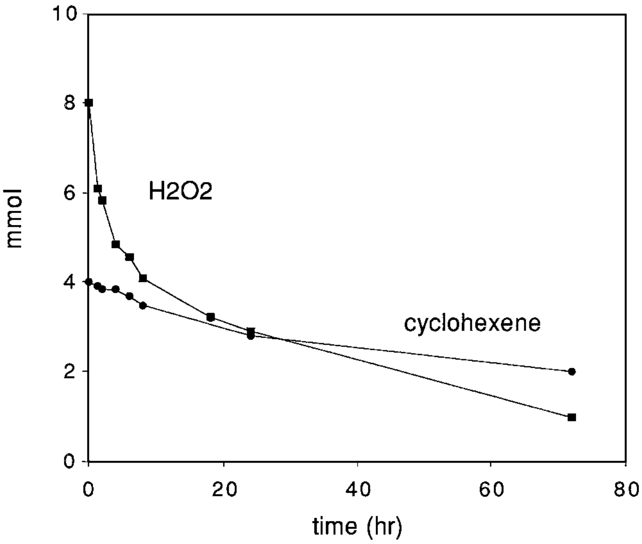


FIG. 5. Hydrogen peroxide and cyclohexene decays in cyclohexene oxidation using sample ZS6 as the catalyst.

TABLE 2

Oxidation of Cyclohexene with Hydrogen Peroxide Catalyzed by Different 1% ZrO_2/SiO_2 Mixed Oxide Samples

Sample no.	Conversion (%)	H_2O_2 consumption (%)	Product selectivity (%) Enol	Enone	Glycol	Glycol monomethyl ether
ZS4	13	12	15		11	70
ZS5	28	60	26	6	22	42
ZS6	28	62	17	6	25	47
ZS5C550	36	59	22	5	18	51
ZS5C800	31	59	19	4	20	52

Note. Reaction conditions: catalyst, 40 mg; substrate, 4 mmol; H_2O_2, 8 mmol; MeOH, 4 ml; *T*, 90°C; 24 h.

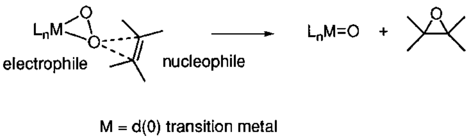
TABLE 3

Oxidation of Different Substrates with 35% Hydrogen Peroxide Catalyzed by a 1% ZrO_2/SiO_2 Mixed Oxide Catalyst

Substrate	Conversion (%)	Products (selectivity %)
Cyclohexene	28	2-Cyclohexen-1-ol (17) 2-Cyclohexen-1-one (6) 2-Methoxycyclohexan-1-ol (47) 1,2-cyclohexanediol (25)
Cyclooctene	41	1,2-Cyclooctanediol (100)
Styrene	53	Benzaldehyde (14) Styrene glycol (17) 1,2-Dimethoxyethylbenzene (68)
2,3-Dimethyl-2-butene	100	2,3-Dimethyl-2,3-dihydroxybutane (22) 2,3-Dimethyl-2-hydroxy-3-methoxybutane (78)
1-Octene	=	
1-Hexene	=	
1-Phenylethanol	17	Acetophenone (76) Unknown (24)
Phenol	=	
Benzyl alcohol	5	Benzaldehyde (100)

Note. Reaction conditions: catalyst sample, ZS6, 40 mg; substrate, 4 mmol; H_2O_2, 8 mmol; MeOH, 4 ml; T, 90°C; 24 h.

The oxidation of olefins shows in general a product distribution similar to that observed for cyclohexene, indicating that the epoxide is the primary product of the reaction, although only products arising from acid hydrolysis of the oxirane ring are actually observed. Since acid centers other than those of silica were not revealed from TPD, we performed two blank experiments.



SCHEME 2

In the first one, a silica sample, prepared according to the method described in the Experimental section for the mixed oxides, was contacted with cyclohexene epoxide in MeOH and water under the conditions used for the catalytic reaction. The aim was to check whether the modest acidity of silica was sufficient to promote the ring opening of the oxirane ring. In the second experiment, cyclohexene epoxide was mixed with 35% hydrogen peroxide in MeOH under the conditions used for the catalytic reactions to check the possible hydrolytic effect of the acid used to stabilize commercial H_2O_2 solutions (apparent pH of approximately 2.5). In both cases after 24 h no epoxide but only cyclohexene glycol and 2-methoxycyclohexan-1-ol were found in the system, proving that under the experimental conditions used the mild acidity of the medium and/or the support is sufficient to hydrolyze the oxirane ring.

