Applied Catalysis A: General 454 (2013) 88–92

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

A novel hydrofobic niobium oxyhydroxide as catalyst: Selective cyclohexene oxidation to epoxide

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ARTICLE INFO

Article history:
Received 5 October 2012
Received in revised form 2 January 2013
Accepted 5 January 2013
Available online xxx

Keywords:
Niobium oxyhydroxide
Hydrogen peroxide
Cyclohexene
Epoxide

ABSTRACT

A surface modified niobium oxyhydroxide catalyst was utilized for the selective liquid-phase oxidation of cyclohexene to epoxide in the presence of hydrogen peroxide. After surface modification with a surfactant (cetiltrimetilamonium bromide -CTAB), the very active niobium oxyhydroxide (NbO_2OH), presented hydrophobic characteristics and good activity for the oxidation of cyclohexene over the heterogeneous catalyst. Furthermore, the hydrophobic material presented a high selectivity toward the formation of the epoxide species. The mass spectrometry analysis of the reaction showed that epoxide species was produced with a selectivity of 60% using 0.2 mL of hydrogen peroxide, with 65% of conversion. The results strongly suggest that the reaction involves oxidizing species generated after the reaction with H_2O_2. The surfactant anchored over the niobium catalyst promotes a better interaction with the nonpolar substrate.

1. Introduction

Many homogeneous and heterogeneous catalysts for the selective activation of C—H bond (oxidation) have been developed in the last years [1–8]. Among them, niobium compounds have been the objects of an increasing interest as peroxo complexes for the oxidation of organic compounds and as precursors for the preparation of niobium oxides [9–11].

Niobium compounds are of great interest in heterogeneous catalysis, due to their promoter and support effects for other metals, increasing the catalytic activity and the stability of the catalysts. Recently, the properties of niobia compounds as active species have been explored by several authors [11,12]. The formation of peroxo species improves the oxidation properties of the niobium catalyst, due to their ability to release active oxygen, promoting the oxidations of different inorganic or organic substrates [13–15]. Not only niobium compounds, but also peroxo complexes of vanadium, molybdenum and tantalum have attracted attention due to their properties to donate active oxygen able to oxidize organic compounds in liquid phase reactions [9]. However most of the works involving the use of niobium reagents for the oxidation of organic compounds in liquid phase take place *via* homogeneous catalysis [10,12]. The oxidation of cyclohexene over heterogeneous niobium catalysts has been studied by the Ziolek's group [16,17]. In a recent work they showed that H_2O_2 can react with amorphous Nb_2O_5 to produce a yellow reactive material, typical of metal peroxo species. We described in a previous work [11] a similar result using a synthetic niobia catalyst obtained by precipitation with sodium hydroxide. Parida et al. [18] described a hybrid titanium complex as an excellent catalyst for epoxidation of cyclohexene using hydrogen peroxide as oxidant. However, the reactions were relatively slow, and, comparing to our work, a higher temperature was necessary to perform the oxidation. These problems, however, have been overcome by the development of a new hydrophobic niobium catalyst [19]. Hybrid catalysts offer the possibility of modulating their surface hydropholicity, increasing the diffusion of the organic compounds on the catalyst surface. In fact, Morandin et al. [20] reported that the increase of the hydrophobicity of zirconia-silica mixed oxides lead to an improvement of the specific activity of the catalysts by three to four times, and allows a better control of the efficiency with which hydrogen peroxide is consumed in the oxidation reaction. Recently, a new class of niobium compounds was developed by pretreatment of a synthetic niobia with H_2O_2 to generate a modified catalyst [11,21]. The synthetic niobium oxyhydroxide obtained in that work can be modified by surfactant treatment generating a new catalyst bearing hydrophobic tail on the surface. The partial hydrophobization of the catalyst provides it the possibility to react with compounds present in polar or nonpolar solvent (amphiphilic properties).

