SHORT PAPER

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Novel bifunctional catalysts of cobalt phthalocyanine bonded to organic-functionalized basic calcined Mg–Al hydrotalcite for autoxidation of mercaptans[†]

Haichao Liu[a,*], Xiyao Yang[b], Guopeng Ran[a], and Enze Min[b]

[a] *Research Institute of Petroleum Processing, Beijing 100083, P. R. China*
[b] *College of Chemistry, Peking University, Beijing 100871, P. R. China*

Two novel bifunctional catalysts, cobalt(II) 2,9,16,23-tetraaminophthalocyanine CoPc$(NH_2)_4$ bound to basic calcined Mg–Al hydrotalcite (Mg/Al=3:1) modified with organic functional groups by complexation and by covalent linkage, respectively, have been found to exhibit higher catalytic activity and stability in 1-octanethiol autoxidation than the corresponding supported CoPc$(NH_2)_4$ catalyst under equivalent reaction conditions.

Cobalt phthalocyanine complexes in the presence of caustic (as a co-catalyst) are very active for the catalytic oxidation of mercaptans to disulfides (sweetening) of gasoline and kerosene. They are thus widely used in the petroleum refining industry.[1] Mercaptans, even when present in very small quantities, are environmentally undesirable contaminants of petroleum products. However, the use of caustic leads to the environmental and economic disadvantages in the refinery because the spent caustic is recognised as a hazardous material.[2,3] To set up a more environmentally friendly process, it is desirable to substitute solid bases for the caustic, and thus attaining an effluent-free system for mercaptan sweetening. Mixed Mg-Al oxides (denoted as Mg(Al)O) derived from the thermal decomposition of hydrotalcites, which are layered double hydroxides, have been regarded as promising solid basic materials.[4,5] Holmgren *et al.* and Liu *et al.* recently reported that bifunctional Mg(Al)O-supported cobalt phthalocyanine catalysts, which possess Co(II) oxidation sites and Mg(Al)O basic sites in cooperative interaction, can effectively oxidise mercaptans to disulfides.[2,3,6] But for these catalysts, we found that the formation of aggregates of the cobalt phthalocyanines on Mg(Al)O during the autoxidation led to their deactivation.[6,7] It is known that the aggregation can be inhibited by anchoring CoPc complexes to supports, such as TiO_2 and SiO_2, modified with organic functional groups.[8-10] However, with respect to the basic Mg(Al)O, it is not known whether they can be functionalised with organic compounds with no damage to their basic sites. Here we report the preparation of two novel bifunctional catalysts of cobalt phthalocyanine bound to basic Mg(Al)O modified with two organosilanes, as well as their catalytic performance in mercaptan autoxidation.

The catalytic properties of the catalysts were studied using the autoxidation of 1-octanethiol as a model reaction. Figure 1 shows the oxygen consumption rate curves of 1-octanethiol autoxidation at 35 °C on three bifunctional catalysts: CoPc$(NH_2)_4$ covalently bonded to modified Mg(Al)O (designated as CoPc-*A*), CoPc$(NH_2)_4$ coordinately bonded to modified Mg(Al)O (CoPc-*B*), and for comparison, CoPc$(NH_2)_4$ impregnated on Mg(Al)O (CoPc-*C*), respectively. All the catalysts exhibited a very short induction period (around 1 min) and high initial activity. In 30 min about 98 and 80% of 1-octanethiol was converted on CoPc-*A*, and CoPc-*B*, respectively, in contrast to mere 45% conversion on CoPc-*C*. After the induction period, the volume of oxygen consumed was nearly linear with time until 30% conversion and then the reaction rate decreased, but the decrease in reaction rate of CoPc-*C* with time was greater than that for the other two catalysts. The reactions on pure CoPc$(NH_2)_4$, Mg(Al)O, and organic-functionalised Mg(Al)O were also conducted for comparison; they were inactive for the autoxidation of 1-octanethiol under identical conditions. After the 1-octanethiol autoxidation the catalyst CoPc-*A*, CoPc-*B* , or CoPc-*C* was filtered off; no leaching of CoPc$(NH_2)_4$ to the reaction solution was observed by atomic absorption spectroscopy and UV spectroscopy, as well as by the blank 1-octanethiol autoxidation in the reaction solution.

