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Niobium containing micro-, meso- and macroporous silica materials as catalysts for the epoxidation of olefins with hydrogen peroxide

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Niobia–silica mesoporous materials (xerogel, aerogel and MCM type) have been synthesized by sol–gel techniques using different co-solvents as templates. All materials are active catalysts in the epoxidation of cyclohexene with hydrogen peroxide, but only meso–macroporous aerogels give a stable and recyclable catalyst.

1. Introduction

The discovery of MCM-type mesoporous materials [1] with their interesting and somehow exceptional physical properties (ordered structure, surface area up 1600 m^2/g, narrow pore-size distribution, pore volume up to 1.2 ml/g, good thermal stability) has pushed the interest of chemists towards the study of new applications for these materials and the development of new synthetic techniques for expanding and improving their properties. Several pathways are known for the synthesis of MCM's. The pH of the reaction medium, aging time and template amount proved of foremost importance in determining the properties of final materials. For example, some years ago, Schumacher *et al.* [2] discovered a new synthesis of MCM-48 utilizing Stober's synthesis of non-porous silica spheres [3]. The procedure consisted in the facile hydrolysis of TEOS and other precursors with an ammonia solution in presence of *n*-hexadecyltrimethylammonium bromide. Compared with the classical hydrothermal process [4] this procedure is faster and produces spherical MCM-48. If metal substituted with e.g. Al, Cr, Ga, Ti, V or Nb, these materials can be used as a catalysts for a variety of reactions such as Friedel–Crafts alkylation, acetalization, oxidation, Diels–Alder reactions, oxidative cyclization. Finally, this synthetic procedure allows to increase the surface area and pore volume of MCM-48 materials, if compared with the classical hydrothermal synthesis.

The demand for more environmentally acceptable processes in oxidation chemistry and the exceptional success of Ti-based silicalites [5] are stimulating an increasing interest towards the use of hydrogen peroxide in catalytic oxidation reactions. Semicrystalline and amorphous mixed oxides based on silica and containing transition metal oxides such as Zr [6], W [7], Ti [8], Nb [9] synthesized by sol–gel have been successfully applied in oxidation reactions with hydrogen peroxide. In particular it has been recently reported [9] that niobia–silica materials can be used as catalysts for the epoxidation of olefins with hydrogen peroxide.

In this work we wish to report our successful attempts to incorporate Nb_2O_5 in the matrix of amorphous MCM-48 type materials and on silicas prepared both as xerogel and aerogel. These samples differ from previously reported examples because the latter were incorporated only on MCM-48 prepared by classical hydrothermal synthesis at high temperature. The MCM samples reported in this work were obtained through the use of co-solvents during synthesis at room temperature. The resulting materials have been used as catalysts in the epoxidation of cyclohexene with hydrogen peroxide under very mild conditions.

2. Experimental section

2.1. Materials

The following materials were used for the synthesis: tetramethoxysilane (TMOS), niobium chloride, hexanol, decanol (Aldrich), *n*-hexadecyltrimethylammonium bromide (Fluka), ethanol and aqueous ammonia (BDH).

The oxidant was 35% hydrogen peroxide (Fluka). Substrates and solvent (methanol) were purchased from Fluka. All chemicals were purum or puriss grade and used without further treatment.

2.2. Methods

BET surface areas and pore size were determined with N_2 at 77 K on a Micromeritics ASAP 2000 apparatus. X-ray powder diffraction analysis was performed using a X'Pert diffractometer operating with Cu Kα Ni-filtered

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radiation, a graphite monochromator, and a proportional counter with a pulse height discriminator. The diffraction patterns were measured step by step (0.05° in2θ). Scanning electron microscopy (SEM) images were taken with a Jeol JSM 5600 LV (low vacuum) microscope. GC-MS measurements were performed on a Hewlett-Packard 5971 mass selective detector connected to a Hewlett-Packard 5890 II gas chromatograph.

2.3. Preparation of Nb_2O_5-MCM type samples

A solution of silica and Nb precursors was prepared by dissolving 114 mg of $NbCl_5$ in 1 ml of methanol followed by the addition of 14.6 ml of TEOS. Separately, *n*-hexadecyltrimethylammonium bromide as synthetic template (9.6 g) was dissolved with stirring in deionized water (200 ml) and a co-solvent (200 ml). To the homogeneous solution containing the surfactant, aqueous ammonia was added (50 ml, 30%) with stirring. The final solution was stirred for 10 min. Then, the solution containing TEOS and $NbCl_5$ precursors was added dropwise. After stirring for 2 h at room temperature, the resulting gel was filtered, washed with water, and dried in air at room temperature. The co-solvents used were ethanol, hexanol and decanol. The different samples obtained were calcined in air (30 ml/min) at 500 °C for 6 h. The samples prepared with this procedure are denoted as 2MNb, 6MNb, 10MNb.

2.4. Preparation of simple Nb_2O_5–SiO_2 xerogel

To a 250-ml beaker were added TMOS (4.8 ml), dissolved in EtOH (14 ml). The mixture was stirred at room temperature for 5 min. After this time, a 30% ammonia solution was added (1.05 ml). Hydrolysis occurred within 5 min. Over the prehydrolyzed mixture, a $NbCl_5$ (114 mg) in MeOH (1 ml) solution was added to obtain 1%wt Nb in silica. Gelation was completed in 5 min. The gel was transparent and was aged for 96 h at room temperature. The xerogel was dried at 110 °C overnight and calcined at 500 °C in air for 150 min: gas flow, 30 ml/min. The sample prepared with this procedure is denoted XNb.