At variance with the results of Maier *et al.* (23) with microporous 3% TiO_2/SiO_2 catalysts in the same reaction using *t*-BuOOH as the oxidant, in the present case no evidence of shape selectivity can be gained from Table 3. Indeed, the reactivity observed for the different olefins parallels the order already observed in the oxidation with d^0 transition metal peroxo complexes in solution (24), i.e.:

$$\text{tetrasubstituted} > \text{trisubstituted} > \text{disubstituted} > \text{monosubstituted}.$$

This behavior is generally considered to be strongly indicative of a metal-centered transformation consisting of the nucleophilic attack of the olefin onto an electron-poor peroxy oxygen formed by interaction of the oxidant with the d^0 transition metal center (Scheme 2).

The effect of different water-miscible solvents on the reaction has been checked in the epoxidation of cyclohexene using sample ZS6 as the catalyst. Results are summarized in Table 4 and show that among the different solvents MeOH is the one that achieves the highest conversion, diglyme yields rather poor results in terms of both activity and selectivity, and dioxane allows one to observe also small amounts

TABLE 4

Oxidation of Cyclohexene with Hydrogen Peroxide Catalyzed by Catalyst ZS6: Effect of Different Reaction Media on the Activity and Selectivity

Solvent	Conversion (%)	Product selectivity (%)				
		Epoxide	Enol	Enone	Glycol	Glycol monomethyl ether
MeOH	28		17	6	25	47
Diglyme[a]	8				8	
Dioxane	25	9	30	16	50	
No solvent	100				100	

Note. Reaction conditions: catalyst sample, ZS6, 40 mg; substrate, 4 mmol; H_2O_2, 8 mmol; solvent, 4 ml; T, 90°C; 24 h.

[a] In this case at least seven unidentified products are formed, accounting for ~90% selectivity.

of epoxide, supporting the idea that it is the primary oxidation product. Interestingly, the highest activity and selectivity is observed in neat cyclohexene, indicating that allylic oxidation can be completely suppressed in the appropriate medium. This result may be interesting also from a practical point of view as the possibility to avoid the presence of the solvent may be quite desirable because no separation is required and because solvent-free reactions are generally more environmentally acceptable. Again, blank experiments in the absence of the active phase carried out as above proved the feasibility of the oxirane ring hydrolysis by silica and by the acidity of H_2O_2, even in the absence of MeOH.

A significant effect on selectivity is also present when a more concentrated H_2O_2 solution (less water present) is used in the reaction. In fact, the use of 50% H_2O_2, while having no influence on the conversion (still 28% with MeOH as the solvent), allows increases in the selectivity to 2-methoxycyclohexan-1-ol up to 80%.

The results reported so far seem to support the idea that matching the polarity of the medium with the polarity of the surface and the reaction requirements may be an important point in controlling the activity and selectivity of these catalysts. In the present case, we are dealing with a highly hydrophilic surface that will certainly have more affinity for water or MeOH rather than for the olefin or hydrogen peroxide. This implies that the concentration of the latter reactants will be much higher in solution than on the surface of the catalyst. When no solvent is used, the conversion is greatly increased. Similarly, in line with this view is the negligible effect of the surface area and the lack of shape selectivity despite the microporosity of the samples. These observations seem to support the idea that the reaction occurs most likely on the external surface of the catalysts.

To check the effect of the surface polarity on the oxidation of cyclohexene, the behavior of the two partially methylated samples in comparison to that of sample ZS6 was analyzed. According to Klein and Maier (9), in the case of 1% TiO_2/SiO_2 maximum activity in the oxidation of cyclohexene with H_2O_2 is observed when methylation of silica is in the 25%–35% range. The results observed with our catalysts in the oxidation of cyclohexene are summarized in Table 5. As can be seen, the most evident effect of methylation is the much lower consumption of hydrogen peroxide that is observed with both catalyst ZS6Me25 and catalyst ZS6Me40. No difference in conversion is observed if 35% H_2O_2 as the oxidant is used, despite the fact that the methylated samples have a surface area that is about double that of the sample ZS6. However, if less water is admitted to the system (50% H_2O_2), an intermediate methylation degree (sample ZS6Me25) allows the conversion of the reaction to significantly increase.

TABLE 5

Effect of Surface Methylation of the Catalyst in the Oxidation of Cyclohexene with Hydrogen Peroxide in MeOH as the Solvent

Sample no.	H_2O_2 conc.	Conversion (%)	H_2O_2 consumption (%)
ZS6	35%	28	62
ZS6Me25	35%	26	34
ZS6Me40	35%	26	32
ZS6	50%	28	60
ZS6Me25	50%	40	38
ZS6Me40	50%	22	25

Note. Reaction conditions: catalyst, 40 mg; substrate, 4 mmol; H_2O_2, 8 mmol; MeOH, 4 ml; *T*, 90°C; 24 h.

