

Catalytic applications of heterogeneous metal-phthalocyanine complexes

The theses of Ph.D. dissertation

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Supervisor:

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1. Introduction

The basic concept of development is to fulfill the requirements of the current generation in a way that the next generations would also be able to fulfill their requirements. For this purpose, chemical industry is of major importance. By using the increasing amount of information in the literature, chemical industry has a key role in the processing of raw materials and also in the reuse of by-products obtained as waste materials. This is the main principle of green chemistry.

One of the most important subjects of green chemistry is catalysis. The principle of catalysis and the applications of various catalysts have been known for a long time, but these days, the role of catalytic reactions has become even more important, mainly in terms of environmental protection and industrial applications.

The subject of my Ph.D. dissertation is the preparation and the catalytic investigation of metal-phthalocyanines. Some of the phthalocyanines are environmentally safe materials, which can be synthesized by facile methods and have favourable catalytic properties, so they may be considered as very promising catalysts.

Metal-phthalocyanine complexes may be suitable catalysts for the degradation of pollutants. The typical toxic contaminants of industrial waste waters are chlorophenols. A possible way for the removal of chlorophenols is oxidation, catalyzed by metal-phthalocyanine complexes.

A similar reaction is the oxidation of 4-chlorophenol by peroxides. This is a "dark" oxidation catalyzed by transition metal-phthalocyanine complexes with electron deficiencies. Other phthalocyanines with filled d orbitals may be employed in photocatalytic oxidations.

After studying the applications of metal-phthalocyanines in oxidation reactions, we investigated other catalytic applications, e.g. hydrogenations. For this reaction, very expensive transition metals and ligands are used, which could be replaced by cheaper metal complexes. Data in the literature suggested that iron complexes may be suitable catalysts for catalytic transfer hydrogenations (CTH), so we decided to study the catalytic transfer hydrogenations of substituted aldehydes and ketones in the presence of iron-phthalocyanine as a catalyst and propane-2-ol as a hydrogen source. This procedure may be an alternative for the application of hydrogen gas, since catalytic transfer hydrogenations take place at atmospheric pressure under mild conditions, in the presence of cheap and natural hydrogen sources.

We intended to prepare active and selective heterogeneous catalysts, to be applied in oxidations and hydrogenations. For industrial applications, heterogeneous catalysts are preferred, because they can be easily handled, removed from the reaction mixture by filtration and reused. Recycling is a basic requirement of the industry and environmental protection. We compared the catalytic performances of homogeneous and heterogenized metal complexes in several reactions. Also, we made a comparison between heterogenized catalysts obtained by different methods.

2. Experimental

2.1. Syntheses of the catalysts

Two methods were employed for the synthesis of metal-phthalocyanines. For the first method, the reaction was performed in a solvent, for the second one, no solvent was used.

Syntheses in solvents

2.1.1. Reaction in 1-octanole

The advantage of this method is the high yield for most metal-phthalocyanines (Zn(Pc), Ni(Pc), Fe(Pc)).

2.1.2. Reaction in nitrobenzene

Some metal-phthalocyanines (Al(Pc), Co(Pc), Cu(Pc)) may be obtained with higher yields than those obtained by 1-octanole.

2.1.3. Reaction in quinoline

Quinoline was used for the syntheses of silicon-phthalocyanine and titanium-phthalocyanine.

Syntheses without solvents

This is the simplest, fastest and cheapest way of preparation. The only disadvantage of this method is the low yield.

The reactants (transition metal chloride : phthalic dinitrile = 1:4) were placed into a beaker and homogenized by stirring. The beaker was covered with a watch glass and placed into a microwave oven. The end of reaction was indicated by the appearance of a dark green or dark blue colour. The reaction vessel was cooled in a fume hood and then the product was ground in a mortar. The fine powder was purified by washing with acetone.