2.5. Preparation of Nb_2O_5–SiO_2 aerogel under acidic conditions

A modified niobium *i*-propylate precursor was synthesized according to the procedure reported in ref. [9].

In a typical procedure, a solution of acetylacetone (acacH, 45 μL), *i*-PrOH (3 ml) and $Nb(Oi\text{-}Pr)_5$ (1.97 ml acac/$Nb(Oi\text{-}Pr)_5$ 2/1 molar ratio) was heated under reflux for 1 h under N_2 with stirring. The modified niobium precursor and TMOS (9.8 ml) were dissolved in *i*-PrOH (10 ml). A hydrolyzing solution consisting of distilled water (6 ml) and nitric acid (0.27 ml) diluted in *i*-PrOH (6 ml) was added dropwise to the alkoxides solution under vigorous stirring. After 90 min, 40 ml *i*-PrOH was introduced into the system. The obtained molar ratios H_2O/alkoxide/acid were 5/1/0.09. The mixture was transferred to a stainless steel autoclave for solvent evaporation under supercritical conditions (experimental conditions: Vc = 48 ml, Tc = 238 °C, Pc = 80 atm), during which gelation occurred yielding, after cooling down to room temperature and venting, a porous white solid. This was calcined at 500 °C in air for 150 min (gas flow 30 ml/min). The sample prepared with this procedure are denoted ANb.

2.6. Dehydration and dehydrogenation activities for isopropanol (DIPA)

Tests were carried out in a gas-flow apparatus. The reactor consisted of a glass tube with a sealed-in quartz bed onto which 100 mg of catalyst were placed. The system was heated at 500 °C for 60 min in air flow (30 cc/min) and then cooled down at 250 °C under nitrogen flow. The reaction feed consisted of a 2 min pulse of a *iso*-propanol in nitrogen mixture obtained by passing N_2 through liquid *iso*-propanol held in a saturator at 15 °C. The reaction effluent was analyzed by GC equipped with FID detector.

2.7. Catalytic oxidation procedures

Catalytic reactions were performed in 10 ml glass vials equipped with a condenser and a small magnetic bar. The catalyst (30 mg), substrate (2 mmol), solvent (methanol, 1 ml) and H_2O_2 (1 mmol) were placed in the vial under N_2 flow. The reaction vessels were sealed and maintained at 25 °C, while an external magnetic stirrer ensured agitation. At different reaction times the vials were opened and analyzed by GC. Product identification was performed by GC-MS analysis and by comparison with authentic samples. Residual H_2O_2 was determined by iodometric titration.

3. Results and discussion

3.1. Preparation

All samples were prepared by sol–gel methods with (MCM-type samples) or without (ANb and XNb) the use of a co-solvent under the conditions reported in the Experimental. Different aliphatic alcohols were chosen because it was previously observed in the case of MCM-41, that the size of the alkyl chain allows to control the surface area and porosity of the final material [4]. In the MCM type samples the preparation conditions led to the formation of a large amount of white gel upon addition of the precursor solution to the template solution, with no need of hydrothermal treatment. All MCM type samples were aged for 2 h with stirring, washed and dried overnight prior to calcination.

In the Xerogel sample, synthesized under basic conditions, gelation occurred in 4–5 min and a homogeneous colorless gel was obtained. The latter was aged in air for 96 h to yield a vitreous xerogel. Subsequent drying in the oven at 110 °C overnight allowed to eliminate organic and inorganic volatiles.

The Aerogel sample did not show any apparent gelation before supercritical evaporation of the solvent. In this case, the latter proved to be a fundamental step for obtaining a transparent gel.

Finally, all samples were calcined at 500 °C in air flow and all contained 1%wt Nb.

3.2. Characterization

X-ray powder diffraction analysis indicated that all samples were completely amorphous except 2MNb. The latter shows a semi-crystalline structure with the presence of a tridimensional cubic phase, typical of MCM-48. In all cases no peaks to be assigned to crystalline Nb_2O_5 were observed. This is a reasonable indication that Nb_2O_5 is well dispersed in the silica matrix [4].

Surface area and pore size distribution were determined from N_2 adsorption/desorption isotherms and some typical ones are shown in figure 1(a) and (b). A summary of the morphological properties of the different samples is reported in table 1

Samples showed different isotherms: 2MNb showed the typical isotherm of cubic MCM-48, classified as a type IV isotherm according to IUPAC nomenclature. The isotherms obtained in the 2MNb and 6MNb samples were similar. The 10MNb sample isotherm is typical of microporous samples. No hysteresis loop between adsorption and desorption branches was exhibited by MCM type materials.

The isotherm of XNb sample is type IV according to IUPAC and it shows a hysteresis loop typical of a mesoporous amorphous xerogel [10]. The aerogel sample (ANb) shows type III isotherm with a type H1 desorption hysteresis loop [9] typical of meso–macro porous materials with a high surface area.

Figure 2(a), (b) shows also some typical pore size distributions (BJH) for Nb_2O_5 containing samples. This is generally rather narrow and falls into the range of small mesopores (about 2–4 nm), but in the case of 2MNb sample an exact calculation cannot be made because of the complicated unit cell of the sample [2]. The aerogel sample (ANb) has large pore size distribution in the range of meso- and macropores. On the contrary, 10MNb sample is extensively microporous. As to 6MNb, some microporosity is suggested by both the isotherm and the BJH distribution.