The same experiments were carried out in the absence of solvent, i.e. under conditions in which the activity and selectivity of the catalysts are maximized. A comparison of the behavior of catalysts ZS6, ZS6Me25, and ZS6Me40 is shown in Fig. 6. Since the reactions are relatively fast, they have been monitored for up to 8 h. As can be seen, the

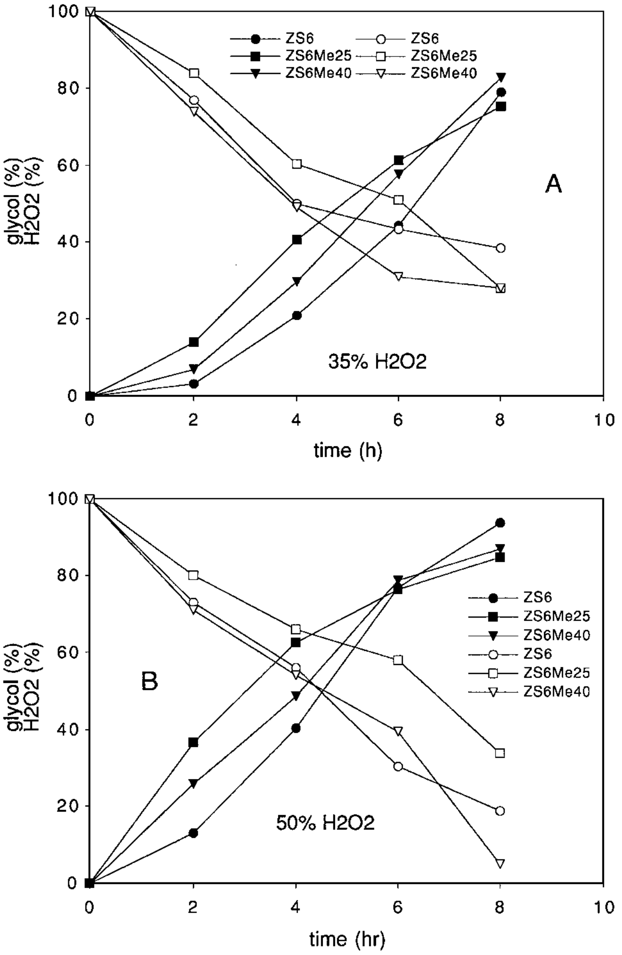


FIG. 6. Cyclohexandiol formation (filled symbols) and hydrogen peroxide consumption (open symbols) in cyclohexene oxidation with 35% H_2O_2 (A) and 50% H_2O_2 (B). Catalysts used: ZS6 (triangles), ZS6Me25 (circles), ZS6Me40 (squares). Reaction conditions: catalyst, 40 mg; substrate, 4 mmol; H_2O_2, 8 mmol; *T*, 90°C.

positive effect of a more hydrophobic support is evident both with 50% H_2O_2 and 35% H_2O_2. In fact, the reaction is faster with sample ZS6Me25 (25% methylation), while sample ZS6 (nonmethylated) is the worst catalyst. An improvement in H_2O_2 consumption is also evident, at least with the 25% methylation sample.

CONCLUSIONS

Although the results reported in this work are largely preliminary, they do show that this class of microporous zirconia–silica mixed oxides can be promising materials to catalyze the oxidation of olefins with hydrogen peroxide. The lack of shape selectivity and the absence of significant effects due to the surface area of the different samples seem to indicate that the reaction is most likely carried out on the external surface of the catalysts, thereby limiting greatly their potential activity. In this respect, an improved synthetic method will be necessary to increase the average pore diameter of the materials. The reactivity order observed in the oxidation of olefins is a strong indication that the reaction proceeds through a heterolytic mechanism in which a nucleophilic olefin attacks a surface-electron-poor zirconium peroxo species. Although in all cases the epoxide is likely involved as the primary reaction oxidation product, the acidity of the medium and/or the support leads to the opening of the oxirane ring. In the absence of solvent, the catalysts show high activity and selectivity (>99% glycol) at moderate temperature. More generally, the activity and selectivity of the catalysts and the extent of decomposition of hydrogen peroxide seem to be controlled by an appropriate polarity of the medium in which the reaction is carried out, by the polarity/acidity of the surface, and by the possibility to carry out the reaction at lower temperatures where the acidity effects of hydrogen peroxide and the silica matrix could be minimized. These effects are still largely unexplored and work is currently underway to tune the surface polarity and the porosity of the catalysts to maximize the activity and selectivity and minimize hydrogen peroxide consumption.

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