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Iron–Phthalocyanine Immobilized on Activated Carbon Black: A Selective Catalyst for Alkane Oxidation

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Carbon black is tested as a support for iron–phthalocyanine within the frame of the oxidation of hydrocarbons with *t*-butylhydroperoxide as oxygen donor. The increased hydrophobicity of the carrier surface, with respect to zeolite Y, changes the adsorption behavior of the components in the reaction mixture towards the alkane. A major improvement in the oxidation conversion and efficiency of cyclohexane has been established. Furthermore, the kinetic isotope effect and the reactivity order of secondary and tertiary carbon atoms measured with adamantane provide evidence for an "oxygen rebound" reaction mechanism, a non-free-radical oxidation pathway where the metallo-complex is responsible for the hydrogen abstraction. © 1996 Academic Press, Inc.

INTRODUCTION

The selective oxidation of alkanes is an important industrial reaction, but is difficult to accomplish. The industrial process uses dioxygen as an oxygen donor in the presence of traces of transition metals. The conversion has to be kept low to achieve high selectivities (1, 2). In nature a group of enzymes, the oxygenation enzymes such as cytochrome P-450, are able to oxidize a broad spectrum of alkanes in a selective way (3). However, enzymes operate optimally under rigorous conditions which make them unattractive for practical use (4). In the last 15 years many attempts have been made to mimic these systems (5–14). One of the best models is iron–phthalocyanine (FePc) encapsulated in zeolites, where the metallo-complex is a mimic of the active heme group and the zeolite that of the protein mantle (14). These systems, however, are hydrophilic models (14) of the enzyme cytochrome P-450, which has a hydrophobic binding site near the active entity (15). Polar molecules of the reaction mixture have a higher affinity for the zeolite than the apolar alkanes. This ends in the exclusion of the alkane from the zeolite supercages and explains the low conversion and efficiency reached with this type of catalyst (14). Organic polymers are not the proper solution to this problem because of their lack of rigidity which enables the complexes to approach each other, leading to auto-oxidation and deactivation (16–18). A more promising material is carbon black. It is known for its good chemical and thermal resistance, as well as its high adsorption qualities (19). Moreover, a previous communication shows that iron–phthalocyanine supported on carbon black is characterized by a high ratio of oxygenase-like to dismutase-like activity in the presence of peroxide (20). It is preferable to activated carbon because of its higher degree of purity (21). Carbon black has already been used as support for TM-complexes for the purpose of O_2 reduction electrodes (22–24).

In this paper we discuss the use of carbon black as a carrier for iron–phthalocyanine in the oxidation of alkanes. A comparison between carbon black and zeolite Y as support materials for FePc will be made. Furthermore, we will show that there exists a relation between the polarity of the carrier surface and the activity of the heterogeneous complex. In the last section of the paper we report the results of a mechanistic study carried out on the carbon-supported iron–phthalocyanine in the oxidation of alkanes.

METHODS

Materials

Dimethylformamide (99%), 1,2-dicyanobenzene (98%), and ferrocene (98%) were obtained from Aldrich. Acetone (p.a.), cyclohexane (99.5%), cyclohexane-d_2 (99.5%), cyclopentanol (99%), dichloromethane (99.5%), and tertiary-butyl hydroperoxide (*t*-BHP; 70% in water) were purchased from Janssen Chimica; adamantane (+99%) was purchased from Aldrich and Fe(II)Pc (98%) from Strem Chemicals. Carbon black Corax N326, a gas black acquired from Degussa, was heated in oxygen at 400°C for 1 h (CB-$O_2$400) according to a procedure described previously (20) (BET surface area: 78.7 $m^2\ g^{-1}$; oxygen content of the surface: 0.89 at%). BL, a powder activated carbon designed for purification in the chemical, food, and pharmaceutical

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industries, was kindly provided by Chemviron Carbon (Iodine Adsorption Number: 1000 mg per gram of carbon). Commercial NaY with a silicon-to-aluminum ratio of 2.47 was acquired from Zeocat.