The use of alcohols with increasing chain length as co-solvents during the preparation of MCM's has a notable effect on the morphological properties of these materials. As shown in table 1, on going from ethanol to hexanol to decanol the surface area, initially very high, first increases to reach a maximum for 6MNb and then drops down to 544 m^2/g for 10MNb. A similar effect occurs to 10MNb in the pore size distribution, whose maximum increases to 3.4 nm, as well as in the pore volume that drops to 0.3 ml/g. These results coupled with the indications of XRD analysis suggest that 2MNb is indeed an MCM-type material, 10MNb is most likely an amorphous, microporous material with only limited short range order, while 6MNb is probably in an intermediate situation. In other words we can say that in ethanol the surfactant is actually organized to work as a template, whereas in decanol, that is completely immiscible with water, it forms mycelles that help the emulsion of

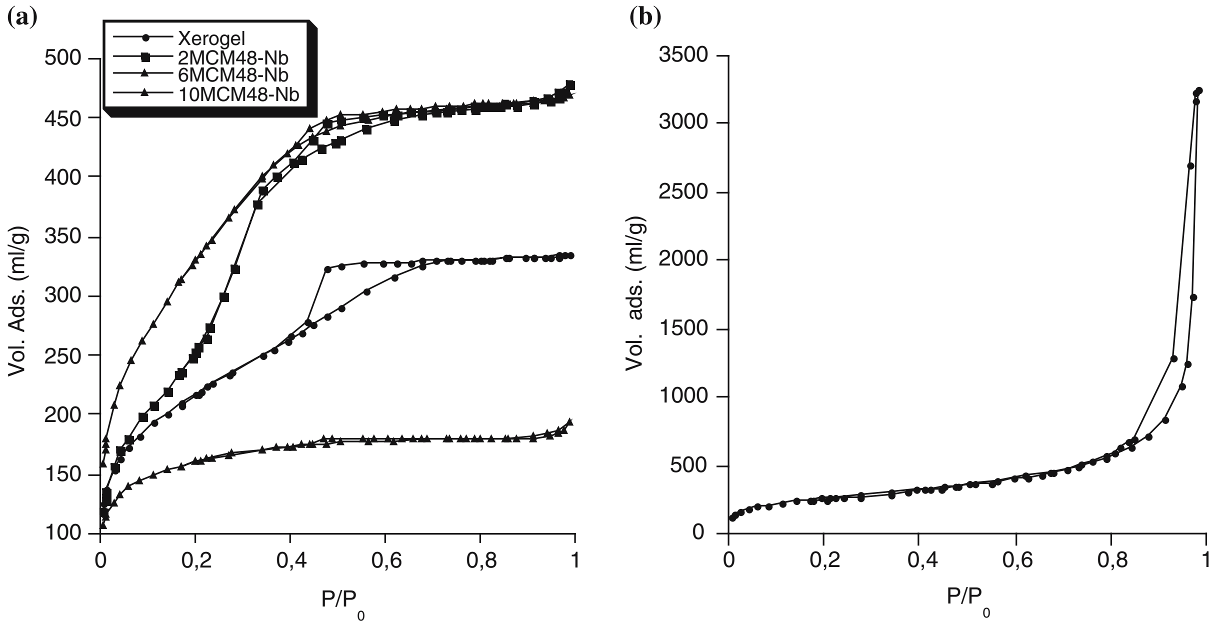


Figure 1. (a) Adsorption/desorption isotherms of 2MNb, 6MNb, 10MNb and XNb catalysts and (b) adsorption/desorption isotherms of ANb catalyst.

Table 1
Morphological and acidic properties of the different niobia samples

Sample	Co-solvent used	Surface area BET (m^2/g)	Pore distribution maxima (nm)	Pore volume (ml/g)	DIPA Conv. (%)at 250 °C
2MNb	Ethanol	974	2.9	0.7	43
6MNb	1-Hexanol	1207	2.7	0.7	65
10MNb	1-Decanol	544	3.4	0.3	60
XNb		768	3.1	0.5	63
ANb		940	35	5.0	61

decanol in water. Under these circumstances, Si–O–Si chain growth during the condensation step probably takes place inside a mycelle giving rise to a more compact, microporous material.

In agreement with these observations, SEM images of these samples (figures 3–7) indicate that only sample 2MNb consists of regular spherical particles, while a disordered, non-uniform agglomeration of spheres to give irregular particles was observed when the chain of the solvent increased. Images typical of glassy materials were obtained for the xerogel sample (XNb).

The aerogel niobia containing sample ANb (figure 7(a)) is constituted by very small particles agglomerated together into large particles. Notably, the ANb sample after four catalytic cycles and recalcination (figure 7(b)) appears with a different structure showing a sintering of the originally small particles. This is not surprising as (vide infra) the recycling procedure involves prolonged agitation, drying and recalcining steps that alter the original morphology of the material.

3.3. *Acidity measurements*

The profile (conversion versus reaction temperature) of the dehydration-dehydrogenation of *iso*-propanol (DIPA) (figure 8), along with the corresponding product distribution has been proposed to give indications on the acidity and basicity of catalysts [11].

