

Thiol-oxidation with zeolite encapsulated phthalocyanines: influence of the solid support

Frédéric Thibault-Starzyk^a, Mark Van Puymbroeck^b, Rudy F. Parton^b,
Pierre A. Jacobs^{b,*}

^a *Laboratoire de Catalyse et Spectrochimie, CNRS – Institut des Sciences de la Matière et du Rayonnement, 6 Boulevard du Maréchal Juin, 14050 Caen cedex, France*

^b *Center for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, 3001 Heverlee, Belgium*

Received 18 May 1995; revised 15 January 1996; accepted 15 January 1996

Abstract

The catalytic activity of zeolite encapsulated cobalt–phthalocyanine for thiol autoxidation varies with the composition of the zeolite support. Different zeolites were compared with carbon supports. The Si/Al ratio in the zeolite appears to be the key factor: it determines the hydrophobicity of the support, and it influences the loading of active complex in the zeolite. Two different types of reaction were tested: in an aqueous alkaline medium, the activity increases with hydrophobicity of the support (thus giving carbon a substantial advantage), while in an organic medium, where the commonly used systems are less efficient, sodium Y zeolite is more active than the usual carbon support.

Keywords: Thiol oxidation; Zeozyme; Zeolites; Encapsulation; Phthalocyanine; Hydrophobicity

1. Introduction

Merox (mercaptan oxidation) is a process used worldwide for the removal of thiols from petroleum fractions [1]. In the Merox process, mercaptans are oxidized to disulfides in an alkaline medium in the presence of a metal phthalocyanine, most often cobalt or vanadium phthalocyanine (CoPc and VPc, respectively). The active complex is in many cases supported on carbon, but different solid supports have been tried successfully [2–8]. Zeolites are very interesting supports for oxidations with transition

metal complexes, especially for phthalocyanines [9–12]. These molecular sieves efficiently protect the active complex encapsulated in their internal volume, and introduce a very important selectivity. However, X is the only zeolite that has been used for the oxidation of thiols [13]. We present here a study of different zeolite types for the support of CoPc for the Merox process, varying the composition and the topology. We have compared these supports with carbon, and have used our catalysts for the oxidation of short chain thiols in an alkaline aqueous phase as well as that of long chain thiols in an organic medium. We have then been able to rationalize the relative reactivities of the different catalysts on the basis of the composi-

* Corresponding author. E-mail: pierre.jacobs@agr.kuleuven.ac.be

tion of the zeolite used. In the organic phase Merox sweetening, we found that zeolite supported cobalt–phthalocyanine is more active than the carbon supported catalyst normally used.

2. Methods

2.1. Preparation of the catalysts

Zeolite X is from Tamino, Y from Zeocat, and USY (Ultra Stable Y zeolite) is from P&Q (USY CBV 720). Zeolite EMT was synthesized as previously described [14]. Si/Al ratios are given in Table 1. The zeolites are exchanged with cobalt, then mixed under nitrogen with 8 equivalents of DCB (dicyanobenzene) per cobalt ion, and heated slowly up to 300°C, and kept at this temperature for 4 h. The material obtained was Soxhlet extracted successively with acetone, dimethylformamide, and again with acetone. The carbon supports were from Norit (C1: hydrophilic, 1000 m²/g) and Degussa (C2: hydrophobic, 82 m²/g). Cobalt phthalocyanine was adsorbed on the carbon support from a dichloromethane solution. CoPc loading in the catalyst was measured by UV–Vis spectroscopy after dissolution of the sample in sulfuric acid, as described by Romanovsky [15].

2.2. Oxidation reactions

2-Mercaptoethanol oxidation was performed at room temperature in pH 9.6 buffered solution

Table 1
CoPc loading of the different catalysts, determined by UV–Vis spectroscopy after dissolution in concentrated sulfuric acid

Catalyst	Loading ($\mu\text{mol/g}$)	Loading (wt%)	Si/Al
CoPcX	522	29.7	1.22
CoPcY	496	28.2	2.45
CoPcEMT	387	2.20	3.6
CoPcUSY	39.3	2.24	13.5
CoPcC1	36.4	2.07	–
CoPcC2	35.8	2.04	–

Table 2

Influence of the temperature on the autoxidation of dodecanethiol, and comparison of carbon with zeolite support

Temp. (°C)	Catalyst	Solvent	Conversion (%) after:	
			4 h	20 h
20	CoPcY	n-hexane	24	26
60	CoPcY	n-hexane	15	21
60	CoPcC2	n-hexane	11	20
80	CoPcY	n-hexane	6	15
120	CoPcY	toluene	–	1

(NaHCO₃/NaOH), saturated with an oxygen flow with vigorous stirring. 0.5 g catalyst were used, with 0.5 g methanol as internal standard for the GC analyses. After addition of thiol (0.08 mol), samples were taken and filtered, and analyzed on a CP Sil 5-CB column from Chrompack, with an FID detector.