Synthesis

FePc complexes were deposited onto the carbon black carrier by impregnation (FePc–CB). Twenty mg FePc was dissolved in a minimal volume of the solvent dichloromethane (±30 ml). Subsequently, 1 g of the carbon black was added. In the case of carbon BL, 52 and 105 mg FePc, respectively, was deposited per gram of carbon. The solvent was vaporized under continuous stirring of the mixture at room temperature. This method has the advantage that the exact quantity of phthalocyanine present on the carrier surface is known.

Iron–phthalocyanine Y zeolite (FePc–Y) was synthesized under nitrogen atmosphere by a solid state adsorption of ferrocene (0.575 g, 1 molecule per supercage) on 5 g NaY air dried at 523 K). Subsequently, the ferrocene-loaded zeolite was mixed with 3.15 g 1,2-dicyanobenzene (excess of 2) and introduced into a Teflon-lined autoclave. The autoclave was heated at 453 K for 24 h. The blue-green solid obtained was successively soxhlet extracted with acetone, dimethyl formamide, and again with acetone, until a colorless extract was obtained. The extractions removed phthalocyanine at the outer surface of the zeolite and unreacted reagents and intermediates from the crude catalyst. The final catalyst was air dried at 343 K (14).

Reaction Setup

The catalytic reactions are carried out in a liquid phase fed batch reactor under continuous stirring, at room temperature (298 K) and atmospheric pressure (0.1 MPa), with acetone (30 ml) as solvent, 5 mmol chlorobenzene as internal standard, 0.5 g catalyst and 50 mmol substrate. The oxidant *t*-BHP is added continuously to the reaction mixture at a rate of 4.38 mmol h^{-1} until 100 mmol is added. The reaction with adamantane is done in dichloromethane as solvent. In the competition reaction of cyclohexane with its deuterated analogue, the reagents and catalyst are reduced with a factor of 1.67, for economical reasons. Identification and quantification of products are made by GC-analysis on a 50-m CP-Sil 5 capillary column purchased from Chrompack, using the appropriate sensitivity factors for a FID detector.

RESULTS AND DISCUSSION

Characterization

The carbon carrier, CB–$O_2$400, was characterized in a previous report (20). XPS shows a surface oxygen concentration around 0.89 at%. Sorption measurements indicate a macroporous structure with pore sizes around 30 nm, a specific surface area of 78.7 $m^2\ g^{-1}$ and without micropores. Its electrophoretic mobility is close to zero in phosphate buffer at pH 7. It shows the highest ratio of oxygenase-like to dismutase-like activity on a set of adsorbents obtained by oxidation of Corax N326. Literature results show that phthalocyanines adsorb on hydrophobic carbon as a monolayer (18, 25). The monolayer dispersion of the FePc complexes on the carbon carrier is a consequence of the strong π–π interaction between the aromatic structure of the carbon surface and the macrocyclic ligand of the complex (26). Our results confirm these findings. Scanning electron microscope pictures (SEM) of the catalyst show no FePc crystals. Evidence pointing towards monolayer distribution is given by comparing the initial reaction rates of oxidation by catalysts with different FePc loadings. When the amount of FePc on the carbon surface is halved the initial reaction rate decreases by a factor 1.5, while a decrease by a factor of two is expected for the reaction rate in the case of monolayer appearance. The deviation of this rule points towards a condition between mono- and multilayer appearance. The fact that the FePc complexes are poorly soluble, even in dichloromethane, by which they are not completely dissolved during the synthesis of the heterogeneous catalyst, can give an acceptable explanation. In the case of monolayer appearance, changes in respectively reaction rate and loading should be directly proportional to one another. The deviation of this rule can be explained by the poor solubility of FePc complexes, even in dichloromethane. Consequently, the FePcC catalyst needs a full coverage of its surface with FePc complexes for optimal functioning.

