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Metal Phthalocyanines Used as Catalysts in Gas Phase Reactions

X. Decomposition and Reduction of NO Catalyzed by Crystalline Monomeric β-Metal Phthalocyanines of the First Transition Period

FRIEDRICH STEINBACH AND HANS-JOACHIM JOSWIG

Institut für Physikalische Chemie der Universität Hamburg, Laufgraben 24,
D-2000 Hamburg 13, Germany

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Monomeric β-metal phthalocyanines (MPc's) of the first transition row (Mn to Cu) have been shown to be good catalysts with respect to both reduction of NO in H_2 flow and decomposition of NO either in H_2 or in He flow in the temperature range of 180 to 425°C. Depending on the central metal atom, in H_2 flow either reduction of NO to N_2 and H_2O (CuPc, NiPc above a certain concentration of NO) or to NH_3 and H_2O (CoPc, NiPc below a certain concentration of NO) is observed. Decomposition (MnPc, FePc) leads to N_2 and O_2, the latter apparently strongly adsorbed by MPc's. From the apparent heats of activation as well as from the degrees of conversion normalized to constant weight of the catalyst, the sequence of catalytic activity with respect to reduction of NO is found to be NiPc > CoPc ≫ CuPc > MnPc > FePc. In contrast, catalytic activity with respect to decomposition of NO shows the following sequence: MnPc > FePc ≫ CuPc > NiPc > CoPc. H_2Pc is found to be inactive.

INTRODUCTION

Solid metal phthalocyanines (MPc's) of 3*d* metals (Mn to Cu) are known to catalyze various reactions of gaseous reactants (*1–9*). The overlap of orbitals of the phthalocyanine system and the central ion allows electron transfer from the metal to the π system of the Pc ligand and vice versa. This enables oxidation and reduction of the complex, addition of axial ligands, and both adsorption on the central ion and catalytic interaction with it.

Reactions of NO according to Eqs. (1) to (5) have been investigated using various materials as catalysts, in particular the noble metals and metal oxides (*10–16*).

$$2NO \rightarrow N_2 + O_2 \qquad (1)$$

$$2NO \rightarrow N_2O + \tfrac{1}{2}O_2 \qquad (2)$$

$$2NO + H_2 \rightarrow N_2 + H_2O \qquad (3)$$

$$NO + \tfrac{5}{2}H_2 \rightarrow NH_3 + H_2O \qquad (4)$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \qquad (5)$$

Catalytic reactions of NO in multicomponent gas mixtures have been reported (*17, 18*).

Recently, the use as catalysts of complexed metal ions, in particular MPc's, has been reported (*7–9, 19–21*). On the other hand, NO is well known to be a stable ligand in a great variety of metal complexes (*22, 23*). The aim of the present study is a systematic investigation of the catalytic activity of MPc's of the first transition row with respect to the selectivity of the reaction pathway. The MPc's differ in population and energy of the metal MOs, whereas the orbital patterns are similar

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and the ligand field order is constant (*24–27*). Therefore, different ways of orbital interaction between central ion and NO are to be expected, which should lead to different activity and selectivity of the different MPc's.

EXPERIMENTAL

A gas chromatographic pulse technique was used to keep to a minimum changes of the catalysts due to long-living adsorption or formation of adduct compounds. Gas chromatographic analysis was carried out with a Perkin–Elmer F 6 gas chromatograph (thermistor detector).

H_2 (Linde, 99.999%) was used as carrier gas in the study of reactions (3) and (4), and He (Linde 99.995%) in the study of reactions (1), (2), and (5); the carrier gas flow was always 30 ml/min. NO pulses (Gerling–Holz, 99.8%) were inserted every 10 min by using a gas inlet valve. Separation of N_2/NO/CO was effected by use of a column of 5A Molecular Sieve (Perkin–Elmer, 2 m long; 6 mm in diameter; temperature, 114°C); separation and identification of NH_3 and H_2O were achieved with Marlophene as column material (Perkin–Elmer, 40 cm long; 6 mm in diameter; temperature, 123°C). In this case, the carrier gas flow had to be 60 ml/min, i.e., the reaction time was shorter. The lower limit of detection of products was about 1×10^{-8} mol.

