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Encapsulation of Vanadium Complexes in Inorganic or Hybrid Matrices *via* the Sol-Gel Method: Application to the Epoxidation of Allylic Alcohols

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Complexos de vanádio foram encapsulados em matrizes inorgânicas (baseadas na hidrólise/condensação de tetrametilortossilicato – TMOS) e híbridas (TMOS e um agente de co-condensação) pelo método sol-gel. Os sólidos resultantes foram testados na epoxidação de álcoois alílicos na presença de hidroperóxido de *terc*-butila (TBHP) como agente oxidante, a 70 °C. Para o catalisador baseado em [VO(salen)], a matriz híbrida levou a maiores freqüências de *turnover* iniciais do que a matriz inorgânica para todos os álcoois testados (*trans*-3-fenil-2-metil-2-propen-1-ol, *trans*-2-hexen-1-ol, *cis*-2-hexen-1-ol, 1-octen-3-ol), o que pode estar relacionado com seu maior diâmetro de poros. Embora não tenha sido observada lixiviação de vanádio nas reações catalíticas, os experimentos de reciclagem com o catalisador híbrido e *trans*-2-hexen-1-ol mostraram perda de vanádio em cada lavagem com Soxhlet (efetuada após cada corrida, usando CH_2Cl_2), totalizando 1,5% em massa após 3 reações. Em 4 corridas sucessivas, mantendo as relações molares iniciais, as conversões decresceram de 100% a 85%, 65% e 40% (em 5h).

Vanadium complexes have been encapsulated in inorganic (based on hydrolysis/condensation of tetramethylorthosilicate - TMOS) and hybrid matrices (TMOS plus a co-condensation agent) using the sol-gel method. The resulting solids were tested in the epoxidation of allylic alcohols in the presence of *tert*-butyl hydroperoxide (TBHP) as the oxidant agent at 70 °C. When the catalyst was based on [VO(salen)], the hybrid matrix led to higher initial turnover frequencies than the inorganic one for all tested alcohols (*trans*-3-phenyl-2-methyl-2-propen-1-ol, *trans*-2-hexen-1-ol, *cis*-2-hexen-1-ol, 1-octen-3-ol), which might be related to its higher pore diameter. Although no vanadium leaching was observed during the catalytic reactions, recycling experiments with the hybrid catalyst and *trans*-2-hexen-1-ol showed that some loss of vanadium took place at every Soxhlet washing (performed after every run, using CH_2Cl_2): a total of 1.5 wt.% after three reactions. In four successive runs, keeping the initial molar ratios, conversions decreased from 100% to 85%, 65% and 40% (in 5h).

Keywords*:* vanadium, epoxidation, allylic alcohols, sol-gel method

Introduction

[VO(acac)$_2$] is one of the best and most extensively studied catalyst for the epoxidation of unsaturated alcohols.[1] The combination [VO(acac)$_2$]/*tert*-butyl hydroperoxide (TBHP) has proved to produce a highly regio- and stereoselective homogeneous system for the epoxidation of allylic[2-4] and homoallylic alcohols.[5] Homogeneous catalysis, however, presents several drawbacks, in particular the recovering of the catalyst at the end of the process, warranting a search for supported-vanadium catalysts. There are several reports about the immobilization of [VO(acac)$_2$] and VO_3^- onto functionalized polystyrene resins.[6-10] The vanadium complexes have also been attached to ion-exchange resins.[11,12] More recently, the microencapsulation of [VO(acac)$_2$] in polystyrene was reported to produce an almost leaching-free system active at room temperature.[13] In the last years, the sol-gel method has been applied as an alternative to immobilize soluble catalysts, using either inorganic[14] or hybrid[15] matrices. Recently, we reported the use of this approach to prepare rhenium- and molybdenum-based epoxidation catalysts,[16,17] as well as ruthenium- and rhodium-based catalysts for the hydrogenation and hydroformylation of olefins, respectively.[18,19] Depending on the characteristics of the matrix, leaching-free systems could be prepared. We wish to report here some results concerning the encapsulation of vanadium catalysts in inorganic and

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hybrid matrices using the sol-gel method and their use in the epoxidation of allylic alcohols.

Experimental

Chemicals

[VO(acac)$_2$], *tert*-butyl hydroperoxide 5.0 mol dm^{-3} in decane, salicylaldehyde, tetramethylorthosilicate (TMOS), *cis*-cyclooctene and the alcohols *trans*-3-phenyl-2-methyl-2-propen-1-ol, *trans*-2-hexen-1-ol, *cis*-2-hexen-1-ol and 1-octen-3-ol were purchased from Aldrich and used as received. [VO(salen)],[20] SalenH$_2$[21] and 1,4-*bis*(triethoxysilyl)benzene[22] were prepared according to the literature. Solvents were treated following standard procedures.