Comparison between Carbon Black and Zeolite Y as Carriers for FePc

Increasing the hydrophobicity in the vicinity of the active TM-complex enhances the activity in the oxidation of hydrocarbons, as has been done by Miki and Sato by anchoring alkyl chains to the hydroxyl groups of a silica surface (27). In this respect a carbon black carrier should also improve the activity of the adsorbed complex. The CB–$O_2$400 support referred to in this article has been found to be the best from a comparative study done on different variants of the Corax N326 (20).

Figure 1 shows the time course of oxidation of cyclohexane on FePc–Y and FePc–CB, respectively. FePc–CB is considerably more active than FePc–Y, in spite of its lower concentration of FePc. Sorption phenomena are responsible for the difference in activity between the two supports. The highly hydrophilic zeolite Y favors adsorption of peroxide and solvent and disfavors that of cyclohexane. Consequently, the actual concentration of the peroxide near the active sites is much higher than in the bulk solution, and vice versa for cyclohexane. Moreover, the oxidation and

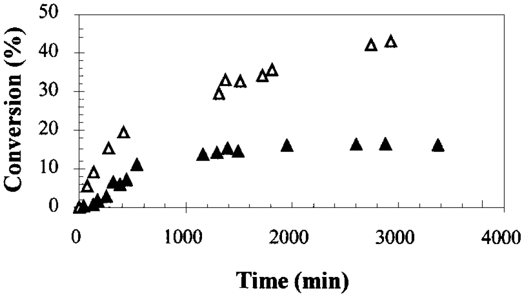

FIG. 1. The oxidation conversion of cyclohexane versus time on (△) FePc–CB and (▲) FePc–Y.

decomposition products will be accumulated on the Y zeolite because of their high hydrophilicity. Decomposition of *t*-BHP into *t*-butanol and O_2 will be the main reaction. On carbon, as a consequence of the high hydrophobicity of the support, the alkane adsorption is improved at the expense of *t*-BHP, *t*-butanol, and the oxidation products. This leads to a better substrate versus oxidant ratio near the active center and a higher rate for oxidation of cyclohexane, compared to decomposition of *t*-BHP. In both cases the conversion reaches a constant level (Fig. 1). With FePc–Y as catalyst the deactivation is due to accumulation of polar components in the zeolite pores, making the active center difficult to reach for the alkane. The oxidation of cyclohexane of FePc–CB, on the contrary, is restarted by adding an extra amount of *t*-BHP, so that the peroxide is the limiting factor. However, oxidative destruction of the phthalocyanine complexes must be taken into account, because of leaching. The release of the complex from he carbon carrier surface has been noticed through a continuous experiment.

The efficiency or peroxide selectivity is defined as the amount of peroxide used for the selective oxidation in proportion to the total amount of peroxide which is converted. The higher efficiency reached with FePc–CB (Fig. 2) is attributed to a favorable sorption of alkane with respect to peroxide.

The positive influence of a higher hydrophobicity of the carrier on the oxidation of non-polar reactants is confirmed in the competitive reaction of cyclohexane and cyclopentanol (Fig. 3). At identical cyclopentanol conversion, the conversion of cyclohexane is notably higher with the iron–phthalocyanine supported on the carbon black compared to Y zeolite. As the hydrophobicity of the support increases, the oxidation of the alkane with respect to the alcohol becomes relatively easier. Cyclopentanol is more sensitive to oxidation, which explains the higher conversion of cyclopentanol with regard to cyclohexane in the competition reaction.

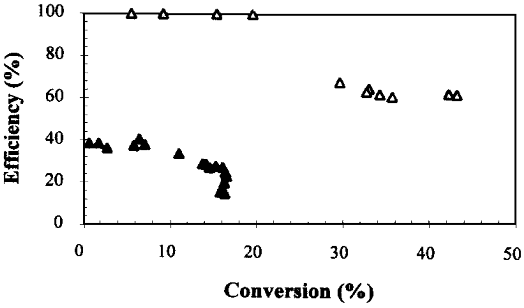

FIG. 2. The efficiency of *t*-BHP as function of the conversion for the oxidation of cyclohexane on (△) FePc–CB and (▲) FePc–Y.