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http://dx.doi.org/10.1016/j.apcata.2013.01.007

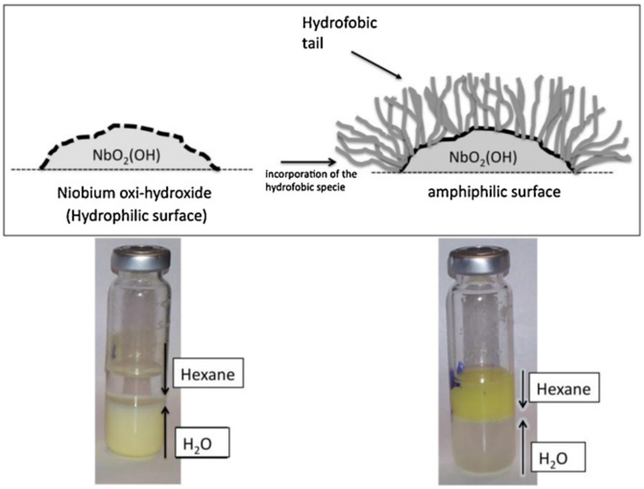

Fig. 1. Schematic illustration of the incorporation of hydrophobic tail over niobium oxyhydroxide and pictures of the hydrophilic catalyst and hydrophobic niobium oxyhydroxide partitioned between water and hexane.

In order to give some contribution to elucidate the chemistry involved in the interaction between niobium species and H_2O_2, we studied in the present work the use of niobium oxyhydroxide and hydrophobic niobium oxyhydroxide (prepared in the presence of CTAB) as heterogeneous catalysts for the oxidation of cyclohexene in the presence of hydrogen peroxide. We observed that the previous treatment of the synthetic niobia with H_2O_2 improved the catalytic activity of the material. An interesting result relative to selectivity for epoxide species was found by anchoring a surfactant on the catalyst surface.

2. Experimental

The hydrophilic catalyst (S2) was prepared treating $NH_4[NbO(C_2O_4)_2(H_2O)]\ (H_2O)_n$ with NaOH (50 mL, 1 mol L^{-1}), followed by heating at 60 °C for 72 h [8]. In the case of hydrophobic catalyst (S3) 15 g of CTAB (cetiltrimetilamonium bromide – $C_{19}H_{42}BrN$) previously dissolved in 105 mL of a mixture water/butanol (80:25) were added. The solid was then filtered, washed with distilled water and dried at 60 °C for 12 h. Fig. 1 presents a scheme of the incorporation of the hydrophobic tails on the catalyst as well as pictures of the catalysts (S2 and S3) partitioned between water and hexane.

The thermal gravimetric analyses (TG) of the materials were made in an SDT-simultaneous TGA-DTA model TA, under N_2 atmosphere with heating rate of 10 °C min^{-1} up to 800 °C.

The acidic properties of the solids were determined by temperature-programmed desorption using ammonia as probe molecule. The NH_3-TPD (Temperature Programmed desorption) profiles were obtained using a Chembet-3000 (Quantachrome) equipment (TCD detector, current of 150 mA, attenuation of 32). About 0.2 g of each solid was treated at 400 °C for 50 min in a continuous flow of helium (80 mL/min) prior to adsorption of NH_3 at 50 °C. After the sample has been purged, the TPD profiles were obtained at a heating rate of 10°/min up to 700 °C.

The resonance Raman spectra was adquired using a (SENTERRA at $\lambda = 532$ nm, power 0.2 mW, objective 50×, integration time 30 s, 4 coadditions and 2 mm laser aperture). The zeta potential variation (PCZ) of aqueous suspensions of the powder as a function of pH was measured by electrophoretic mobility using a Zetasizer 3000 (from M/s Malvern Instruments Ltd., UK) equipment.

The oxidation reactions of cyclohexene were performed using a mixture of 2 mmol of the reactant, 50 mg of the catalyst in acetonitrile (20 mL) and 0.1 mL of aqueous hydrogen peroxide 30% at 25 °C. The cyclohexene conversion was monitored by UV (Spectrovision), with scan between 250 and 800 nm and GC–MS (Hewlett-Packard 5890 Series II with MSD 5971A).

3. Results and discussion

3.1. Catalytic tests

3.1.1. UV–vis spectroscopy analyses

The kinetic of the conversion of cyclohexene over synthetic niobium oxyhydroxide, monitored by UV–vis spectroscopy is shown in Fig. 2a. The results clearly show that the surface modified catalyst (S3) was more efficient than the hydrophilic catalyst (S2), allowing a conversion of approximately 80% after 180 min of reaction, while S2 lead to only 15% of conversion.

Furthermore, to verify the absence of heat and mass transfer limitations, the Koros-Nowak test [22] was employed. This test was carried out with different amounts of catalyst (15, 30, and 50 e 100 mg) as shown in Fig. 2b. The similarity of the conversion in all the systems indicates that there are no heat or mass transfer limitations in our measurements.