Catalyst preparation

*Catalysts based on [VO(acac)$_2$], **I***. 6 cm^3 (40.3mmol) of TMOS, 5 cm^3 of THF, 10 cm^3 of methanol, 0.20 g (7.54 10^{-4} mol) of [VO(acac)$_2$] and 2.5 cm^3 of deionized water (pH 2.0, adjusted with concentrated HCl) were mixed in a rounded bottom flask. After 20 min under magnetic stirring, 10 cm^3 of a 1.81 mmol dm^{-3} solution of K_2CO_3 were added to the homogeneous solution and a greenish-blue gel was formed. Upon drying under vacuum, a red-brown solid was formed. It was then crushed in a mortar, washed with CH_2Cl_2 in a Soxhlet and dried again under vacuum.

*Catalysts based on [VO(salen)], **II***. 1 g (*ca.* 4.0 mmol) of salenH$_2$, 24 cm^3 (161.3 mmol) of TMOS, 12 cm^3 of 1,4-*bis*(triethoxysilyl)benzene (co-condensation agent, in the case of a hybrid matrix), 40 cm^3 of methanol and 10 cm^3 of deionized water (pH 2.0, adjusted with concentrated HCl) were mixed in a beaker. After 70 min under magnetic stirring, 12 drops of concentrated HCl were added to the solution, which was then allowed to stand for one week. The resulting gel was dried under vacuum for two days and crushed in a mortar. The granules were allowed to react with 1.2 g (4.5 mmol) of a solution of [VO(acac)$_2$] in CH_2Cl_2 for 24 h. The green solid was washed with CH_2Cl_2 in a Soxhlet, and dried under vacuum at room temperature.

All materials were stored under air at room temperature.

Catalyst characterization

Nitrogen adsorption isotherms were determined at -196 °C with a Micromeritics ASAP 2010 automated porosimeter. All calculations were performed using the associated Micromeritics software. Samples were degassed at 80 °C for a minimum of 24 h prior to measurements.

Vanadium concentrations were determined by X-ray fluorescence using a Shimadzu EDX-700 equipment (rhodium lamp and K_α line from vanadium) or through ICP-EAS (Perkin Elmer Optima 3000 DV). Infrared spectra were recorded on a Bomem MB Series FT-IR spectrometer (resolution: 4 cm^{-1}).

Catalytic experiments

All experiments were carried out at 70 °C in a Schlenk flask equipped with a septum. In a typical experiment, 5 cm^3 of toluene, 466 mg of the inorganic catalyst (0.155 mmol V), 498 mg of 1-octen-3-ol (3.88 mmol), 100 μl of cyclooctane (internal standard) and 0.52 cm^3 of a solution of TBHP in decane (5.12 mmol) were employed. For recycling experiments, the catalyst was separated by filtration, washed with CH_2Cl_2 in a Soxhlet, dried under vacuum and used in a new run. GC analyses were performed in an HP5890 series II gas chromatograph, equipped with an HP5 capillary column (50 m x 0.2 mm) and a flame ionization detector. Conversions of the substrates were determined using calibration curves obtained with standard solutions. Products were identified by GC/MS using an HP5973 equipment. TBHP consumption was determined by iodometric titration.

Results and Discussion

The first experiments were carried out using [VO(acac)$_2$] in order to determine the viability of immobilization with this type of species in matrices derived from hydrolysis/condensation of tetramethylorthosilicate without significant losses in its catalytic activity. Further experiments, already using [VO(salen)], involved also the use of a co-condensation agent, which was expected to decrease the degree of 3D-cross-linking, and thus the rigidity of the matrix.

Preparation and characterization of the catalysts

The solids based on [VO(acac)$_2$] (catalyst **I**) were prepared according to a method previously described for the preparation of molybdenum-based catalysts.[17] This procedure, however, could not be applied to [VO(salen)]: although several solvents were tested (THF, THF/CH_2Cl_2, CH_3CN), the complex always crystallized outside the matrix. An alternative route was then evaluated: the ligand was firstly immobilized into an hybrid or inorganic matrix, and then allowed to react with [VO(acac)$_2$]. The success of the reaction was proved by FT-IR analyses: the band at 680 cm^{-1}, characteristic of the acac$^-$ ligand,[23] disappeared while the band assignable to ν_{sym}(V=O) was shifted from 997 to 980 cm^{-1}, in good agreement with the literature.[20] Solids based on [VO(salen)] (catalysts **II**) are called **a** or **b** depending on the nature of the matrix, inorganic or hybrid (using the co-condensation agent), respectively.