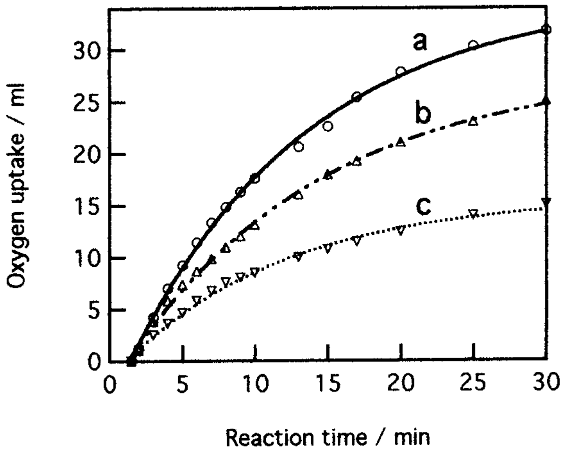

Fig.1 Oxygen consumption plots for the autoxidation of 1-octanethiol at 35°C catalysed by CoPc-*A* (a), CoPc*B* (b), and CoPc-*C* (c).

We examined the stability of the catalysts by recycling the catalysts three times. Thus, the catalysts were washed with 1-octane and then a further 1 ml of 1-octanethiol was added after one reaction cycle. As shown in Table 1, the catalyst CoPc-*C* was completely deactivated after the first run, which may be due to the aggregation of CoPc$(NH_2)_4$ molecules. In contrast, CoPc-*A* and CoPc-*B* were active during the second run although their initial reaction rates were reduced. Moreover, the CoPc-*A* still showed over 50 % conversion of 1-octanethiol to the corresponding disulfide even in the third run, giving a total of ~45 000 catalytic turnovers. The better performance of CoPc-*A* compared to CoPc-*B* is probably due to higher stability of the covalent C-N bonds on CoPc-*A* than the coordination bonds of H_2N–Co(II) on CoPc-*B*, resulting in higher dispersion of CoPc$(NH_2)_4$ on CoPc-*A* during the autoxidation. Such effect of coupling methods on the stability was

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[*] To receive any correspondence, present address: Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: haichliu@chem.s.u-tokyo.ac.jp

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Table 1 Catalytic activities in successive runs

	Initial rate V_0 / ml min^{-1} μmol-Co^{-1}			Conversion[a] (%)		
Catalyst	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
CoPc-*A*	5.6	3.5	1.0	100	95	55
CoPc-*B*	3.9	1.9	0.4	100	78	30
CoPc-*C*	2.3	0	-	72	0	-

[a] After oxidation for 1 h.

also reported in polymer-attached cobalt phthalocyanine catalysts by Schutten *et al.*[11]

In conclusion, the cobalt phthalocyanine $CoPc(NH_2)_4$ chemically attached to the organic-functionalized Mg(Al)O was achieved by formation of a C–N covalent bond (CoPc-*A*), as well as by complexation (CoPc-*B*). The two coupling methods most likely improved the $CoPc(NH_2)_4$ dispersion on the support, thus resulting in the two highly active catalysts with enhanced stability relative to the supported catalyst (CoPc-*C*). The basic calcined hydrotalcites can be modified by the grafting of organosilanes that contain organic functional groups without affecting their basic sites. This modification not only can provide chemically active sites for attaching organometallic complexes on calcined hydrotalcites but also can modify their hydrophobicities. Further research along this line may open up a new way for broadening the diversity of the calcined hydrotalcites as promising solid basic materials in catalytic activity.