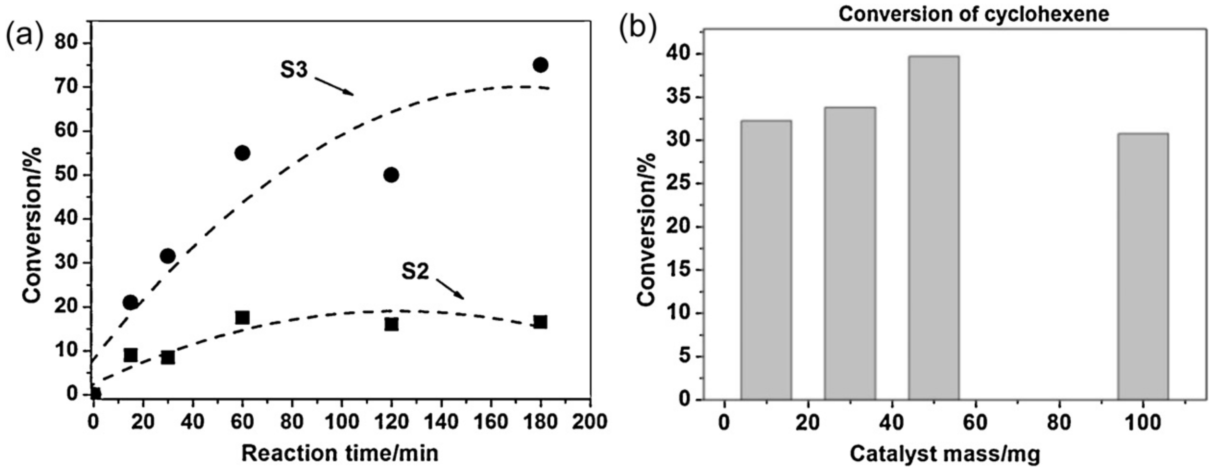

Fig. 2. Kinetic of the reaction of cyclohexene oxidation with hydrogen peroxide monitored by UV–vis spectroscopy (a), and the oxidation with different amounts of catalyst (b) ($T = 25$ °C; 1.0 mL of H_2O_2; 1 h of reaction).

Table 1
Reactions of cyclohexene with hydrophylic (S2) and hydrophobic (S3) niobia at 25 °C for 1 h.

Reaction	Conversion (%)	Seletivity (%)				
		2-Cyclohexenol	Cyclohexanol	2-Cyclohexen-1-one	1,2-Cyclohexanodiol	Cyclohexene oxide
No catalyst (only H_2O_2)	8	–	1	4	2	–
S2[a]	18	9	–	12	9	1
S3 (without H_2O_2)	5	–	3	–	–	–
S3[a]	55	6	–	–	4	28
S3[b]	65	–	–	8	7	60

[a] V_{H2O2} = 0.1 mL;
[b] V_{H2O2} = 0.2 mL; time of reaction = 1 h.

3.1.2. GC–MS analyses

In order to identify the species formed during the reaction, the products were analyzed by GC–MS (Table 1). The material treated with the surfactant presented a higher conversion of the cyclohexene when compared to other catalysts under mild conditions. The results show that the reaction of cyclohexene (0.978 mmol) over the hydrophobic catalyst (S3) in the presence 0.1 mL of H_2O_2 (2.94 mmol) gave 55% of conversion (28% selectivity to cyclohexene epoxide) after 1 h of reaction. The same reaction with 0.2 mL of H_2O_2 lead to a better result: a conversion of 65% was obtained with a high selectivity toward the cyclohexene epoxide (60%). These results are better than those found in the literature. For example, the homogenous Nb-catalysts sodium tetraperoxo-niobate was selective for the formation of the epoxide (73% selectivity), but the rate of conversion was very low (7%) [7]. Ziolek et al. [16] obtained 72% conversion of cyclohexene when Nb was incorporated into mesoporous silicate, however, using pure Nb_2O_5 and H_2O_2 the conversion was only 49%.

The presence of the hydrophobic tails on the surface of the catalyst lead to a much higher conversion of cyclohexene when compared to the hydrophilic catalyst S2 (respectively 55% and 18% using 0.1 mL H_2O_2). This may be due to the increased area of contact between the catalyst S3 and the nonpolar cyclohexene. Furthermore, the presence of the hydrophobic part over the catalyst decreases the capacity of oxidation of the material, which permits the formation of cyclohexene epoxide without further reaction process such as the formation of diol, since the peroxo groups are active in the opening of ring [17].