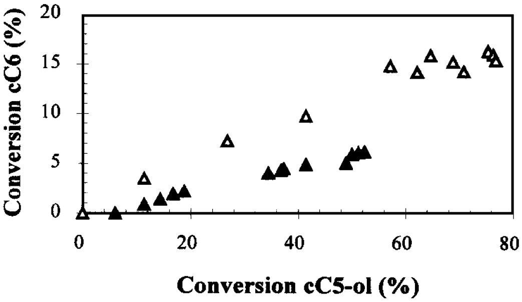

FIG. 3. The conversion of cyclohexane as a function of the conversion of cyclopentanol for the competitive oxidation reaction on (△) FePc–CB and (▲) FePc–Y.

The polarity of the support has to be accommodated to that of the substrate and products, so that the substrate adsorbs readily at the active center and the products desorb easily. In this way an ideal substrate-to-oxidant ratio is created and consecutive reactions are limited.

Regeneration of the catalyst, by washing with acetone and drying in an oven at 333 K, failed. The activity dropped considerably and decomposition of peroxide became the main reaction. This is the opposite of what is observed on FePc–Y, which seems to be undamaged after regeneration. Probably, the supercage in a Y zeolite creates a superior protection of the phthalocyanine against radicals and other reactive species.

Mechanistic Study

Mechanistic insight into the oxidation of alkanes on FePc–CB catalysts has been gained on the basis of two reactions, namely the oxidation of adamantane and the competitive oxidation of cyclohexane and its deuterated analogue.

The oxidation ratio of secondary to tertiary carbon atoms of adamantane is a good indication for the mechanism. Fenton chemistry, where the active entity is a hydroxyl radical, corresponds to a value of the ratio below 0.05 (28). In the case of free radical chemistry, where RO° or ROO° species derived from the peroxide are responsible for hydrogen abstraction, the ratio is between 0.5 and 1.2 (28). Gif chemistry, characterized by the higher selectivity towards the oxidation of secondary with respect to tertiary carbon atoms, gives ratios between 0.5 and 17 (28). With cytochrome

P-450 (29), homogeneous porphyrine complexes (30), and FePc–Y embedded in membranes (31), all examples of oxo-chemistry, the ratio is between 0.05 and 0.6. When there is no difference between the reactivity of secondary and tertiary carbon atoms, the value of the ratio is 3.

With FePc–CB, the secondary/tertiary ratio varies between 0.21 and 0.29. This is in the range characteristic of oxo-chemistry, but the interference of alkoxy or alkylperoxy radicals cannot be excluded. These radicals could be responsible for the abstraction of hydrogen from the alkane forming an alkyl radical that can freely react with molecular oxygen. Performing the oxidation of cyclooctane with *t*-BHP and FePc–CB once while flushing the reaction mixture with nitrogen and a second time under air gives a definite answer. The formation of the products follows the same curve in the presence or absence of molecular oxygen. The alcohol and ketone are therefore not the result of the decomposition of the alkylhydroperoxide, which is formed through the reaction of the alkyl radical with molecular oxygen, but are derived from the direct interaction of the alkyl radical with the metal-oxo species. The activated oxygen atoms have electrophilic properties, which makes tertiary carbon atoms more suitable for oxidation than secondary ones, because of the inductive donating effect of the alkyl groups. A minor part of the products are chlorinated (Fig. 4). This points out that alkyl radicals are formed, which react with chlorine radicals from the solvent instead of recombining with the hydroxyl group. Within the chlorinated products the secondary/tertiary ratio is larger compared to the oxygenated products. Hence, tertiary radicals generated at the active site recombine faster with the active oxygen species than secondary alkyl radicals which diffuse more easily from the active center to react with the chlorine radicals present in the medium (Fig. 5).