2.2. Heterogenization of the complexes

2.2.1. Preparation of anchored complexes

1,5 g of Al_2O_3 was suspended in 30 ml of methanol in a 3-necked flask. Then, 386,7 mg of phosphotungstic acid hydrate, dissolved in 25 ml of methanol, was added dropwise under stirring in an argon atmosphere, at room temperature. Finally, 0,1 mmol of metal-phthalocyanine, dissolved in 40 ml of dimethylformamide, was slowly added to the suspension, followed by stirring, washing, filtration and drying.

2.2.2. Preparation of encapsulated complexes

Encapsulation of the $\text{Fe}(\text{Pc})$ complex in zeolite was performed by internal ligand synthesis under argon atmosphere. The Fe^{2+} containing zeolite was prepared by ionic exchange (2 g of sodium zeolite and 40 ml of 1N FeSO_4 solution was left under stirring at 50°C for 3 h). The ion-exchanged zeolite was filtered and washed with ion exchanged water and methanol and dried under argon. Then the mixture of zeolite, 2 g of phthalic dinitrile and 3 g of diphenyl was heated to 205°C and the melted material was stirred under argon for 4 h and cooled to room temperature. The product was subjected to Soxhlet extraction by acetone for 48 h and then the free Fe^{2+} ions were exchanged to Na^+ ions by a NaCl solution. The solid was filtered and dried.

2.2.3. Characterization of the heterogenized complexes

The metal content of immobilized complexes was determined by ICP-AES. A JOBLIN YVON 24 ICP-AES equipment was used. The heterogenized complexes were characterized by FT-IR spectroscopy, by using a Bio-Rad Digilab Division FTS 65A/896 instrument. The IR spectra of the free complex ($\text{Fe}(\text{Pc})$), the support and the heterogenized catalysts ($\text{Fe}(\text{Pc})/\text{NaY}$, $\text{Fe}(\text{Pc})/\text{Al}_2\text{O}_3$) were recorded.

The zeolite encapsulated iron-phthalocyanine catalyst was characterized by X-ray diffraction (Philips PW – 1830). This method was used for structural investigation of the zeolite encapsulated complex.

The surface of the catalyst prepared by Augustine's method was characterized by SEM (a Hitachi 520 microscope).

2.3. Catalytic reactions

2.3.1. Oxidations

The catalytic activities of homogeneous phthalocyanines and heterogenized iron(II)-phthalocyanines were studied for the oxidation of 4-chlorophenol. The aqueous solution of the reactant was poured into an Erlenmeyer flask, which was covered to exclude light. Then, the catalysts and oxidizing agents were added. The reactions were performed under continuous stirring at atmospheric pressure and 25 °C, by controlling the pH. After reaction, the reaction mixture was filtered by a layer of SiO₂. Analysis was performed by HPLC-1, by using an RP-18 column.

The importance of heterogeneous catalysts is based on their easy recovery and recycling. After the catalytic reaction, the reaction mixture was left until the heterogenized catalyst settled down on the bottom of the liquid phase, so the supernatant could be easily removed. Then the reactant and the oxidizing agent was added and the reaction was re-started under the same conditions.

2.3.2. Catalytic transfer hydrogenation

The hydrogen source was propane-2-ol, which was also a solvent. Propane-2-ol was poured into a Schlenk vessel, 0,038 mmol of iron(II)-phthalocyanine complex was added and then the vessel was flushed with argon. For the hydrogenations of aldehydes, the solution of 0,095 mmol of NaOH and 0,5 ml of propane-2-ol was added. For the hydrogenations of ketones, the amount of NaOH was increased to 0,38 mmol. The amount of reactant (aldehyde or ketone) was 0,38 mmol, which was dissolved in 0,5 ml of propane-2-ol and injected into the reaction vessel. The reaction temperature was 80 °C, the reaction time was 4 h and 12 h for aldehydes and ketones, respectively. During reactions, magnetic stirring was applied.

For the heterogenized iron(II)-phthalocyanine, the reaction was performed similarly. In order to obtain fair conversions, the amounts of reactants and the reaction time were modified. For the reactions of aldehydes, 0,04 g of heterogenized complex and 0,19 mmol of NaOH was used. For the reactions of ketones, the amount of NaOH was 0,38 mmol. The reaction time was 6 h and 12 h for aldehydes and ketones, respectively. The amount of reactant was 0,38 mmol. During reactions, magnetic stirring was applied.