The distribution of products and the conversions at 250 °C (table 1) were analyzed to get some insights on the acid–base properties of these materials. The main reaction product for all samples is propylene ($>95\%$) with only small amounts of acetone and diisopropyl ether at all temperatures. In the case of ANb a larger amount of acetone ($\approx 15\%$) was observed. This type of product distribution is a good indication for the presence of acid sites and good uniformity of the acidic properties for 6MNb, 10MNb, XNb (Conversion at 250 °C 60–65%). The lower activity observed for 2MNb (43% conversion at 250 °C) is indicative of a lower acidity. On the other hand, the larger amount of acetone observed for the ANb sample suggests that the latter may also contain basic sites [11].

3.4. *Oxidation of cyclohexene*

The oxidation of cyclohexene (Scheme 1) with 35% hydrogen peroxide was chosen as the reference reaction to compare the behaviour of the different catalysts. Cyclohexene is an interesting test reagent, because the low stability of the corresponding epoxide allows to test

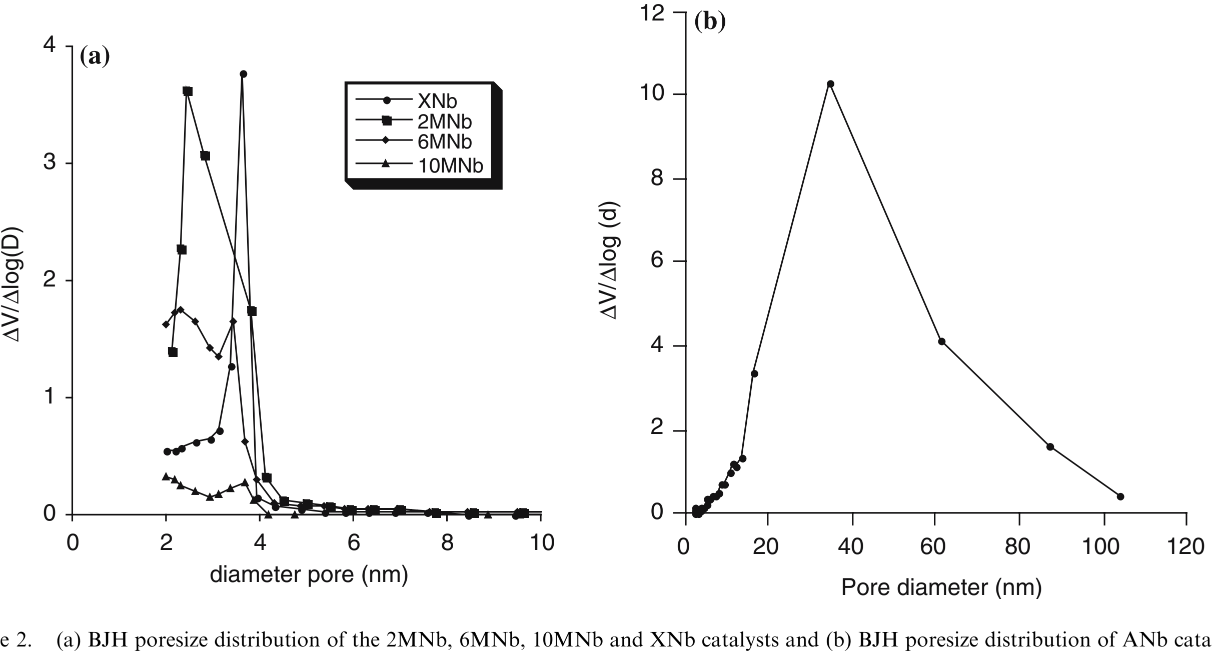


Figure 2. (a) BJH poresize distribution of the 2MNb, 6MNb, 10MNb and XNb catalysts and (b) BJH poresize distribution of ANb catalysts.

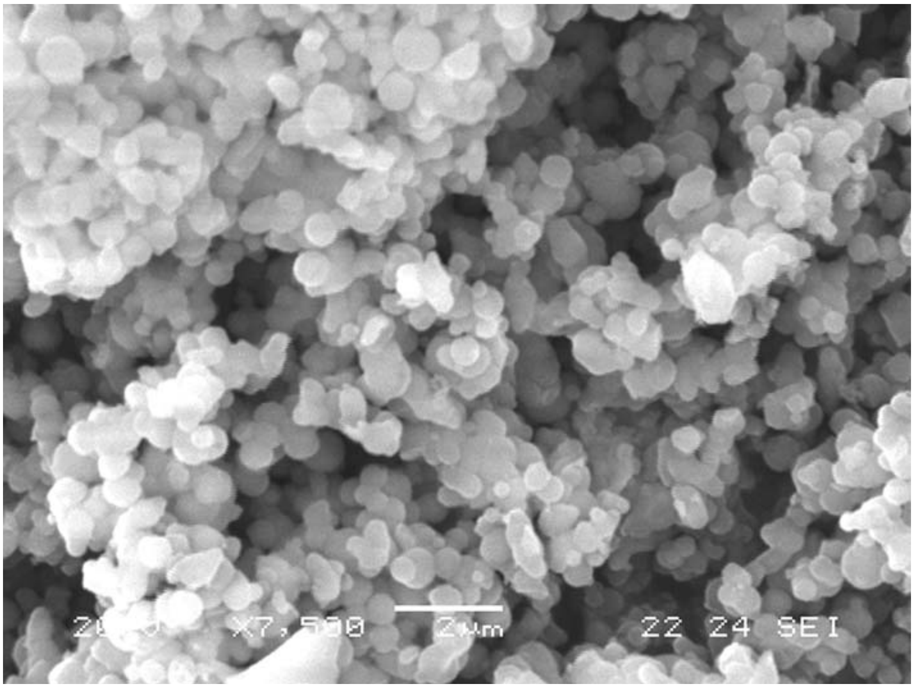


Figure 3. A SEM image (×7500) of 2MNb.