No leaching problems with the catalysts were revealed in the experiments. Thus, the S2 and S3 materials can be used as truly heterogeneous oxidative catalysts for the epoxidation process.

The influence of the hydrogen peroxide amount on the rate of conversion was studied and the results are displayed in Fig. 3a. Clearly, the increase of hydrogen peroxide favors the cyclohexene conversion, which can be explained by the formation of peroxoniobate from the reaction between H_2O_2 and the surface niobium [11]. In Fig. 3b a schematic representation of the entire process is depicted showing the reaction of H_2O_2 that leads to the formation of a peroxoniobate reactive group at the surface of the catalyst and to the conversion of cyclohexene.

The results suggest that the functionalization occurs in the surface OH groups attached to niobium. This fact decreases the formation of peroxos groups (oxidant groups) resulting from the reaction of these OH groups with the H_2O_2 added (Fig. 3b). Thus, due to the prevention of formation of peroxo group by anchoring of a surfactant group, the material reduces its oxidative ability becoming more selective for partial oxidation products. Furthermore, one evidence that leaching of organic groups does not occur is that after several reuses the material continues with hydrophobic properties, since it keeps itself in the interface between a polar and the other nonpolar solvents, as shown in Fig. 4a. Additionally, leaching tests were performed and the results were negligible conversion.Several reuse tests were conducted to ensure the stability of the catalyst. After each reaction, the catalyst was recovered by centrifugation and weighed to check a possible loss of mass with the recovery process. The cyclohexene conversion results are shown in Fig. 4b. It can be observed that after six reuses the cyclohexene conversion remained very similar, which proves the stability of the catalyst. It is also interesting to note that the material after reuse stays with the hydrophobic property because it stays at the interface of polar and nonpolar liquids, as shown in Fig. 4b.

3.2. Characterization of the materials

The acidic properties of the materials were investigated by temperature-programmed desorption using a mmonia as probe molecule. TPD-NH_3 profiles are shown in Fig. 5a. In both materials, S2 and S3, adsorbed ammonia began to desorb at a temperature above 250 °C and exhibited the peaks centered at nearly 320 °C. The relatively low desorption temperature indicates the presence of weak acid sites on the surface of S2 sample. The S3 material exhibited similar NH_3-TPD profiles and less acidity than S2, and

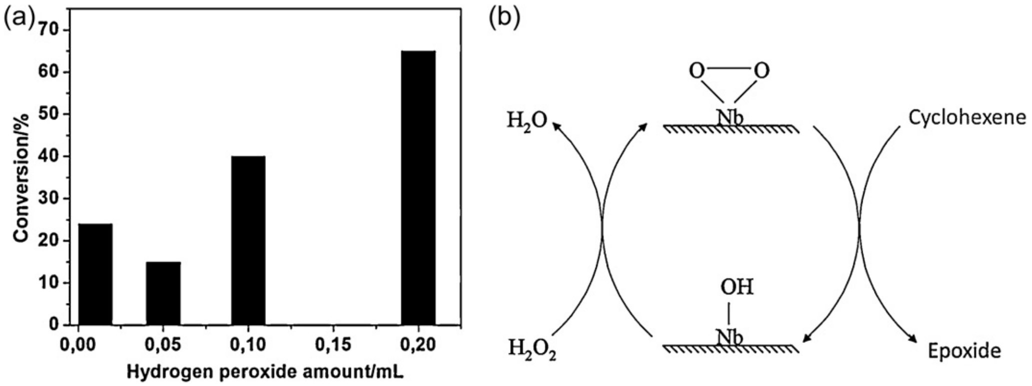

Fig. 3. Influence of H_2O_2 amount in ciclohexene conversion (a) and a schematic illustration of the entire process involving the formation of a peroxoniobate reactive group and conversion of cyclohexene.

