Phthalocyanines on Mineral Carriers, 2*

Synthesis of Cobalt(II) and Copper(II)-phthalocyanines on $\gamma$-Al$_2$O$_3$ and SiO$_2$

Dieter Wöhrle** and Uwe Hündorf
Organische und Makromolekulare Chemie, Universität Bremen, D-2800 Bremen 33, FRG
Günter Schulz-Ekloff and Erwin Ignatzek
Institut für Angewandte und Physikalische Chemie, Universität Bremen, D-2800 Bremen 33, FRG

Z. Naturforsch. 41b, 179–184 (1986); received August 19, 1985
Phthalocyanines, Mineral Carriers, Alumina, Silica

The reaction of metal loaded $\gamma$-Al$_2$O$_3$ and SiO$_2$ with benzene-1,2-dicarbonitrile (2) resp. 1H-isoindole-1,3(2H)diimine (3) results in the $\beta$-modification of metallized phthalocyanines (1; metals: Cu(II), Co(II)). 1 is formed with an average yield of 48–64% in uniform distribution on the carriers from the reaction with 2. The sizes of the surface areas of the supports are not changed significantly by loading with 1. Non-uniform distribution or even unsupported crystals of 1 are found if the synthesis is carried out with 3.

1. Introduction

The catalytic activities of carrier-free metallized phthalocyanines and their polymeric analogues have been the subject of many papers [2—9]. In heterogeneous catalysis the low dispersion of carrier-free 1 is a disadvantage. Therefore many attempts have been made to deposit 1 on supports like $\gamma$-Al$_2$O$_3$ [10–13], SiO$_2$ [14, 15] or coal [16–18].

Especially, inorganic supports exhibit the advantage that they are more resistant thermally, chemically and mechanically than other supports like organic polymers. Also, the carriers might have an advantageous influence on the catalytic activity. Such catalysts were particularly investigated in oxidation resp. hydrogenation reactions and in O$_2$ reductions (fuel cell) [3, 10, 13, 19–23].

Up to the present time, 1 was deposited on the supports by precipitation or sublimation. It has been shown by us, that faujasite supported 1 can be prepared by the reaction of transition metal ion exchanged zeolite with benzene-1,2-dicarbonitrile (2) resulting in a highly dispersed 1, since only one phthalocyanine molecule can be encapsulated by a supercage of the faujasite framework [1].

The aim of this work is to develop a method for synthesizing 1 directly on supports such as $\gamma$-Al$_2$O$_3$ and SiO$_2$. Therefore, reactions between supports charged with metal ions and benzene-1,2-dicarbonitrile (2) resp. 1H-isoindole-1,3(2H)diimine (3) were carried out. In such a way, uniform distribution and strong attachment to the supports are expected, which might improve the catalytic properties of the produced phthalocyanine/support system.

---

* 1. Communication s. Ref. [1].
** Reprints request to Prof. Dr. D. Wöhrle.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen 0340–5087/86/0200–0179/$ 01.00/0
2. Results and Discussion

\( \gamma \text{-Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) were selected as carriers having identical grain sizes (5–20 \( \mu \text{m} \)) in order to rule out possible grain size effects in the comparative studies on the influence of the combination of support on the catalytic activity. First, the supports are charged with metal salts (Tab. I). An amount of metal salt for the doping of the amorphous carriers is used, which is sufficient for the formation of monomolecular layers of \( \text{I} \) on the carriers.

Charging of \( \gamma \text{-Al}_2\text{O}_3 \) with \( \text{Co(II)} \) and \( \text{Cu(II)} \) salts is most successful in acetone. For acidic \( \text{SiO}_2 \), the taking up of basic ammonia complexes of \( \text{Co(II)} \) and \( \text{Cu(II)} \) salts in water is the best method. In the case of silica, the mechanism of cation exchange was investigated. In ammonia, the exchange of two protons against one tetrammine \( \text{Cu(II)} \) ion results in finely dispersed metal cations [24].