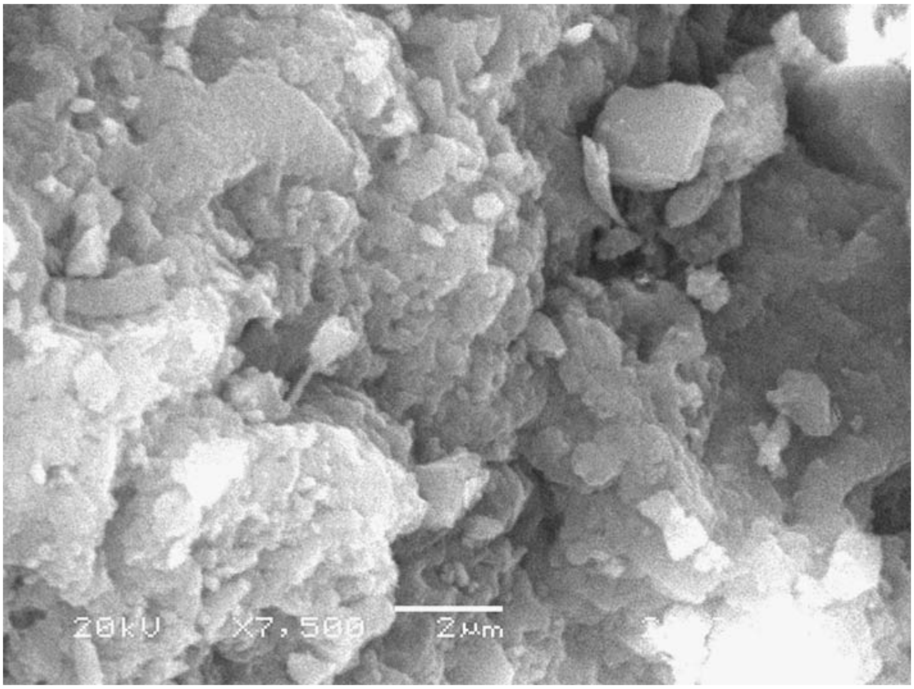


Figure 4. A SEM image (×7500) of 6MNb.

the selectivity properties of catalysts. Reactions were carried out in methanol, a solvent that is commonly preferred for industrial applications, as it is cheap and completely miscible with hydrogen peroxide. The reaction was carried out at room temperature (25 °C) because it is most interesting with respect to economic issues and because it helps preserving the catalysts from metal leaching. Other experiments at different temperature (50 and 70 °C) were carried out but, although the conversions were higher, the final yield to epoxide did not increase because of an increase in the amount of ring-opening products.

In general, the use of fresh catalysts led to the formation of large amounts of cyclohexandiol methyl ether

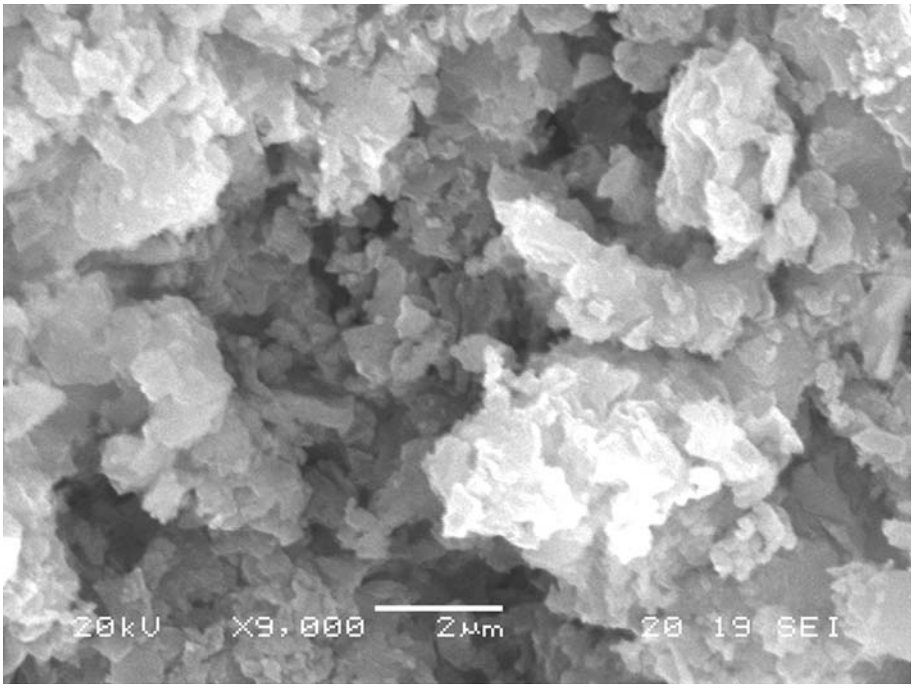


Figure 5. A SEM image (×9000) of 10MNb.