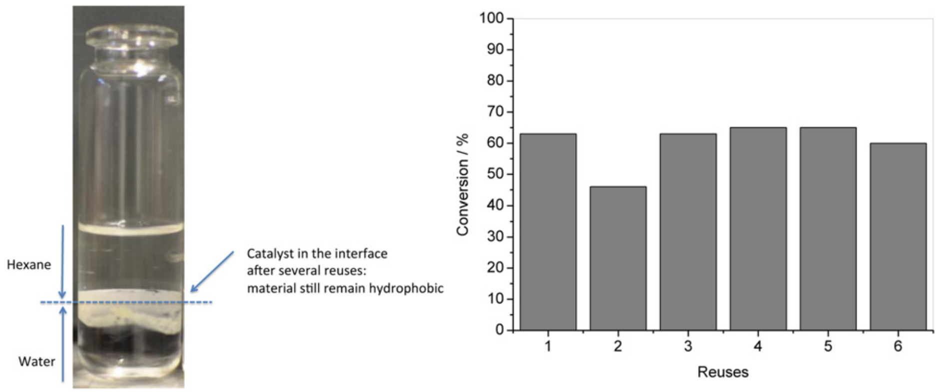

Fig. 4. Picture of catalyst in the interface of a biphasic system (hexane/water) after six reuses (a) and reuses tests of the catalysts (b) ($m = 50$ mg; Vol $H_2O_2 = 0.2$ mL; Vol cyclohexene = 10 mL; 60 min of reaction).

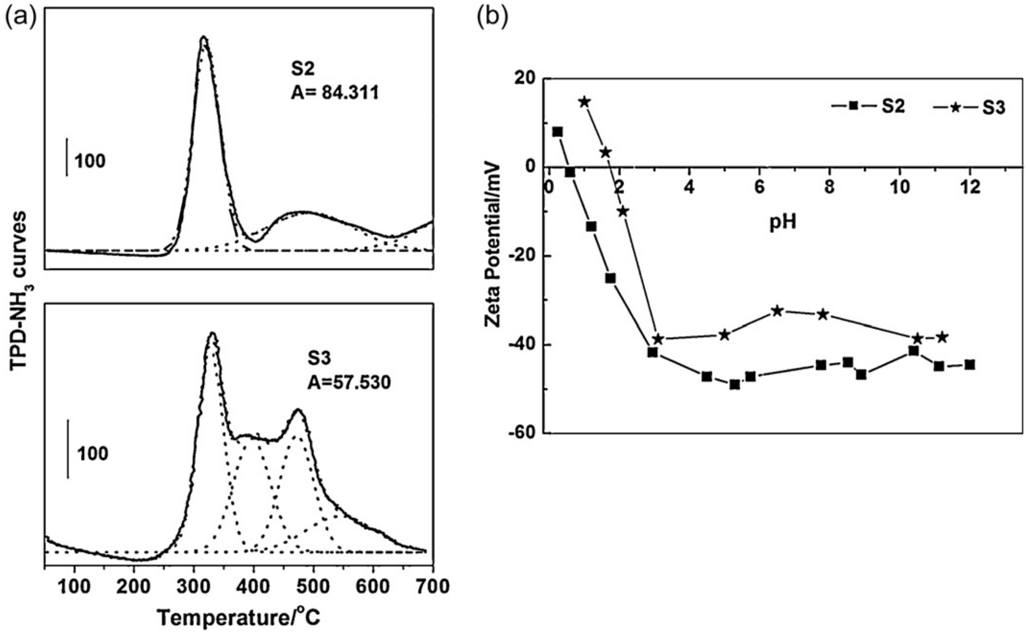

Fig. 5. TPD-NH_3 profile of the S2 and S3 samples (a). The pH dependence of zeta potentials for S2 and S3 (b).