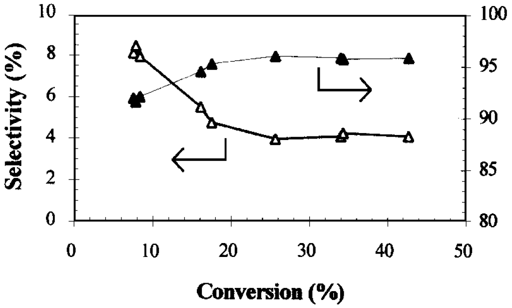

FIG. 4. The portion of (△) chlorinated and (▲) oxygenated compounds in the product pool for the oxidation of adamantane on FePc–CB.

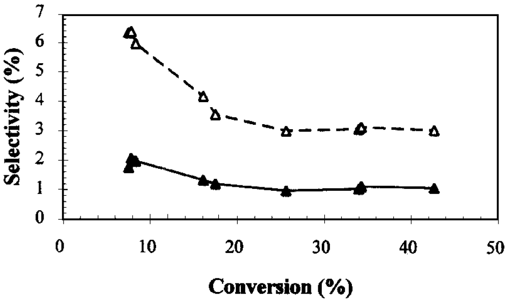

FIG. 5. The selectivity of (△) 2-chloro-adamantane and (▲) 1-chloro-adamantane within the products for the oxidation of adamantane on FePc–CB.

When the kinetic isotope effect (KIE), defined as the ratio of the reaction rate constants of, respectively, the hydrogen and deuterium abstraction, is larger than unity, hydrogen abstraction occurs as the rate determining step of the reaction. The KIE value is indicative of the reaction mechanism. It is approximately 2 for Gif chemistry (32), less than 2 for Fenton chemistry (32), below 2.5 in the case of free-radical oxidations (33), and between 2 and 22 for oxo-chemistry (33–36). Bent and linear transition states (TS) are associated with KIE below and above 6, respectively (34, 37). At room temperature the theoretically highest possible KIE is 6.2 (36). On account of secondary isotope effects and tunneling effects this number is frequently exceeded. Secondary isotope effects contribute to KIE for one or two units at most and are the result of hydrogen transfers in non-rate-determining reaction steps. Tunneling can be responsible for very large deviations of the theoretical maximum and goes back to the uncertainty principle of Heisenberg. This means that the energy actually needed for breaking the chemical bond is less than the theoretical activation energy. This phenomenon is only applicable for light entities such as an electron, a hydrogen atom, and a deuterium atom and is more pronounced when the mass drops (36). The contribution of tunneling is derived from the temperature dependence of the KIE (34, 37). Table 1 shows the values of the KIE for the competitive oxidation of cyclohexane and cyclohexane-d_{12} on FePc–CB performed at three different temperatures.

These numbers are corrected by extrapolation to zero conversion, because of the decreasing concentration ratio ($cC_6/cC_6\text{-}d_{12}$) upon increasing conversion. The KIE is larger than unity, so hydrogen abstraction takes place as the rate-determining step. The formation of chloroadamantane points to a radical hydrogen species. The KIE at room

TABLE 1

Kinetic Isotope Effect (KIE = k^H/k^D) at Three Different Temperatures for the Competitive Oxidation of Cyclohexane and Deutero-Cyclohexane on FePc–CB

Temperature (K)	k^H/k^D
274	11.05
299	9.03
328	7.26

TABLE 2

Difference between the Activation Energies, Ratio of the Pre-exponential Factors (A^H/A^D) Derived from the Arrhenius Plot, and Theoretical Ranges Where Tunneling Effects Have to Be Considered

	$E_A^D - E_A^H$ (kcal mol^{-1})	A^H/A^D
FePcC	1.38	0.86
Tunneling conditions* (34)	>1.2	<0.7

* The tunneling conditions shown are those which are met when a tunneling transfer of a hydrogen atom takes place in the rate determining step.

temperature exceeds 6.2, but not by more than a factor of 2. The contribution of tunneling is small, according to the difference between the activation energies ($E_A^D - E_A^H$) and to the ratio of the pre-exponential factors (A^H/A^D) (Table 2) which are extracted from the slope and the intercept by plotting $\ln(k^H/k^D)$ as a function of the reciprocal of the temperature. For this the competitive oxidation of cyclohexane and its deuterated analogue have been carried out at three temperatures (Table 1).