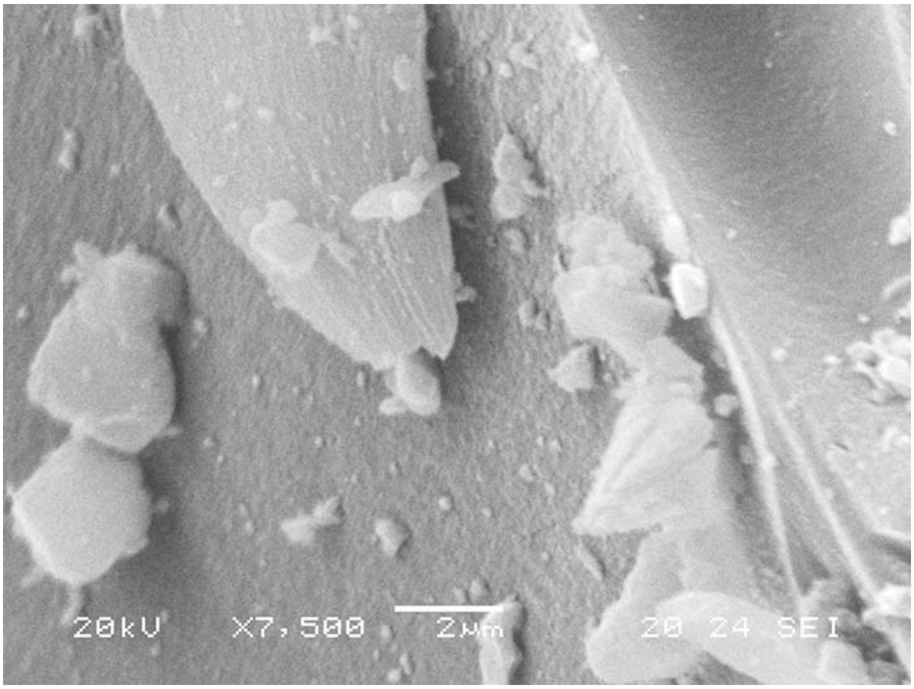
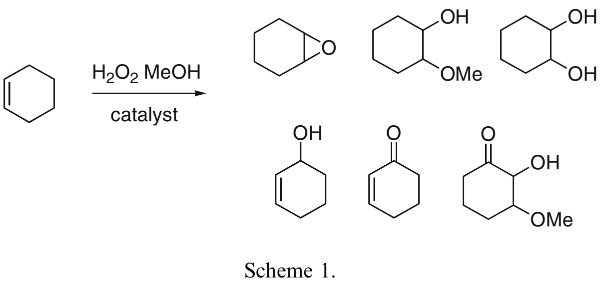


Figure 6. A SEM image (×7500)of XNb.



Scheme 1.

arising from methanolysis of the epoxide initially formed, with consequent lowering of selectivities and yields. Other by-products were observed as indicated in Scheme 1. A typical reaction profile reporting the conversion and the selectivity to epoxide is shown in figure 9. The conversions, selectivities and yields to epoxide after 22 h are reported in table 2, where the data for the fresh catalysts correspond to the first catalytic cycle. As can be seen, the conversion did not show any direct correlation with the