The metal concentrations of the supports described in this paper are about 3 wt\%. The carriers containing \( \text{Cu(II)} \) and \( \gamma \text{-Al}_2\text{O}_3 \) containing \( \text{Co(II)} \) are stable to tempering up to 250 °C [24]. Only when heating \( \text{Co(II)} \)-salt-charged \( \text{SiO}_2 \) to 250 °C an autoreduction takes place to give a gray product containing \( \text{Co}^0 \). The formation of \( \text{Co}^0 \) was proven with energy dispersive analysis of X-radiation (EDAX). Debye-Scherrer powder photographs do not indicate any \( \text{Co}^0 \). From the fact that no \( \text{Co}^0 \) lines are found in the Debye-Scherrer powder photographs the conclusion can be drawn that the \( \text{Co} \) particles are < 5 nm. Therefore, also the cobalt salts must be finely dispersed on the carrier prior to the autoreduction to \( \text{Co}^0 \). The reaction of \( \text{2} \) or \( \text{3} \) with metals or metal salts is the preferred way for synthesizing \( \text{I} \) in high yields [8]. At 250 °C, \( \text{2} \) resp. \( \text{3} \) react with the metal charged supports in the stoichiometric ratio of phthalocyanine formation. \( \text{I} \) is formed in yields between 45 and 72% (Tab. I). The intensively colored blue products contain more than 10 wt\% of \( \text{I} \). Cobalt-containing supports give higher yields of \( \text{I} \) with \( \text{2} \) while copper charged carriers give higher yields with \( \text{3} \). During after-treatment 1H-isoidole-1,3(2H)dione (phthalimide) was found as by-product. The degree of drying of the metal charged carriers prior to the phthalocyanine synthesis was found to influence strongly the yield of \( \text{I} \) as well as the side product phthalimide. Drying at \( T > 573 \text{ K} \) reduced the yield of \( \text{I} \) whereas drying at low \( T \) (\( \sim 323 \text{ K} \)) gave large fractions of phthalimide. 523 K was found to be an optimum. ESR analysis of \( \text{Cu(II)} \)-charged \( \text{SiO}_2 \) shows that at 573 K not exactly known changes occur in the bonds of the metal ions on the surface [24].

![UV/VIS-spectra](image)

Fig. 1. UV/VIS-spectra (in conc. sulfuric acid) of \( \text{I} \) (Mt = Co) (a) and \( \text{I} \) (Mt = Cu) (b) after separation from the support reacted with \( \text{2} \).

Table I. Charging of metal salts and phthalocyanine (I) on \( \gamma \text{-Al}_2\text{O}_3 \) and \( \text{SiO}_2 \).

<table>
<thead>
<tr>
<th>Support</th>
<th>Metal salt</th>
<th>Metal salt Method</th>
<th>Uptake of metal salt (%)</th>
<th>Metal content (wt%)</th>
<th>Yield of I (%)</th>
<th>Content of I on the support (wt%)</th>
<th>Yield of I (%)</th>
<th>Content of I on the support (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma \text{-Al}_2\text{O}_3 )</td>
<td>CoCl(_2)</td>
<td>A</td>
<td>82.7</td>
<td>2.8</td>
<td>55.0</td>
<td>11.9</td>
<td>44.4</td>
<td>9.8</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>CoCl(_2)</td>
<td>B</td>
<td>99.9</td>
<td>3.3</td>
<td>64.3</td>
<td>16.1</td>
<td>50.4</td>
<td>12.2</td>
</tr>
<tr>
<td>( \gamma \text{-Al}_2\text{O}_3 )</td>
<td>CuCl(_2)</td>
<td>A</td>
<td>93.3</td>
<td>3.4</td>
<td>47.6</td>
<td>11.4</td>
<td>72.4</td>
<td>17.1</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>CuCl(_2)</td>
<td>B</td>
<td>99.8</td>
<td>3.6</td>
<td>50.4</td>
<td>12.7</td>
<td>63.8</td>
<td>14.5</td>
</tr>
</tbody>
</table>
The phthalocyanine 1 was quantitatively removed from the carriers with conc. sulfuric acid. From the extinctions quantitative determinations of 1 on the carriers were made [25]. The electronic spectra of metal free and metal containing phthalocyanines in conc. sulfuric acid differ significantly in the range of \( \lambda = 740 - 840 \text{ nm} \) [25, 26]. The bands at \( \lambda = 784 \text{ nm} \) (1, \( M_t = \text{Co} \)) resp. \( \lambda = 791 \text{ nm} \) (1, \( M_t = \text{Cu} \)) are typical for metallized phthalocyanines with \( D_{4h} \) symmetry (Fig. 1). Metal-free phthalocyanines are not formed in the reactions of the metal-charged supports with 2 resp. 3. UV/VIS spectra in conc. sulfuric acid also indicate the purity of the reaction products. Comparing the intensive absorptions at \( \sim 800 \text{ nm} \) with the low intensive absorptions at approximately 220 nm shows that impurities such as polyisoinidolenines absorbing in the UV region intensively at \( \lambda < 400 \text{ nm} \) can be excluded [27].