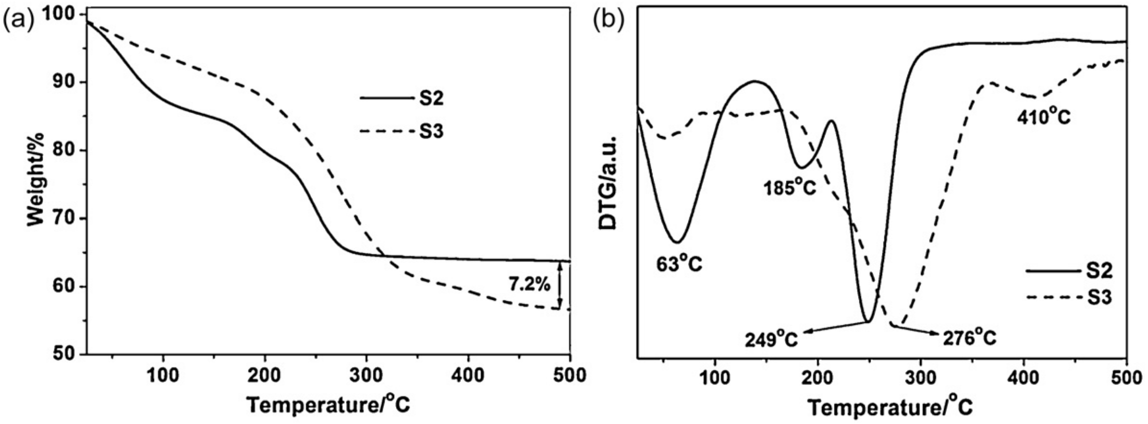

Fig. 6. TG analyses of the catalysts S2 and S3 under oxygen atmosphere.

a decrease of approximately 32% of the acid sites was observed by incorporating the surfactant. This suggests that the surfactant molecules are bound to the surface by substituting hydroxyl groups.

The surface changes of the materials were studied by zeta potential measurements. The variation of zeta potential with pH for the aqueous suspensions is shown in Fig. 5b. The zeta potential was found to be approximately pH 0.59 and pH 1.71 for S2 and S3,

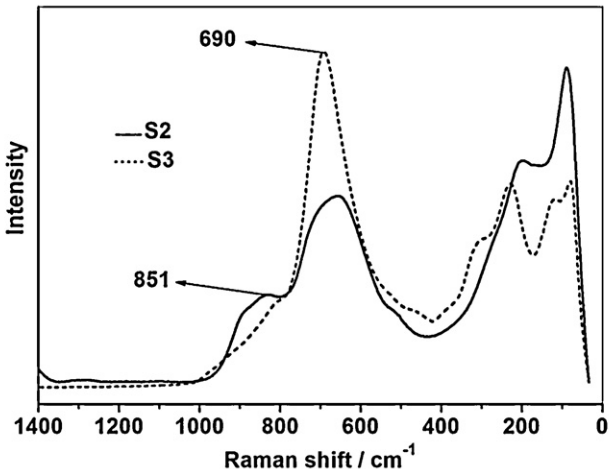

Fig. 7. Raman spectra of investigated catalysts.

respectively. It is likely that there are more negative ions at the S2 particle surface compared to S3. The treatment of the hydrophilic catalyst (S2) with CTAB surfactant causes great changes in the surface of the material. The higher pH at zero charge suggests that the surfactant presence leads to a decrease of Brönsted acid sites (Fig. 5b). Considering the difference in PCZ values of S2 and S3 it can be obtained that the 1.32×10^{23} surfactants sites were generated on the surface of the catalyst S3.

The catalysts showed a mass loss related to dehydration and dehydroxylation of the surface and bulk up to 300 °C (Fig. 6a). The hydrophobic catalyst (S3) still showed a mass loss after 300 °C likely due to the surfactant decomposition. Fig. 6b shows the temperatures of various events occurring during thermal analysis. Interestingly, the hydrophobic material had a lower water loss, due to the presence of the surfactant on the catalyst surface.

Raman spectra of investigated catalysts are reported in Fig. 7. The spectrum of S3 is dominated by a broad band at 690 cm^{-1}, which is typical for all niobium oxides and is assigned to the vibrations of Nb–O–Nb bridges from slightly distorted octahedral NbO_6 [23,24]. The weak band around 850 cm^{-1} can be assigned to the symmetric stretching mode of Nb-O surface species, this kind of bond being present in highly distorted octahedral NbO_6 structures. Raman band between 150 and 300 cm^{-1} is due to the bending modes of Nb—O—Nb linkages [24–27].

4. Conclusion

High conversions can be achieved for the oxidation of cyclohexene to epoxide specie with high selectivity, using a synthetic niobium oxyhydroxide prepared in the presence of CTAB surfactant as an efficient heterogeneous catalyst. The presence of the hydrophobic moiety was verified by TG measurements. These novel results describe, for the first time, the use of a synthetic niobium oxide in liquid phase at low temperature (25 °C) in the presence of hydrogen peroxide without metal impregnation. Furthermore, the catalyst can be reused without deactivation, which is an advantage compared to others catalytic systems.

Acknowledgments

This work was supported by the CNPq, CBMM (Brazil), and FAPEMIG.