Dodecanethiol oxidations were performed in an autoclave, with 0.5 g catalyst, 5 ml decane as internal standard for the GC analyses, and 200 ml solvent (see Table 2). After addition of the thiol (19.2 ml) at the chosen temperature, 9 bar oxygen pressure was built up in the autoclave. Vigorous stirring was maintained during the reaction. A closed autoclave under oxygen pressure was necessary because the solvent used would very quickly evaporate in a constant gas flow. Samples were centrifuged before GC analyses, done on a CP Sil 5-CB column from Chrompack, with an FID detector.

3. Results and discussion

The amount of CoPc supported by the zeolite (the so-called loading) diminishes with increasing Si/Al ratio, with a fairly good correlation with the decrease of the exchange capacity (Table 1). Although it is not directly linked to the number of available cobalt ions (an important proportion of the metal will remain free), the amount of CoPc formed is more important when there is more cobalt in the zeolite. Other factors depending on the Si/Al ratio can have an effect (acidity of the lattice, hydrophobicity, ...). The

loading of the carbon supports does not depend on the nature of the material, but was chosen during the synthesis so that the complex does not form a multilayer.

We have compared the different supports in two different reaction models: oxidation of low molecular weight thiols in an alkaline aqueous medium, and oxidation of long chain thiols in an organic medium. Long chain thiols are weakly soluble in water, and their oxidation must be done in an organic phase. This reaction has been much less studied, because it is more delicate to perform in the laboratory, although its industrial and environmental interest is certain.

All the catalysts we studied show good activity for the autoxidation of mercaptoethanol in an alkaline aqueous phase (Fig. 1). For comparison with already described catalysts, we have used as reference supports the X zeolite, used by Schulz-Ekloff et al. [13], and two carbon supports, because charcoal is the standard industrial support. C1 is an active carbon, with many oxygen containing groups on the surface, and thus a hydrophilic character. C2 is a very hy-

drophobic carbon black. The support by itself shows some activity, and results with the bare carbon and with cobalt exchanged Y zeolite are also shown on Fig. 1. Selectivity was in all cases 100% for the disulfide, and there was no trace of deeper oxidation products. Turnover numbers (TON: number of catalytic cycles performed by each catalytic site) are difficult to calculate, because the number of accessible complexes in a zeolite is not always well known. We provide an estimation of turnover rates (TOR: number of catalytic cycles performed by each catalytic site in one hour) in Fig. 1, assuming that all complexes are active. Considering that not all the complexes are accessible, the actual TOR's are in fact very probably much higher, and our estimation only gives a strict minimum.

The conversion never reached 100%. This was not due to deactivation of the catalyst, because any further added thiol was converted at the same rate, with no sign of deactivation. This limited conversion was rather explained by diffusion limits in our experimental setting: disulfide can form a separate phase and dissolve

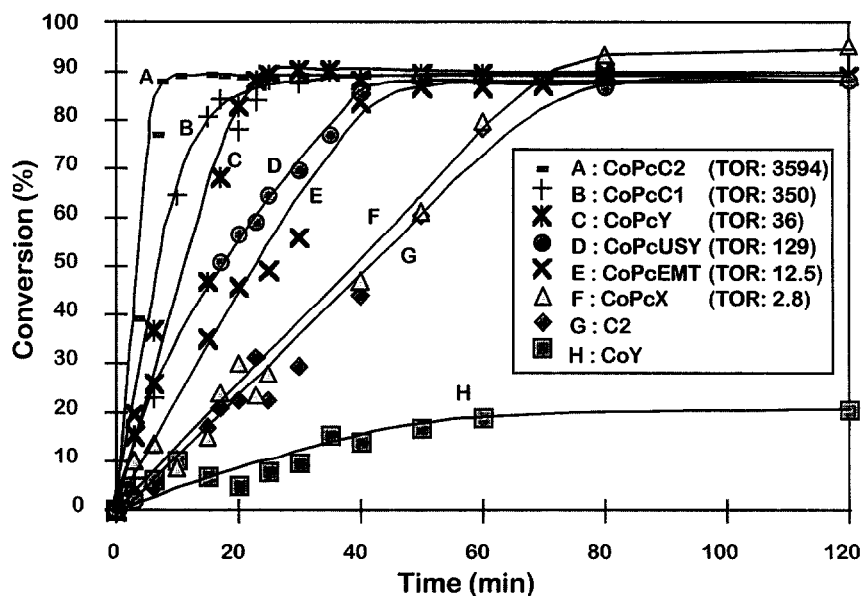


Fig. 1. Oxidation of mercaptoethanol in aqueous solution on the different catalysts at 25°C. TOR are estimated turnover rates, in h⁻¹ (see text).

some of the thiol, that will no longer be readily accessible.