For the recycling experiments, the stirring was stopped, the catalyst was sedimented and the liquid-phase reaction mixture was carefully removed. Then fresh propane-2-ol was added, the reaction vessel was flushed with argon and the reactant was applied in the presence of 0,5 ml of NaOH, after dissolution in 0,5 ml of propane-2-ol. The reaction was started by stirring. Further recycling experiments were performed similarly.

After reactions, the samples were filtered on a short column packed with SiO₂, and analyzed by gas chromatography. The alcohols were identified by using reference compounds. The products obtained from aldehydes were analyzed by a DB-5 capillary column, and the products obtained from acetophenone and its derivatives were analyzed by a HP-1 capillary column.

3. Novel scientific results

1. We have established the optimized preparation condition of 8 different metal-phthalocyanine complexes and using this method we have prepared these complexes. The prepared complexes were applied successfully in the oxidative degradation of 4-chlorophenol –which is a characteristic poison of industrial waste water – using different oxidants.
2. Having done a comparison of different metal-phthalocyanine complexes and different oxidants in the oxidative degradation of 4-chlorophenol we have established that the Fe(Pc) complex and *t*-BuOOH is the most effective system for the „dark” oxidation.
3. Considering the potential industrial application of the above reaction, we have prepared an immobilized Fe(Pc) complex, using two different preparation methods. The Fe(Pc) complex was grafted into the Al₂O₃ surface and it was built inside the NaY zeolite. The heterogenized complexes were characterized by spectroscopic methods: the complex was identified by FT-IR spectroscopy and the amount of complex was determined by ICP-AES method.
4. The heterogenized complexes were applied in the oxidative degradation of 4-chlorophenol and we could prove that our catalysts were active in the above reaction. Having known the amount of complex in the heterogenized catalysts, we could calculate and compare the TOF values. Our results show that the complex, anchored onto the Al₂O₃ surface had the highest TOF value in this reaction.
5. The most important advantage of the heterogenized complexes is the possibility of recycling, consequently we have applied our catalysts in 3 subsequent runs of the above reaction. Both our heterogenized complexes were active in the oxidative degradation of 4-chlorophenol, but they behaved differently: the complex, built inside the zeolite showed originally smaller activity, but during the recycling experiments it did not lose this activity. Meanwhile the other

immobilized complex during the recycling experiments gradually loses its activity, it did not have a stable activity.

6. To extend the catalytic applicability of Fe(Pc) complex, we have studied the usability of this complex in the catalytic transfer hydrogenation of carbonyl group. It is well known the application in oxidation reaction of Fe(Pc) however only a few examples can be found its application in reductions. Another challenge of these examination was the possibility to replace the usually applied rare transition metal complexes by cheap, readily available metal complexes, like: Fe.
7. Using benzaldehyde and acetophenon as starting materials we have established the optimized conditions of CTH reaction in homogeneous and heterogeneous conditions. We have studied the CTH reactions of differently substituted aldehydes and ketones in the optimum condition. A significant effect of substituents was observed, what we have explained in connection with the mechanism of CTH reaction.
8. The Fe(Pc) complex, anchored into the Al₂O₃ surface was applied in the CTH reaction of aldehydes and ketones. We had to establish the optimum condition of CTH reaction in heterogeneous circumstances and in this condition we studied the reactions of different aldehydes and ketones. Good and/or excellent activities were observed for the differently substituted aldehydes and ketones. In other words we could prove that the immobilized Fe(Pc) is a good catalyst for the CTH reaction of aldehydes and ketones.
9. Our results show that all of the substituted ketones were less reactive than the acetophenon, inspite of the fact that the substituents were electron donating substituents. The results of aldehydes show that the benzaldehydes, having electron donating substituents always had excellent conversion. This experimental fact can be rationalized by the different reactivity of the different carbonyl functionality.