Some characteristics of the catalysts are presented in Table 1. The nitrogen adsorption/desorption isotherms obtained for all catalysts are a mixture of type I and IV, *i. e.* a mixture of microporous and mesoporous systems (Figure 1).[24,25] The volumes adsorbed at the lowest relative pressures represent *ca*. 50 and 42% of the total pore volume for catalysts **IIa** and **IIb**, respectively, corresponding to a significant proportion of micropores. The micropore size distribution is also shown in Figure 1, being narrower for catalyst **IIa**. Catalysts **Ia** and **IIa** presented the same characteristics. The hysteresis loop observed for catalyst **IIb** suggests the presence of ink-bottle or narrow-mouth shaped pores.[26]

Catalytic experiments

Initially, [VO(acac)$_2$] and [VO(salen)] were tested in the epoxidation of cyclooctene in a toluene solution using a molar ratio [V]:[olefin]:[TBHP] = 1:50:60. In such conditions, conversions were around 45% and 25%, respectively, in 2h. The lower activity of [VO(salen)] could be assigned to the complete decomposition of TBHP. When this experiment was repeated doubling the amount of TBHP, 64% conversion to epoxide was observed before deactivation (4h). Both systems turned out to be more stable in the epoxidation of *trans*-2-hexen-1-ol: using a molar ratio [V]:[alcohol]:[TBHP] = 1:50:66, 70% and 95% conversions were obtained in 5h in the presence of [VO(acac)$_2$] and [VO(salen)], respectively. Therefore, the inorganic systems **Ia** and **IIa** were prepared and tested in the epoxidation of the same alcohol, but now using a molar ratio [V]:[alcohol]:[TBHP] = 1:25:33. A lower proportion between

Table 1. Characteristics of the catalysts

Catalyst	V loading wt.%	BET surface area / m^2 g^{-1}	Porous volume[a] cm^3 g^{-1}	Average pore diameter / nm
Ia	1.25	634	0.37	2.10[b] (1.05)[c]
IIa	1.61	586	0.34	2.33[b] (1.17)[c]
IIb	1.21	436	0.29	2.65[b] (1.59)[c]

Methods: [a] Single point; [b] 4V/A by BET; [c] Horvath-Kawazoe.