In an aqueous phase, zeolite supported catalysts are less active than those on carbon, sometimes by several orders of magnitude. The relatively high decrease of thiol concentration with the carbon supports can be partially explained by the ability of carbon to generate free radicals that can initiate the reaction, and to adsorb thiols more strongly than zeolites. In the zeolitic series, the reaction rate increases with increasing Si/Al ratio in the support. Among the various factors linked to this ratio, hydrophobicity plays the most important role in this particular case, and comparison of the two carbon supports is meaningful here. On the more hydrophobic support C2, the reaction is two to three times faster than on C1. Considering only the turnover rate in an alkaline aqueous medium, supports for CoPc show the following catalyst reactivity order:

X zeolite < Y, EMT zeolites < USY zeolite < C2

The activity of CoPc on USY even reaches the same order of magnitude as that observed with the hydrophilic carbon. Considering the reactivity per gram of catalyst, Y zeolite is the best candidate in the zeolitic series, because it realizes the best compromise between hydrophobicity and loading.

In an organic phase, the situation is greatly modified, and Y zeolite gives now the most active catalyst, even compared to the carbon supported ones (Table 2). The main limitations to the reaction are the weak ionization of the thiol into the thiolate, and the solubility of oxygen. Because of the decrease of oxygen solubility when temperature increases, the reaction rate also decreases, and there is no significant conversion at 120°C, below 9 bar oxygen¹. We are presently studying the optimization of the encapsulated complex by various substitutions. These results indicate a possible improvement of the industrial Mercox process using catalysts supported on zeolites, which offer more

flexibility and reactivity control than carbon supports.

In conclusion, hydrophobicity is a key factor for the autoxidation of mercaptans in aqueous medium on zeolite supported cobalt phthalocyanines. Y zeolite is the zeolitic support giving the best compromise between complex loading and hydrophobicity. For the oxidation of long chain thiols in an organic medium, zeolites can compete with carbon supports used in industry, and open interesting possibilities.

Acknowledgements

This work was supported by the Belgian Government in the scope of an Interuniversity Attraction Pole (I.U.A.P.) (this paper does not contain official viewpoints of the Belgian government). FTS thanks the Commission of the European Communities for a Post-Doctoral Fellowship in the Human Capital and Mobility Program. RFP thanks the Belgian National Fund for Scientific Research for a research position as Post-Doctoral Researcher. The authors are grateful to Prof. Viaene (Fysicochemische Geologie, K.U. Leuven) for taking the XRD diffractograms, and to Eddy Feijen for providing the EMT.

References

- [1] B. Basu, S. Satapathy and A.K. Bhatnagar, *Catal. Rev.-Sci. Eng.*, 35 (1993) 571.
- [2] V. Iliev, A. Andreev, D. Wöhrle and G. Schulz-Ekloff, *J. Mol. Catal.*, 66 (1991) 5.
- [3] M.E. Pérez-Bernal, R. Ruano-Casero and T.J. Pinnavaia, *Catal. Lett.*, 11 (1991) 55.

¹ Oxygen solutions in apolar solvents are nearly ideal solutions, and Henry's law gives a satisfactory approximation of the concentration of the gas in the solvent. With $\Delta H^{\text{vap}} = 6.81 \text{ kJ mol}^{-1}$ for oxygen, this law predicts a decrease of 50% in oxygen solubility on going from 20 to 120°C. If the concentration is such that the redox potential of the reaction is not reached, the reaction will completely stop.

- [4] T. Buck, D. Wöhrle, G. Schulz-Ekloff and A. Andreev, *J. Mol. Catal.*, 70 (1991) 259.
- [5] Y.G. Akopyants, S.A. Borisenkova, O.L. Kaliya, V.M. Derkacheva and E.A. Lukyanets, *J. Mol. Catal.*, 83 (1993) 1.
- [6] D. Wöhrle, T. Buck, U. Hündorf, G. Schulz-Ekloff and A. Andreev, *Makromol. Chem.*, 190 (1989) 961.
- [7] K.H. Van Streun, R. Tennebroek, P. Piet and A.L. German, *Makromol. Chem.*, 191 (1990) 2181.
- [8] E.T.W.M. Schipper, Ph.D. Thesis, Eindhoven (1994).
- [9] D.E. De Vos, F. Thibault-Starzyk, P.P. Knops-Gerrits, R.F. Parton and P.A. Jacobs, *Macromol. Symp.*, 80 (1994) 157.
- [10] P.P. Knops-Gerrits, D.E. De Vos, F. Thibault-Starzyk and P.A. Jacobs, *Nature*, 369 (1994) 543.
- [11] D.E. De Vos, F. Thibault-Starzyk and P.A. Jacobs, *Angew. Chem.*, 106 (1994) 447; *Angew. Chem. Int., Ed. Engl.*, 33 (1994) 431.
- [12] R.F. Parton, I.F.J. Vankelecom, M.J.A. Casselman, C.P. Bezoukhanova, J.B. Uytterhoeven and P.A. Jacobs, *Nature*, 370, (1994) 541.
- [13] G. Schulz-Ekloff, D. Wöhrle, V. Iliev, E. Ignatzek and A. Andreev, *Stud. Surf. Sci. Catal.*, 46 (1988) 315.
- [14] E. Feyen, K. De Vadder, M.H. Bosschaerts, J.L. Lievens, J.A. Martens, P.J. Grobet and P.A. Jacobs, *J. Am. Chem. Soc.*, 116 (1994) 2950.
- [15] B.V. Romanovsky, *Acta Phys. Chem.*, 31 (1985) 215.