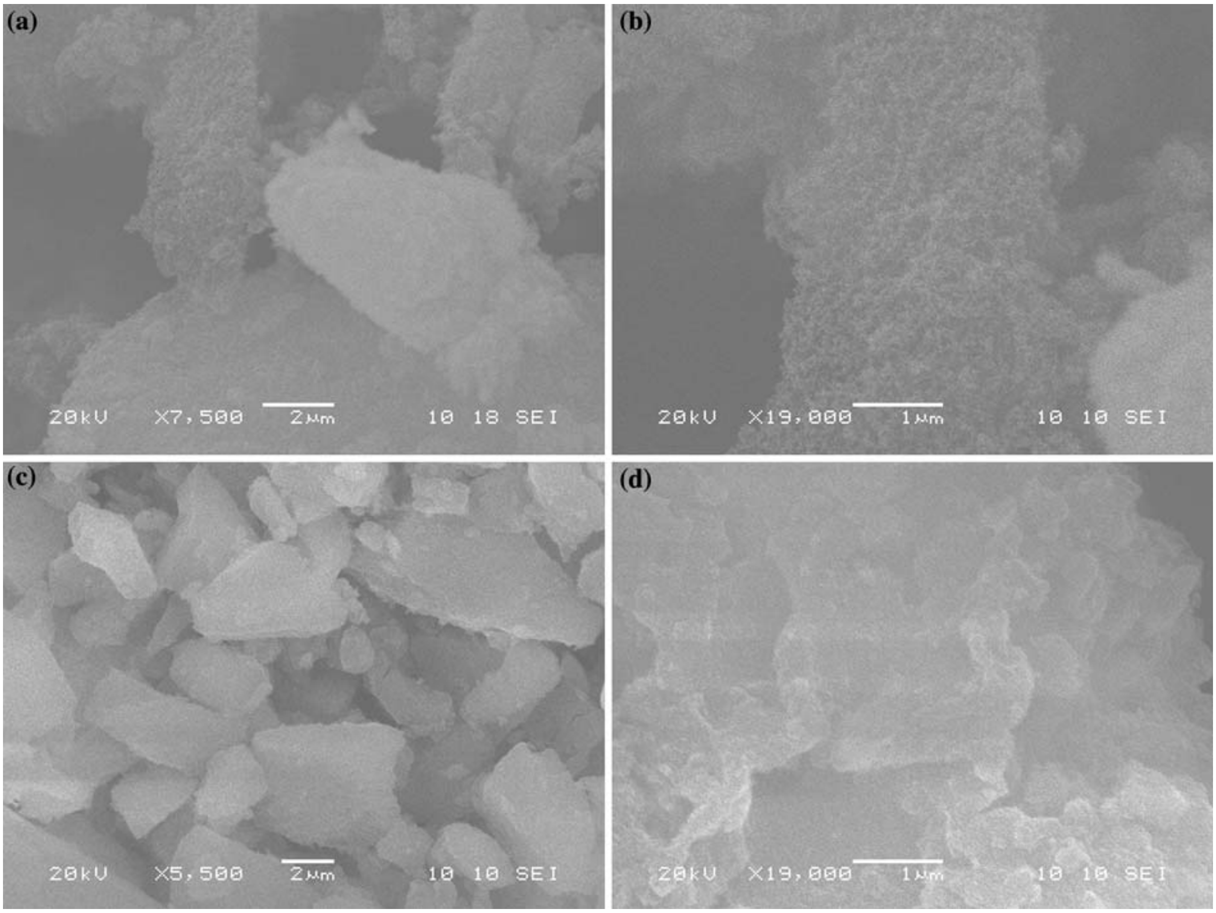


Figure 7. SEM images of fresh ANb: (a) (×7500), (b) (×19000). SEM images of used ANb: (c) (× 5500), (d) (× 19000).

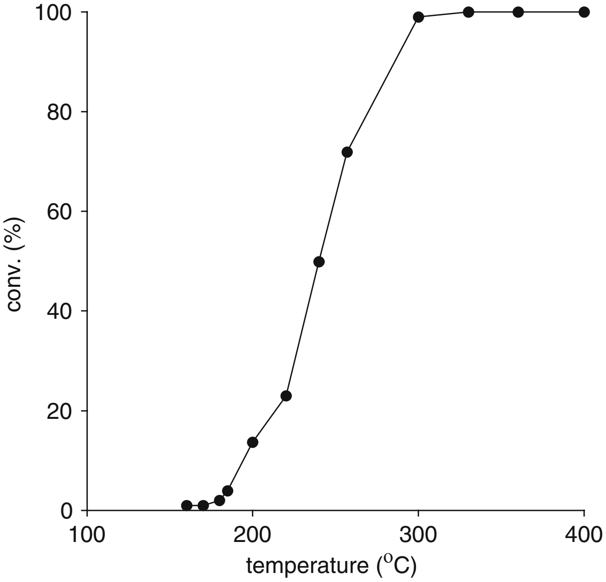


Figure 8. A typical (ANb sample) conversion versus temperature profile for the decomposition of *i*-propanol.

acidity test results, selectivities to epoxide are from moderate to low, while the efficiency in the consumption of hydrogen peroxide is always very high (95–100%).

The overall reactivity is summarized in table 2, where the results obtained with an amount of $NbCl_5$ identical to the amount of Nb present in the different samples, dissolved in MeOH and used as a reference homogeneous catalyst are also reported. As shown, simple correlations with the morphological and/or acidic properties of the materials cannot be identified. For

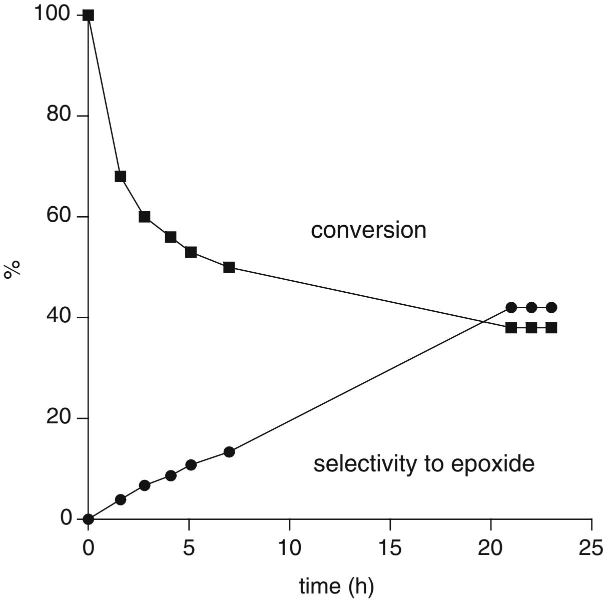


Figure 9. A typical (ANb sample) conversion and selectivity to epoxide versus time plot for the oxidation of cyclohexene.

Table 2
Effect of catalyst recycling in the oxidation of cyclohexene with hydrogen peroxide catalyzed by different niobia catalysts

Sample	Cycle[a]	Conv (%)	Epoxide selectivity (%)	Epoxide yield (%)	H_2O_2 eff. (%)
2MNb	1st	44	40	18	96
	2nd	23	41	9	96
	3rd	26	34	8	95
	4th	13	20	3	95
6MNb	1st	67	18	12	99
	2nd	61	39	24	98
	3rd	46	56	26	100
	4th	34	57	20	98
10MNb	1st	54	39	21	99
	2nd	41	55	23	95
	3rd	31	47	15	100
	4th	32	13	4	98
XNb	1st	60	13	8	96
	2nd	55	40	22	96
	3rd	37	43	16	96
	4th	17	5	1	95
ANb	1st	42	38	16	100
	2nd	30	44	13	99
	3rd	13	54	7	98
	4th	30	39	12	99
$NbCl_2$ Hom.		76	24	18	95

[a] Between the 3rd and 4th cycle a recalcination at 500 °C was performed.

example, one would expect a higher selectivity for sample 2MNb (the least acidic) with respect to other catalysts. Instead, 10MNb and ANb give similar results. Only in the case of 6MNb the higher conversion could be due to its larger surface area, however the observed low selectivity to epoxide is not in agreement with its relatively low acidity. With the exception of XNb, in most cases the total amount of epoxide observed is very similar to the one achieved for the $NbCl_5$ homogeneous species that appears to be the most active catalyst.