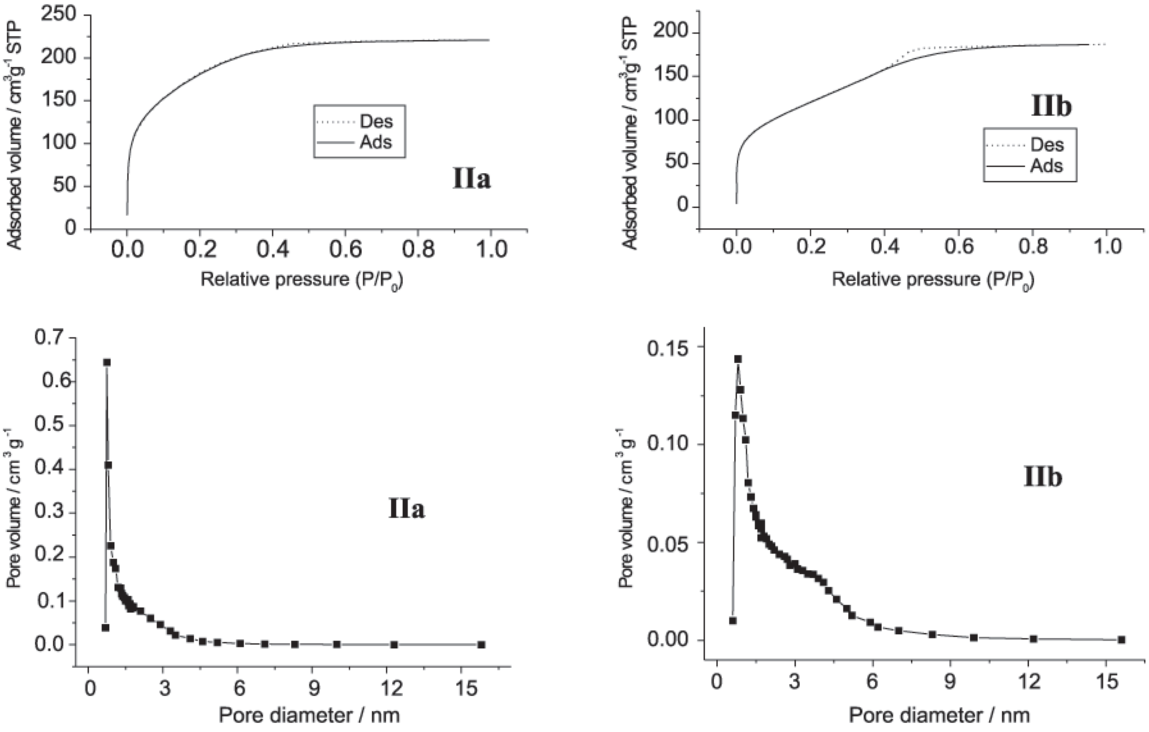

Figure 1. Nitrogen adsorption/desorption isotherms (top) and micropore size distributions (bottom) for catalysts **IIa** and **IIb**.

Table 2. Performance of catalysts **IIa** and **IIb** in the epoxidation of allylic alcohols[a]

Substrate	Catalyst **IIa**			Catalyst **Iib**		
	Conv.	TOF h^{-1}	TON	Conv.	TOF h^{-1}	TON
trans-3-phenyl-2-methyl-2-propen-1-ol	43%	8	10.8	42%	13	10.5
trans-2-hexen-1-ol	80%	19	20	92%	25	23
cis-2-hexen-1-ol	54%	15	13.5	67%	20	16.8
1-octen-3-ol	51%	14	12.8	63%	18	15.8

[a] [V]:[substrate]:[TBHP] = 1:25:33; reaction temperature: 70°C; reaction time: 2h. TON: turnover number = mol of epoxide per mol of vanadium in 2h; TOF: initial turnover frequency, calculated at low conversion (15 min).

alcohol/vanadium was employed since a decrease in catalytic activity, owing to diffusion problems arising from the encapsulation of the complexes, was expected. After 5h, a complete conversion of *trans*-2-hexen-1-ol to its epoxide was observed for system **IIa**; with system **Ia**, conversion was only 76%. Since catalysts based on [VO(salen)] appeared to be more active even when encapsulated, catalyst **IIb** was also prepared in order to determine whether a change in the characteristics of the matrix would affect the resulting catalytic activity. Thus, catalysts **IIa** and **IIb** were tested in the epoxidation of several allylic alcohols with different nucleophilic character of the double bond and steric demands (Table 2). The lowest initial turnover frequency was observed for the primary trisubstituted alcohol, probably due to its higher steric demand. The least nucleophilic secondary allylic alcohol (*i.e.* the less reactive) 1-octen-3-ol was epoxidized in almost the same rate as the primary disubstituted alcohol *cis*-2-hexen-1-ol. This unexpected result can also be ascribed to different steric demands associated with the diffusion of the substrate through the pore system. In spite of the different initial turnover rates observed for catalysts **IIa** and **IIb** with the same alcohol, the final conversions (after ~5h) were the same, as shown in Figure 2 for the epoxidation of *trans*-2-hexen-1-ol and 1-octen-3-ol. The higher initial turnover frequencies observed for catalyst **IIb**, whatever the alcohol tested, can be assigned to structural differences between the matrices, in particular to its larger pore diameter (Table 1, Figure 1). Since total consumption of TBHP was never observed with the encapsulated systems, the deactivation of the catalysts after *ca*. 4-5h under reaction can be tentatively ascribed to pore blockage.

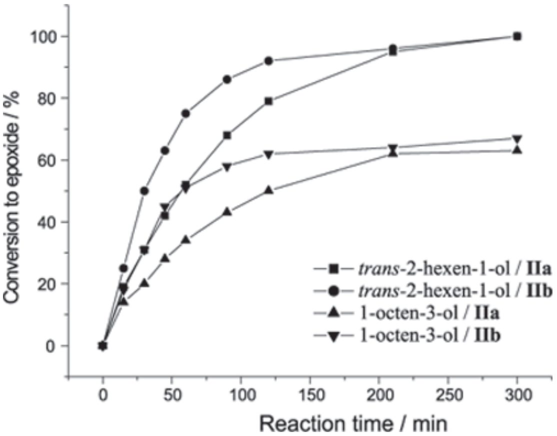

Figure 2. Performance of catalysts **IIa** and **IIb** in the epoxidation of *trans*-2-hexen-1-ol and 1-octen-3-ol. [V]:[alcohol]:[TBHP] = 1:25:33; 70 °C, in toluene.