References

[1] M.S. Niasari, S.H. Banitaba, J. Mol. Catal. A: Chem. 201 (2003) 43–54.
[2] I.R. Guimaraes, A. Giroto, L.C.A. Oliveira, M.C. Guerreiro, D.Q. Lima, J.D. Fabris, Appl. Catal. B: Environ. 91 (2009) 581–586.
[3] W.F. de Souza, I.R. Guimaraes, M.C. Guerreiro, L.C.A. Oliveira, Appl. Catal. A: Gen. 360 (2009) 205–209.
[4] Z.Y. Cai, M.Q. Zhu, J. Chen, Y.Y. Shen, J. Zhao, Y. Tang, X.Z. Chen, Catal. Commun. 12 (2010) 197–201.
[5] J. Tong, Y. Zhang, Z. Li, C. Xia, J. Mol. Catal. A: Chem. 249 (2006) 47–52.
[6] D. Mandelli, M.C.A van Vliet, R.A. Sheldon, U. Schuchardt, Appl. Catal. A: Gen. 219 (2001) 209–213.
[7] M. Torres, I.W.C.E. Arends, J.A. Mayoral, E. Pires, G. Jiménez-Osés, Appl. Catal. A: Gen. 425–426 (2012) 91–96.
[8] M. Guidotti, R. Psaro, I. Batonneau-Gener, E. Gavrilova, Chem. Eng. Technol. 34 (2011) 1924–1927.
[9] D. Bayot, M. Devillers, Coord. Chem. Rev. 250 (2006) 2610–2626.
[10] L.C. Passoni, M.R.H. Siddiqui, A. Steiner, I.V. Kozhevnikov, J. Mol. Catal. A: Chem. 153 (2000) 103–108.
[11] L.C.A. Oliveira, T.C. Ramalho, M. Gonçalves, F. Cereda, K.T. Carvalho, M.S. Nazzarro, K. Sapag, Chem. Phys. Lett. 446 (2007) 133–137.
[12] L.J. Burcham, J. Datka, I.E. Wachs, J. Phys. Chem. B 103 (1999) 6015–6024.
[13] I.R. Guimaraes, L.C.A. Oliveira, P.F. Queiroz, M.C. Pereira, J.D. Fabris, J.D. Ardisson, Appl. Catal. A: Gen. 347 (2008) 89–93.
[14] A.C. Silva, D.Q.L. Oliveira, L.C.A. Oliveira, A.S. Anastácio, T.C. Ramalho, J.H. Lopes, H.W.P. Carvalho, C.E.R. Torres, Appl. Catal. A: Gen. 357 (2009) 79–84.
[15] L.C.A. Oliveira, M.F. Portilho, A.C. Silva, H.A. Taroco, P.P. Souza, Appl. Catal. B: Environ. 117–118 (2012) 29–35.
[16] M. Ziolek, Catal. Today 90 (2004) 145–150.
[17] M. Ziolek, P. Decyk, I. Sobczak, M. Trejda, J. Florek, H.G.W. Klimas, A. Wojtaszek, Appl. Catal. A: Gen. 391 (2011) 194–204.
[18] K.M. Parida, M. Sahoo, S. Singha, J. Catal. 276 (2010) 161–169.
[19] W.F. de Souza, M.C. Pereira, L.C.A. Oliveira, Fuel 96 (2012) 604–607.
[20] M. Morandin, R. Gavagnin, F. Pinna, G. Strukul, J. Catal. 212 (2002) 193–200.
[21] A. Esteves, L.C.A. Oliveira, T.C. Ramalho, M. Gonçalves, A.S. Anastacio, H.W.P. Carvalho, Catal. Commun. 10 (2008) 330–332.
[22] R.M. Koros, E.J. Nowak, Chem. Eng. Sci. 22 (1967) 470.
[23] J.M. Jehng, I.E. Wachs, Chem. Mater. 3 (1991) 100–107.
[24] A.A. McConnel, J.S. Anderson, C.N.R. Rao, Spectrochem. Acta A 23 (1976) 1067–1076.
[25] D. Stosic, S. Bennici, V. Rakic, A. Auroux, Catal. Today 192 (2011) 160–168.
[26] I.E. Wachs, J.-M. Jehng, G. Deo, H. Hu, N. Arora, Catal. Today 28 (1996) 199–205.
[27] X. Gao, S.R. Bare, B.M. Weckhuysen, I.E. Wachs, J. Phys. Chem. B 102 (1998) 10842–10852.