A KIE of 9.03 implies a symmetric linear hydrogen transfer between the active metal-oxo entity and the alkane, without interference of the leaving group of the oxidant (34–37) (Fig. 6). Small tunneling effects and probably some contribution of secondary isotope effects are responsible for the increase of KIE from 6.2 to 9.03.

The first reaction step involves the abstraction of a hydrogen atom from the alkane by a triplet-like oxygen atom in the phthalocyanine–$[FeO]^{3+}$ complex (38). This complex is formed by an oxygen transfer between *t*-BHP and Fe(III). The hydrogen abstraction leads to the formation of an alkyl radical and a phthalocyanine–$[FeOH]^{3+}$-stabilized hydroxyl radical. Consequently, these two radicals recombine to form a product. The highly active hydroxyl radical prevents the alkyl radical from diffusing into the reaction mixture. Chloroadamantane, being only a minor fraction of the oxidation products, points to a fast recombination of the two radical species. This overall reaction mechanism is known as the "oxygen rebound" mechanism, and fits the shunt path followed by cytochrome P-450 in the presence of mono-oxygen donors (35, 38–40). Figure 7 gives a schematic presentation of the reaction mechanism.

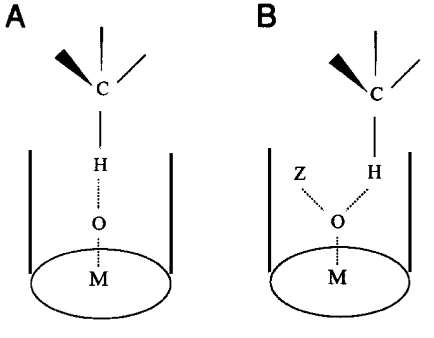

FIG. 6. A schematic presentation of the transition state (TS) in case of the oxygen rebound mechanism: (A) linear TS at high KIE and (B) bent TS at low KIE, with Z the leaving group of the oxidant (*t*-BuO–) (34).

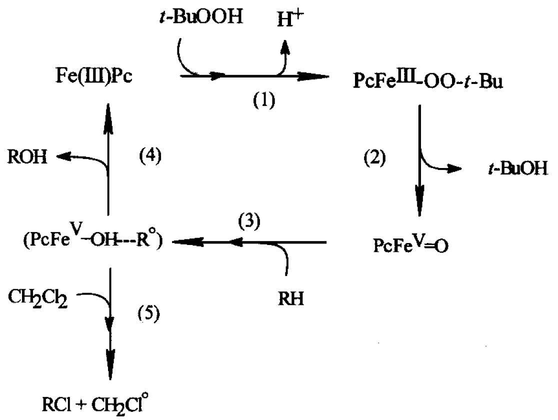

FIG. 7. Reaction mechanism for the oxidation of alkanes on FePc–CB (35, 38–40): (1) and (2): formation of the triplet-like active oxygen species; (3): hydrogen abstraction; (4): recombination of the alkyl radical with the hydroxy radical, forming the alcohol; (5): capture of the alkyl radical by the chlorine radical.

CONCLUSIONS

Carbon black proves to be an appropriate carrier for FePc complexes within the framework of the oxidation of alkanes. The increased hydrophobicity of the support surface, compared to zeolite Y, alters the adsorption behavior to the benefit of the alkane. This leads to a more ideal substrate/oxidant ratio near the active center, which explains the higher activity and efficiency reached with FePc–CB.

The oxygen rebound mechanism, discovered by Groves, applies to the carbon supported iron–phthalocyanine. This means that an electrophilic oxygen species is responsible for the hydrogen abstraction, forming an alkyl radical and a phthalocyanine–$[FeOH]^{3+}$-stabilized hydroxyl radical. A fast recombination of these two radicals leads to the formation of the alcohol.

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