Although no vanadium leaching was observed during the catalytic reactions, recycling experiments with catalysts **IIb** and *trans*-2-hexen-1-ol showed that some loss of vanadium took place at every Soxhlet washing (performed after each catalytic reaction): 0.9 wt.% vanadium leaching after the first washing; 0.3wt.% after the second and third washings, totalizing 1.5 wt.% after three reactions. In four successive runs, keeping the initial molar ratios, conversions decreased from 100% to 85%, 65% and 40% (in 5h). These results suggest that, besides pore blockage, a modification (or degradation) of the complex might take place during each reaction, with the modified species being insoluble in toluene.

Finally, the non optimized results described in this work are similar to those reported for polystyrene microencapsulated [VO(acac)$_2$],[13] being a promising alternative to the immobilization of soluble vanadium complexes.

Conclusions

[VO(salen)] was successfully encapsulated in inorganic or hybrid matrices *via* the sol-gel method. The resulting systems are active in the epoxidation of allylic alcohols but the initial turnover frequency seems to depend on the characteristics of the pore system. Although the systems were not optimized, the catalyst based on the hybrid matrix could be used in at least 4 runs. The low total amount of vanadium leached cannot account for the observed decrease in catalytic activity in successive runs.

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References

1. Jørgensen, K.A.; *Chem. Rev.* **1989**, *89*, 435.
2. Sharpless, K.B.; Michaelson, R.C.; *J. Am. Chem. Soc.* **1973**, *95*, 6136.
3. Sharpless, K.B.; Verhoeven, T.R.; *Aldrichimica Acta* **1979**, *12*, 63.
4. Itoh, T.; Jitsukawa, K.; Kaneda, K.; Teranishi, S.; *J. Am. Chem. Soc.* **1979**, *101*, 159.
5. Mihelich, E.D.; Daniels, K.; Eickhoff, D.; *J. Am. Chem. Soc.* **1981**, *103*, 7690.
6. Bhaduri, S.; Ghosh, A.; Khwaja, H.; *J. Chem. Soc., Dalton Trans.* **1981**, 447.
7. Bhaduri, S.; Khwaja, H.; Khanwalkar, V.; *J. Chem. Soc., Dalton Trans.* **1982**, 445.
8. Yokoyama, T.; Nishizawa, M.; Kimura, T.; Suzuki, T.; *Chem. Lett.* **1983**, 1703.
9. Yokoyama, T.; Nishizawa, M.; Kimura, T.; Suzuki, T.; *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3271.
10. Kumar, A.; Das, S.K.; *J. Catal.* **1997**, *166*, 108.
11. Linden, G.L.; Farona, M.; *Inorg. Chem.* **1977**, *16*, 3170.
12. Pesiri, D.R.; Moritia, D.K.; Walker, T.; Tumas, W.; *Organometallics* **1999**, *18*, 4916.
13. Lattanzi, A.; Leadbeater, N.E.; *Org. Lett.* **2002**, *4*, 1519.
14. Blum, J.; Avnir, D.; Schumann, H.; *Chemtech* **1999**, *29*, 32.
15. Lindner, E.; Schneller, T.; Auer, F.; Mayer, H.A.; *Angew. Chem. Int. Ed.* **1999**, *38*, 2155.
16. Dallmann, K.; Buffon, R.; *Catal. Commun.* **2000**, *1*, 9.
17. Teixeira, S.; Dallmann, K.; Schuchardt, U.; Buffon, R.; *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 167.
18. Dallmann, K.; Buffon, R.; *J. Mol. Catal. A: Chem.* **2002**, *185*, 187.
19. Campos, J.D.R.; Buffon, R.; *New J. Chem.* **2003**, *27*, 446.
20. Haas, G.R.; Kolis, J.W.; *Tetrahedron Lett.* **1998**, *39*, 5923.
21. Appleton, T.G.; *J. Chem. Educ.* **1977**, *54*, 444.
22. Loy, D.A.; Jamison, G. M.; Baugher, B.M.; Myers, S.A.; Assink, R.A.; Shea, K J.; *Chem. Mater.* **1996**, *8*, 656.
23. Di Bella, S.; Lanza, G.; Gulino, A.; Fragalà, I.L.; *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2709.
24. Kimura, T.; Sugahara, Y.; Kuroda, K.; *Chem. Mater.* **1999**, *11*, 508.
25. Oliveira, E.C. de; Pastore, H.O.; *Stud. Surf, Sci. Catal.* **2002**,*141*, 297.
26. Brinker, C.J.; Scherer, G.W.; *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press: San Diego - CA, 1990, pp. 522-525.

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