MPc's and H_2Pc (BASF) were purified by a twofold sublimation in high vacuum (5×10^{-5} Torr) at about 450°C. After 12 hr of heating at 290°C in H_2 or He flow in a Duran reaction tube (*3*) the stable β-polymorph was formed, the crystal modification being checked by ir spectroscopy (Beckman IR 20 A). The BET surface area was determined gravimetrically by using a Sartorius electrobalance to be in the range of 1 to 15 m^2/g (see Table 1). To increase the surface in experiments in He flow, sublimed MPc's were milled for 20 min in a double-ball mill. The degree of

TABLE 1

Reaction of NO Pulses in Flow of H_2 or He

MPc	MnPc				FePc			CoPc				NiPc			CuPc			
Flow	H_2	H_2	He	He	H_2	H_2	He	H_2	H_2	H_2	He	H_2	H_2	He	H_2	H_2	H_2	He
BET surface area (m^2/g)	2,7	2,7	2,7	2,7	3,6	3,6	13,7	1,6	1,6	1,6	4,9	1,5	1,5	5,7	1,2	1,2	1,2	5,0
Weight (mg)	125	125	125	125	250	250	500	250	250	250	500	180	250	500	250	250	250	500
T_{entr} (°C)	200		200		—	—	200	180	180	180	400		130[a]	300	220	220	220	300
T_{max} (°C)	400	395	380	388	285	281	299	407	407	407	415	390	367	380	425	425	425	402
$NO \cdot 10^5$ mol	1,3	3,1	1,7	2,6	1,3	2,7	3,4	1,4	1,9	2,6	3,5	3,1	1,4	3,0	0,7	1,0	1,8	3,5
$N_2 \cdot 10^7$ mol	4,4	6,2	2,1	2,6	—	—	3,0	4,6	5,1	6,7	0,2	29,7[a,b]		0,4	0,9	1,3	1,8	0,8
$NH_3 \cdot 10^7$ mol	—	—			—	—				9,0		—	46,5[a]		—	—	—	
ΔNO (%)	6,8	4,0	2,5	2,1	—	—	1,7	6,5[c]	5,4[c]	8,7	0,1	19,3	32,2	0,24	2,7	2,6	2,0	0,44

[a] Break-off of measurements.

[b] No analysis for N_2.

[c] No analysis for NH_3.

conversion for the different products was determined as a function of reaction temperature starting from the highest and going to lower temperatures. The reason for this procedure is discussed together with the results.

RESULTS

Degree of Conversion in Hydrogenation and Decomposition

Three reactions proceeding according to Eqs. (1), (3), and (4) were studied. In the presence of H_2 (carrier gas) a distinction of reaction (1) from reaction (3) was possible only for rather high degrees of conversion, since the detection of H_2O is not very sensitive. This is due to adsorption of H_2O in the stainless steel tubes of the flow system. Therefore, decomposition of NO was studied separately using He as carrier gas; moreover, the amount of catalyst was doubled in these experiments (see Table 1). Formation of N_2O according to Eq. (2) was observed as a side reaction accounting for 2 to 7% of the total conversion of NO. The results are summarized in Table 1.

MnPc

The degree of conversion to N_2 in H_2 flow as a function of reaction temperature is shown in Fig. 1. Starting with measurements at the uppermost temperature, consecutive pulses showed an initial isothermal decrease of N_2 formation, but this reached a fairly constant lower limit after about five consecutive pulses. Therefore, isothermal decrease of degree of conversion during subsequent reaction at lower temperatures could be neglected. Formation of NH_3 was not observed; H_2O was detected only at reaction temperatures above 380°C. Hence, it is concluded that the main reaction pathway follows Eq. (1) even though O_2 was not detected. At temperatures around 300°C oxygen is adsorbed strongly by MnPc (*28*). The isothermal decrease of N_2 formation also leads to the conclusion that there is oxygen adsorption: decomposition of NO is inhibited by the adsorbed oxygen generated during previous pulses. Inhibition of NO decomposition by oxygen has been observed previously (*16*).

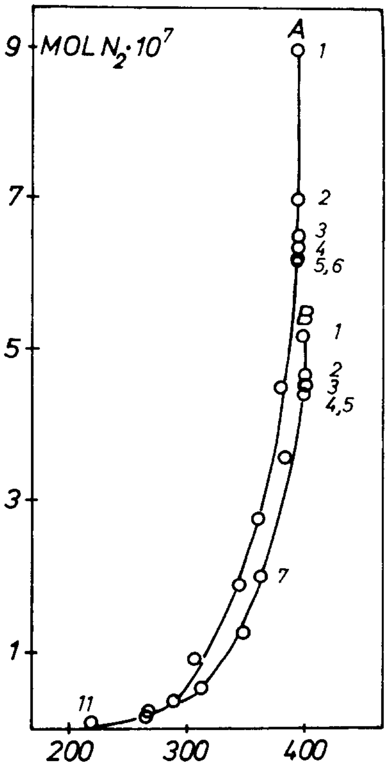

FIG. 1. Formation of N_2 in H_2 flow on MnPc. (A) $3.12 \cdot 10^{-5}$ mol NO per pulse; (B) $1.29 \cdot 10^{-5}$ mol NO per pulse. Numerals indicate the pulse number.