These observations, in particular the poor influence of the morphological properties of solids on the reactivity, cast some doubts on the actual heterogeneous nature of these reactions, especially in view of the high activity observed for the homogeneous catalyst.

3.5. *Catalyst recycling*

Catalyst recycling tests were carried out for all heterogeneous samples. The oxidation of cyclohexene was tested with fresh samples, followed by a series of recyclings, the solids being isolated by filtration from the previous reaction mixture. After each cycle, the recovered solids were always dried for 20 h in the oven at 110 °C and reused. At the same time catalyst free solutions were reacted with fresh oxidant and substrate, stirred for further 22 h and checked for residual activity. After the third cycle all samples were recalcined at 500 °C before running a fourth cycle. A summary of the results obtained in the different cycles is collected in table 2. As can be seen, cycle after cycle and even after recalcination there is a constant loss of activity (conversion) as well as a change in epoxide yield. It must be emphasized that the catalyst free solutions separated from each reaction mixture showed a residual activity and a further 5–15% conversion was observed. This is a clear indication that Nb is leached from the heterogeneous materials to form soluble oxy-hydroxy (or -methoxy) species that might be similar in nature to the species formed from $NbCl_5$. If we roughly assume that the soluble species have a similar activity, no matter where they come from, we can estimate that solid catalysts lose 10–20% Nb during each cycle. The only exception is the aerogel catalyst (ANb) for which the different reaction solutions show no residual activity after separating the catalyst and a significant revamping of activity of ANb is observed after calcination.

It is interesting to notice that the chain length of the co-solvent used for the preparation has an effect on the loss of activity after the 4th cycle. This observation seems to show that the co-solvent has an effect not only on the morphological properties of the materials but also on the stability of the active phase, that is higher for longer co-solvent alkyl chain.

In the case of 6MNb, 10MNb, XNb and ANb samples, after each cycle, the selectivity to epoxide increases (at least before calcination).

This effect is conceivably due to the heterogeneous catalysts, since the selectivity of the soluble species is low and presumably remains the same during the different cycles.

It could be suggested that niobium in an amorphous silica matrix can change its coordination geometry (and hence its selectivity), while in 2MNb (Nb_2O_5-MCM48) the presence of an ordered semi-crystalline structure does not allow this change in coordination, but only leaching of active phase. Finally, the calcination after the third cycle probably eliminates residual organics, but restores neither the initial activity nor the selectivity of catalysts.

Only in ANb sample, after recalcination, the conversion increases from 13% to 30% and the selectivity to epoxide returns to the initial value. We can infer that probably, only ANb sample is a truly heterogeneous catalyst. The loss of activity for this material could be related to structure collapsing, as observed by the SEM pictures (figure 7(a), (b)), due to repeated stirring cycle by cycle.

3.6. Comparison with previous samples

With respect to previous work already reported on niobia–silica catalysts [9] it appears that the high Nb dispersion suggested by XRD data is not determining for the stability of the catalysts. Indeed, XRD data do not give a direct indication of the size of the different Nb_2O_5 domains, they merely show that these domains are amorphous (hence conceivably small) and it is possible that different synthetic techniques will lead to Nb_2O_5 domains of different size. We can hypothesize that Nb_2O_5, albeit dispersed in the matrix, when in contact with H_2O_2 can form niobic acid type species that are soluble and partly responsible for the catalytic activity. The high catalytic activity observed with $NbCl_5$ in methanol solution could well be attributed to niobic acid. In fact, $NbCl_5$ reacts with MeOH producing HCl and species such as $Nb(MeO)_xCl_y$ that, in the presence of hydrogen peroxide, can easily hydrolyze to give Nb species related to those obtained by leaching of Nb in the catalytic reaction mixtures.

If the results here reported are compared to those of Novak *et al.* [9] on the stability of Nb_2O_5-MCM-41 made by classical hydrothermal methods and to those of Somma [9] on Nb_2O_5-SiO_2 aerogels, it appears that a high temperature, high pressure treatment (in autoclave) is determining for obtaining active and stable catalysts, as the ANb catalyst here reported, where the metal is strongly held in the matrix and is not released during epoxidation reactions. When such a treatment is not foreseen in the preparation procedure (as in most of the catalysts reported in the present work), leaching may become quite significant.

4. Conclusions

The results reported in this paper clearly show that the *sol–gel* and the template preparation methods are a viable way to obtain micro and mesoporous Nb_2O_5-SiO_2 mixed oxides materials with either semi-crystalline or amorphous structure. These materials are active in the epoxidation reactions with H_2O_2 under very mild conditions (RT), although the selectivity is moderate. Differences in the catalytic activity between amorphous and crystalline samples are not observed. Yields to epoxide are similar and there is no direct correlation between the selectivity to epoxide and the acidity of the catalysts determined by decomposition of *i*-propanol.

However, recycling data have clearly shown that these materials cannot be considered as truly heterogeneous catalysts. Only the aerogel sample shows a good stability during the reaction. Therefore in dealing with sol–gel made samples for liquid phase catalysis, one should always take into account stability issues and carefully deal with possible leaching problems.

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