- 10.** The most important advantage of the immobilized catalysts is the easy handling and the possibility of recycling. The Fe(Pc) complex, anchored into the Al₂O₃ surface was active in 3 subsequent runs in this reaction. Using benzaldehyde as a starting material, the conversion did not decrease in these experiments, meanwhile we observed a little decrease in conversion in the case of acetophenone.

- 11.** Our main goal was successfully fulfilled, because we could develop a cheap, heterogeneous catalyst, which can catalyze the CTH reaction of aldehydes and ketones with reasonable activity. At the same time we could fulfill the other motivation, as well, namely we can replace the expensive rare metals (Ru, Ir) with a cheap, readily available metal like Fe in the reduction reaction.

4. Publication list

4.1. Papers related to the Theses

1. P. Kluson, M. Drobek, A. Zsigmond, J. Baranyi, **P. Bata**, S. Zarubova, A. Kalaji
Environmentally friendly phthalocyanine catalysts for water decontamination—Non-photocatalytic systems
Applied Catalysis B: Environmental 91 (2009) 605–609 IF: 5,252
2. **P. Bata**, A. Demjen, F. Notheisz, A Zsigmond
Comparative Study of Immobilized Phthalocyanines in Oxidative Degradation
The Open Catalysis Journal, 5 (2012) 50-55 IF:-
3. **P. Bata**, F. Notheisz, P. Kluson, A. Zsigmond
Preparation and application of heterogenized iron(II)-phthalocyanine in oxidation and reduction reactions
Hungarian Journal of Chemistry (2014) IF:-
4. **P. Bata**, F. Notheisz, P. Kluson, A Zsigmond
Iron-phthalocyanine as a new, efficient catalyst for catalytic transfer hydrogenation of carbonyl functionality
Appl. Organometallic Chem. (submitted for publication) IF: 2,011
5. A. Zsigmond, **P. Bata**, M. Gyémánt, A. Czeglédi, P. Kluson
Application of heterogenized metal complexes in hydrogenation reactions: a comparison of hydrogenations and CTH reactions
Chemical Papers (in preparation) IF: 0,879

4.2. Paper not related to the Theses

1. A. Zsigmond, **P. Bata**, M. Fekete, F. Notheisz
Catalytic dehydration of glycerol under mild condition: an environmental friendly acrolein production
Journal of Environmental Protection 1 (2010) 201-205 IF: 0,178

4.3. Oral presentations related to the Theses

1. **P. Bata**, D. Bárdfalvy, F. Notheisz, A. Zsigmond
New, efficient heterogeneous catalyst for catalytic transfer hydrogenation, Proceedings of the 11th Pannonian International Symposium on Catalysis, Obergurgl, Austria, September 3-7, 2012, page 97.
2. A. Zsigmond, **P. Bata**, F. Notheisz, P. Kluson
Catalytic transfer hydrogenation of carbonyl group using iron catalys, ISHHC-16, Hokkaido University, Sapporo, Japan, 2013, Program and Abstracts, 2RRR-7, page 181.
3. **P. Bata**, R. Szucs, A. Zsigmond, F. Notheisz
The oxidative degradation of xanthane biopolymer, *MTA Katalízis Munkabizottsági Ülés (2012) Budapest*
4. **P. Bata**, D. Bárdfalvy, A. Zsigmond
Catalytic transfer hydrogenation on heterogenized metal complexes, *MTA Katalízis Munkabizottsági Ülés (2012) Szeged*
5. **P. Bata**
Catalytic application of heterogenized metal-phthalocyanine, *MTA Katalízis Munkabizottsági Ülés (2014) Budapest*

4.4. Oral presentations not related to the Theses

1. **P. Bata**, Dehydrtation of glycerol to acrolein, *A Szegedi Ifjú Szerves Kémikusok Támogatásáért Alapítvány 9. tudományos előadóiülése*, Szeged (Hungary), 2009
2. **P. Bata**, Dehydration of glycerol to acrolein, *XXIX. Országos Tudományos Diákköri Konferencia, Kémiai és Vegyipari Szekció*, Debrecen (Hungary), 2009, p. 105

Cummulative impact factors: 8,32