In He flow, decomposition of NO was observed to follow quite similar patterns to those in the presence of H_2. In consecutive pulses an isothermal decrease of N_2 formation was observed; at 380°C the steady state degree of conversion amounted to 75% of the value observed in the first pulse. In the entire temperature range, formation of N_2 was about one half of the conversion observed in the presence of H_2; apparently, adsorbed oxygen is partly removed by reaction with H_2.

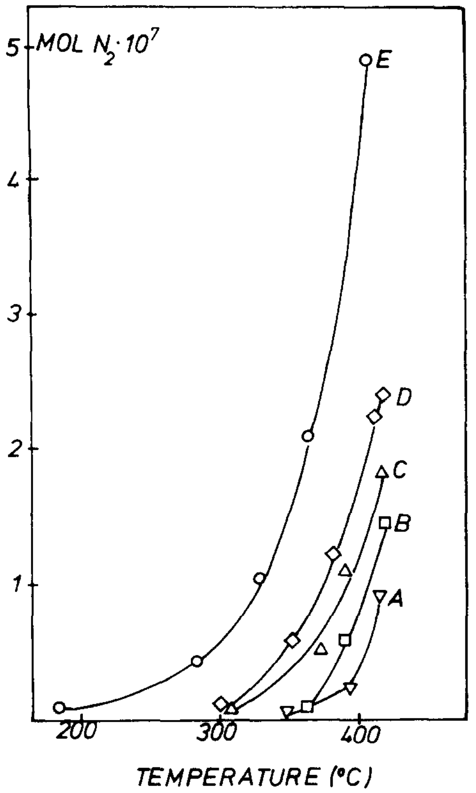

FIG. 2. Formation of N_2 in H_2 flow on CoPc. Five consecutive measurements (A–E): (A) 28.25 $\cdot 10^{-6}$ mol NO per pulse, (B) 19.6$\cdot 10^{-6}$ mol NO per pulse, (C) 16.5$\cdot 10^{-6}$ mol NO per pulse, (D) 9.3$\cdot 10^{-6}$ mol NO per pulse, and (E) after 40 hr of heat treatment at 290°C in H_2 flow, 9.3$\cdot 10^{-6}$ mol NO per pulse.

FePc

No significant differences were detected in the formation of N_2 with respect to the presence of H_2 or He. Decomposition of NO is inhibited, as is seen from the isothermal decrease of the degree of conversion in subsequent pulses: 7.1 $\times 10^{-7}$ mol N_2 in the first pulse, falling to a steady state value of 2.95 $\times 10^{-7}$ mol N_2 in the seventh pulse at 300°C in He flow. Besides NO decomposition, a reaction of NO with FePc forming an FePc–NO adduct (*29*) was observed. At temperatures above 205°C the adduct begins to be decomposed, hence, with increasing temperature increasing amounts of NO pass the catalyst without being withheld by adduct formation. At 205°C 70% of NO per pulse were observed to form the FePc–NO adduct.

CoPc

The degree of conversion of NO to N_2 in H_2 flow as a function of reaction temperature is shown in Fig. 2 for different amounts of NO per pulse. A marked increase of catalytic activity during sequential experiments was observed. Catalytic activity finally remained constant as given by curve E even after repeated periods of further catalytic measurements and heat treatment. Formation of NH_3 and H_2O was measured using pulses containing 2.66 $\times 10^{-5}$ mol NO. Formation of H_2O and N_2 was observed to start simultaneously shortly below 200°C, whereas formation of NH_3 was observed to start at 300°C. In He flow, only at 415°C was N_2 observed and then in an amount scarcely above the detection limit. Consequently, hydrogenations of NO according to Eqs. (3) and (4) are the main reaction pathways with CoPc, whereas decomposition of NO has no significance.

NiPc

A positive induction period was also observed with NiPc, and it was much more pronounced than with CoPc. Figure 3 shows sequences of isothermal increases of N_2 formation as a function of the age of the catalyst (pulse number). The initial degree of conversion was very small (1.8 $\times 10^{-8}$ mol N_2) but was followed by an increase of activity during use of the catalyst. The increase of activity was still continuing even after 20 pulses. By keeping the catalyst under H_2 flow, regardless of the temperature, a substantial decrease of activity occurred. A corresponding pattern was found with respect to formation of H_2O, whereas no formation of NH_3 was detected up to 405°C; this confirms that only reaction (3) was being observed.