Experimental

The Mg–Al mixed oxide (Mg(Al)O) was obtained by calcination of the hydrotalcite with a Mg/Al molar ratio of 3:1 at 500 °C in air for 8 h.[5] The Mg(Al)O was then functionalised with two organosilanes with epoxy and amine groups, respectively, on the surface as follows: to a suspension of vacuum-dried Mg(Al)O (2 g) in dry toluene (15 ml), 80 mg of $(CH_3O)_3SiCH_2CH_2CH_2OCH_2CH(O)CH_2$ or $(CH_3O)_3SiCH_2CH_2CH_2NH_2$ was added. The mixture was stirred at 85 °C for 8 h. Afterwards, the solid was separated, extracted thoroughly with dried toluene and methanol to remove residual unreacted silanes, and then dried under vacuum at 80 °C. The organic groups coupled to the Mg(Al)O were identified by FT-IR and XPS spectra; thermal analysis showed that these two organosilane compounds were quantitatively bonded to the Mg(Al)O surface.[12] The catalysts were prepared in two ways, by covalent linkage of $CoPc(NH_2)_4$ through the reaction between $-NH_2$ of the phthalocyanine ring system and the epoxy groups on the modified Mg(Al)O surface (the catalyst obtained was denoted as CoPc-*A*) and by complexation of $CoPc(NH_2)_4$ through the amine groups on the modified Mg(Al)O surface (denoted as CoPc-*B*). The covalent attachment of $CoPc(NH_2)_4$ was performed by adding 1 g of modified Mg(Al)O with epoxy groups to a DMSO solution of $CoPc(NH_2)_4$ (15 ml), followed by stirring the suspension at 80 °C for 24 h (CoPc-*A*). In the similar procedure, by using modified Mg(Al)O with amine groups, the coupling of $CoPc(NH_2)_4$ by complexation was done at room temperature (CoPc-*B*). After the coupling, the final products were extracted extensively with DMSO or pyridine until all unreacted $CoPc(NH_2)_4$ was removed, and then further washed with DMSO and methanol. The resulting catalysts were dried under vacuum at 80 °C. For comparison, a supported $CoPc(NH_2)_4$ catalyst was also prepared directly by impregnation of newly calcined Mg(Al)O with a DMSO solution of the $CoPc(NH_2)_4$ at room temperature (denoted as CoPc-*C*).

The catalytic 1-octanethiol autoxidation reactions were carried out in a thermostated double-walled glass flask equipped with a high-speed stirrer.[6,10] 60 mg of catalyst containing 0.48 μmol of $CoPc(NH_2)_4$, 5 ml of dry *n*-octane and oxygen were introduced to the reaction flask. After the injection of 1 ml of 1-octanethiol, the reaction started at 35 (±0.1) °C under constant oxygen pressure (1 atm), and the oxygen depletion was monitored with a gas buret to evaluate the catalytic activity and initial reaction rate (ml min^{-1} μmol Co^{-1}). The reaction solution was analysed by GC–MS, and $C_8H_{17}SSC_8H_{17}$ was the only 1-octanethiol oxidation product. Also, no H_2O_2 was produced. Therefor, the conversion of 1-octanethiol proceeds according to the following equation, $4\ C_8H_{17}SH + O_2 \rightarrow 2\ C_8H_{17}SSC_8H_{17} + 2\ H_2O$.

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References

1 B. Basu, S. Satapathy and A.K. Bhatnagar, *Catal. Rev*., 1993, **35**, 571.
2 R.D. Gillespic, J.C. Bricker, B.J. Arena and J.S. Holmgren, U.S. Patent 5413701, 1995.
3 J. J. Alcaraz, B. J. Arena, R. D. Gillespic and J.S. Holmgren, *Catal. Today*, 1998, **43**, 89.
4 F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11** 173.
5 H.C. Liu, X.Y. Yang, G. P. Ran, E.Z. Min, J.K. Liu, P.L. Ying, Q. Xin and C. Li, *Chin. J. Chem.*, 1999, **17**, 319.
6 H.C. Liu, G.P. Ran, E.Z. Min and X.Y. Yang, *Chin. J. Mol. Catal*., 1998, **12**, 221.
7 H.C. Liu, X.Y. Yang, G.P. Ran and E.Z. Min, Acta. Phys.-Chim. Sini., 1999, **15**, 918.
8 A.P. Hong, S.D. Boyce and M.R. Hoffmann, *Environ. Sci. Technol*., 1989, **23**, 533.
9 T. Buck, D. Wohrle, G. Schulz-Ekloff and A. Andreev, *J. Mol. Catal*., 1991, **70**, 259.
10 Y.G. Akopyants, S.A. Borisenkova, O.L. Kaliya, V.M. Derkacheva and E.A. Lukyanets, *J. Mol. Catal*., 1993, **83**, 1.
11 J.H. Schutten and J.Zwart, *J. Mol. Catal*., 1979, **5**, 109.
12 H.C. Liu, Doctoral Thesis, Research Institute of Petroleum Processing, Beijing, China, 1996.