Transmission FT-IR spectra of the reaction products, obtained from the metal charged carriers and 2 resp. 3, confirm the statements drawn of the electronic spectra. The IR spectra exhibit between 1800 and 600 cm\(^{-1}\) typical absorptions for C—C and C—H of 1 (Fig. 2) [28]. Additionally, characteristic absorptions of metal-free 1 as N—H in-plane bending at 1000 cm\(^{-1}\) and N—H out-of-plane bending at 716 cm\(^{-1}\) are not present [28, 29].

Scanning electron micrographs clearly show differences in the morphology of the reaction products formed from metal-charged supports with 2 or 3 (Fig. 3). When using 3, isolated crystals of 1 located either on or even separately from the carriers are
formed. In contrast when using 2, crystals of 1 cannot be detected. All 1 formed in this reaction is on the surface of the supports γ-Al₂O₃ and SiO₂. The fact that the morphology of the employed supports does not differ in REM from supports charged with 1 (from 2) indicates uniform layer formation on the carriers. With the aid of Debye-Scherrer powder photographs clear statements on the modifications of the phthalocyanines formed can be made. In the reactions of the metal-charged supports with 2 or 3 the thermodynamically stable β-modifications are formed due to the high reaction temperatures [25, 30]. No indications for the α-modifications are present. In comparison to 2, the isoindolenine 3 reacts much more easily under formation of 1 [8]. This might be the reason for the non-uniform distribution of 1 obtained from the educt 3.

Transmission VIS microscope spectrophotometry of single particles also permits modification assignment. The solid state spectra of the products synthesized from metal charged supports and 2 (Fig. 4) correspond to those of sublimed layers of the β-modification of 1 (Mt = Cu, Co) on fused silica [31]. However, no exact assignments to metal-free or metal-containing parts are possible here due to small differences with respect to location and form of their visible absorption bands. The average thickness of the phthalocyanine layers can be estimated by the transmission photometry. According to Lambert-Bouguer's law a linear relation exists between absorbance and surface concentration. After dividing by the density of 1, an average layer thickness is obtained. Repeated and statistic measurements resulted in a value for the extinction E = 0.86 at λ = 695 nm for 1 (Mt = Co) on SiO₂. Corresponding to the calibration curve in [30] the surface concentration amounts to 0.018 mg · cm⁻². Hence, the layers of the β-modification of metallized 1 (density = 1.61 g · cm⁻³) have an average thickness of about 120 nm. Since the distances of neighboring 1 in the direction of the stack axes are 0.48 nm there are in average approximately 250 molecule layers present. For the other samples in Table I around 200 molecular layers on the supports are found. BET measurements of the surface areas of the carriers were made prior to as well as after charging with 1: γ-Al₂O₃ (127 m²/g), CoPc (11.9 wt%)/γ-Al₂O₃ (95 m²/g); SiO₂ (283 m²/g), CoPc (16.1 wt%)/SiO₂ (330 m²/g). Theoretically, the surface areas of formed β-phthalocyanines in a monomolecular arrangement would be for CoPc (11 wt%)/γ-Al₂O₃ 165 m²/g and for CoPc (16.1 wt%)/SiO₂ 223 m²/g. Therefore, monomolecular layer formation on the carrier is possible. Due to the evidence of the β-modification of 1 on the carrier detected by Debye-Scherrer powder photographs layers with a thickness >5 nm (>10 layers of 1) must be present at the external geometric surfaces of the grains. Because of the mean pore sizes (=6 nm for SiO₂) only very few layers of 1 can be formed in the pores, i.e. on the internal surface of the grains. It can be assumed that a large fraction of the formed 1 is located on the internal surface of the porous grains of the supports. A uniform deposition of 1 at the external geometric surface only, having 0.1% of the total surface, should result in an extensive plogging of the pore volume, which is, however, not found by the BET measurements.