However, when pulses of 1.44×10^{-5} mol NO instead of 3.1×10^{-5} mol NO were used, simultaneous formation of H_2O and NH_3 was observed with a steady increase of the degree of conversion from pulse to pulse, as was found for the formation of N_2 and H_2O. When measurements were interrupted, the degree of conversion had reached a value of 32% (see Table 1). In an immediately subsequent experiment, again with 3.1×10^{-5} mol NO per pulse, formation of NH_3 was not detectable, i.e., the reaction pathway is dependent on the amount of reactant per pulse. The same results were found in analogous experiments performed subsequently at 325°C; owing to continuous increase of activity, the degree of conversion to NH_3 was observed to be about 27%, though temperature was 40°C lower.

CuPc

Hydrogenation of NO was observed to occur according to Eq. (3) only, the beginning of formation of N_2 and H_2O both being detected at 200°C. No influence of heat treatment on activity was observed. Decomposition of NO according to Eq. (1), as studied separately in He flow, was observed to occur with degrees of conversion of some 0.1%, 1.1×10^{-7} mol N_2 in the first pulse decreasing to a steady state value of 0.8×10^{-7} mol.

H_2Pc

H_2Pc was found to be totally inactive.

Comparison of Activities

A comparison of the degrees of conversion normalized to constant reaction temperature (400°C) and to constant weight of catalyst (250 mg in H_2 flow, 500 mg in He flow) is given in Table 2. Surface areas, though different in runs in H_2 and runs in He due to milling in the latter case, were constant within a factor of three for the different MPc's. It will be seen that the ranking of the activities of the MPc's will not become uncertain because of differences in BET surface areas.

Keeping in mind the induction period shown by CoPc and NiPc and considering

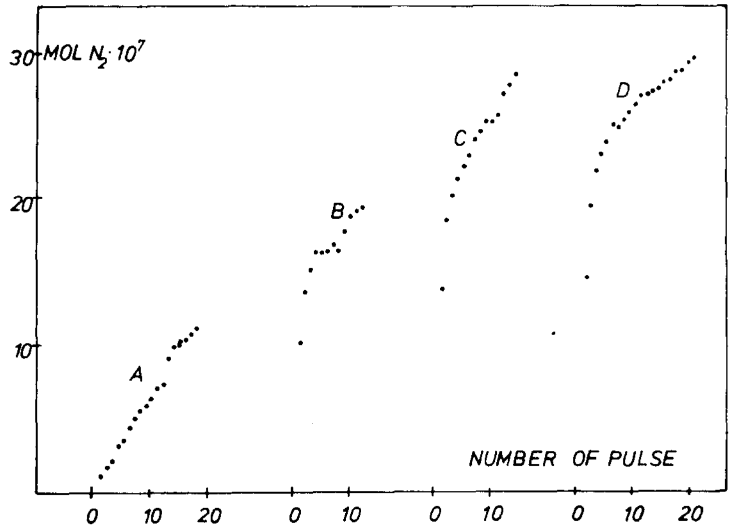

FIG. 3. Formation of N_2 in H_2 flow on NiPc in consecutive pulses of $3 \cdot 10^{-5}$ mol NO. (A) 385°C, (B) 395°C, (C) 388°C, and (D) 380°C.

TABLE 2

Degree of Conversion (10^7 mol NO) Normalized to 400°C with Carrier Gas H_2 (Normalized to 250 mg of MPc) and with Carrier Gas He (Normalized to 500 mg of MPc)

MPc	MnPc	FePc	CoPc	NiPc	CuPc
H_2	26.0	—	22.4	82.5	3.6
He	21.0	8.9[a]	0.4	0.9	1.6

[a] Extrapolated to 400°C by use of the Arrhenius plot. No measurement above 300°C owing to instability of FePc.

the fact that the high degree of conversion listed for MnPc is due to decomposition of NO rather than to hydrogenation, the following sequence of catalytic activity with respect to hydrogenation of NO is observed: NiPc > CoPc ≫ CuPc > MnPc > FePc. The BET surface areas of NiPc, CoPc, and CuPc do not differ to such an extent to alter that sequence of catalytic activity. Since formation of H_2O was detected even with the low degree of conversion on CuPc but was not detected with the high degree of conversion on MnPc (see above), it can be concluded that the activity with respect to hydrogenation is higher with CuPc than with MnPc; even so, there might be a very small amount of hydrogenation hidden among the decomposition, and therefore the completely inactive FePc has been placed at the end of the sequence. In contrast, the catalytic activity with respect to the decomposition of NO shows the following sequence: MnPc > FePc ≫ CuPc > NiPc > CoPc. The first position of MnPc is confirmed, even taking into account the rather low BET surface area, the second position of FePc is unchanged by reducing the degree of conversion in the ratio of the BET surface areas. In conclusion, it is seen that those MPc's catalyzing well the decomposition of NO are poor catalysts with respect to hydrogenation of NO and vice versa.