Reactions of the metal-containing supports SiO₂ and γ-Al₂O₃ with 2 are a simple method for obtaining uniform charging of metallized 1 on the supports. Further studies with the aim to prepare monomolecular layers of 1 are going on. Investigation of the catalytic activity of the supports charged with 1 in heterogeneous gas and liquid phase oxidation has begun.

3. Experimental

UV/VIS spectra of 1 in conc. sulfuric acid were obtained on a Perkin Elmer 554. Transmission VIS microscope spectrophotometry of the supports charged with 1 was carried out with an MMSP [32]. FT-IR transmission spectra were recorded with a
Nicolet 5 DX (KBr pellets). Scanning electron microscopy was carried out by ISL-100 (Intern. Sci. Inst., Cambridge, USA). The sample was attached to an aluminum metal sheet and then treated with gold vapor. The crystallinities were checked by X-ray powder diffraction using CuKα radiation. The surface area was obtained by using a dynamic method for the determination of the nitrogen physisorption capacity at 77 K [33]. Metal contents of the samples were determined by complexometric methods [34].

2 was purified by recrystallization from H2O/ETOH (3:1) with activated charcoal. Further purification was accomplished by sublimation. 3 was synthesized by introduction of ammonia into a solution of 2 in methanol [35]. The employed supports γ-Al2O3 (Art. Nr. 39800, surface area 127 m²/g, grain size 5—20 μm) and SiO2 (Art. Nr. 39806, surface area 283 m²/g, grain size 5—20 μm, pore diameter 6 nm, pH 6.5—7) were obtained from Riedel de Haen, FRG.

Preparation of the metal-charged supports

In all reactions 7.6 wt% CoCl₂ and 7.9 wt% CuCl₂ related to the weight of the support were used. This corresponds to 3.3 wt% resp. 3.6 wt% metal content on the support at total absorption. The amount of metal salt taken up by the support was determined by complexometric measurements of the metal ions remaining in the filtrates of the reaction mixtures [34].

a) Method A

1 g γ-Al₂O₃ was added to a solution of 5.85×10⁻¹⁴ mol metal salt in 20 ml acetone. The suspension was refluxed for 2 h. After cooling the mixture was filtered and the amount of Co(II) or Cu(II) determined in the filtrate. The residue was washed twice with 100 ml water and dried as described in Method A.

b) Method B

1 g SiO₂ was given to a solution of 5.85×10⁻¹⁴ mol metal salt in 20 ml water. Under moderate stirring the mixture was saturated with NH₃. After further stirring (30 min) it was filtered and the amount of free metal salt determined in the filtrate. The residue was washed twice with 100 ml water and dried as described in Method A.

General instructions for the synthesis of phthalocyanine charged supports

0.5 g metal charged support is mixed with 2 or 3. The molar ratio 2: metal on the support is 4:1. The mixture is filled into a glass ampoule (Duran 100x12 mm), which is then evacuated and flushed with dry nitrogen three times. The ampoule is sealed at 10 Pa and heated at 250 °C for 4 h. When opening the cold ampoule NH₃ can be detected if 3 is used. The dark blue product is treated with acetone in a Soxhlet extractor for 4 h. Phthalimide can be detected (IR, MS) in the filtrate. The residue is dried 1 h at 50 °C and normal pressure, then stirred 24 h with 50 ml 1 N HNO₃, filtered, and washed with water to neutrality. It was then dried 24 h at 50 °C over P₂O₅ in vacuo.

Determination of the amount of 1 on the support: 0.01 g of the sample was stirred in 100 ml conc. H₂SO₄. The absorbance of 1 is determined and this value compared with the ε values of 1:1 (Mt = Cu) at λ = 791, ε = 2.4 × 10⁻⁵; 1 (Mt = Co) at λ = 784, ε = 1.7 × 10⁻⁵.

The authors wish to thank Dr. P. J. Plath (Universität Bremen) for valuable discussions and H. Prüfer for the VIS-transmission measurements.