Activation Energy in Hydrogenation and Decomposition

Degrees of conversion being rather low and the reaction order being close to zero, with the exception of CuPc, Arrhenius plots can be evaluated from the temperature dependence of the degree of conversion by using the zero-order relation between the degree of conversion and the rate constant. Since the reaction time is constant in pulse experiments, the logarithm of the degree of conversion can be plotted against reciprocal temperature; the slope of the straight line furnishes the activation energy. The results obtained by evaluation of the products of the different reaction pathways are given in Table 3. The degrees of conversion used in this procedure were measured—after the initial period of deactivation (e.g., MnPc) or activation (e.g., NiPc) at the highest temperature ($T_{\max}$ in Table 1) had been ended—by subsequent stepwise decrease of catalyst temperature until the degree of conversion had reached zero.

As is seen in Table 3, the activation energies of decomposition of NO were found to have higher values than those of hydrogenation of NO. For MnPc the activation energy of decomposition of NO in H_2 flow was found to be lower than in He flow, probably because of the decrease of the inhibiting influence of oxygen in the reducing gas. The value of 48.5 kJ/mol found for the formation of H_2O on CoPc is an average of 65 and 36, the activation energies of formation of the corresponding stoichiometric compounds N_2 and NH_3. The good agreement of both values found for the reaction on CuPc, computed from the separately measured formations of N_2 and H_2O, again shows that hydrogenation is the main reaction pathway with this catalyst. The value given for the formation of H_2O on NiPc is not as exact as the values found for other MPc's since the activation of NiPc was still increasing during measurement. Formation of NH_3 not being detected at the amount of NO used, the value given represents the activation energy of Reaction (3). Even with the limits of error being rather large for this value, it is seen that activation energy of Reaction (3) is significantly lower for NiPc than for CoPc.

Comparing the different MPc's with respect to activation energies and degrees of conversion, it is seen that high catalytic activity (high degree of conversion at a given temperature) is accompanied by low activation energy of the respective reaction, and that low catalytic activity (low degree of conversion at a given temperature) is connected with high activation energy. Hence, the conclusions based on comparison of degrees of conversion are confirmed by the energetics of the interaction between catalyst and reactant.

Reaction of NO in the presence of CO

Thermodynamics show that reduction of NO by CO according to Eq. (5) is possible. This reaction was studied in He flow with FePc, CoPc, and CuPc, chosen because of their different selectivities, by passing pulses of CO/NO mixtures over the catalysts, starting with pulses of pure NO (3.5×10^{-5} mol) and increasing subsequently the percentage of CO until only 5 mole% of NO was present in a single pulse. In all mixtures, with all catalysts, degrees of conversion were significantly lower than those observed for pulses of pure NO. This might be because, owing to the electronic similarity of NO and CO, they compete for the active sites formed by the metal ions.

DISCUSSION

Two qualitative approaches, based on MO diagrams of MPc's and making use of either molecular orbital or crystal field theory, have been shown to be of great utility in understanding the catalytic activity of complexed metal ions in MPc's in various reactions including decomposition and hydrogenation of NO (*8*).

In the following discussion the activity and selectivity of MPc's will be compared with results reported for metal oxide catalysts in order to show that the catalytic activity of MPc's is not due to the catalytic activity of traces of oxides formed during the reaction in the presence of NO and O_2. In hydrogenation of NO with oxides of Cu, Ni, or Fe as catalysts, conversion to NH_3 *and* N_2 is observed (*15*). The dependence of NH_3 formation on NO inlet is found to be similar with oxides and with NiPc. However, at low NO concentrations, comparison of the 27% degree of conversion to NH_3 at 325°C observed with NiPc with the threshold temperature of NH_3 formation of ~400°C reported with Ni oxide shows that the catalytic activity of NiPc is higher than that of Ni oxide,

TABLE 3

Apparent Heat of Activation (kJ/mol) for Reaction Products of Different Reaction Pathways with Carrier Gas H_2 and Carrier Gas He

MPc	MnPc		FePc		CoPc		NiPc		CuPc	
Carrier gas Product	H_2	He	H_2	He	H_2	He	H_2	He	H_2	He
N_2	75.5	88	—	96	63	—	—[a]	—	50	—
NH_3	—		—		35.5		—[a]		—	
H_2O	—		—		48		21–29		50	

[a] No experiments.

even though larger BET surface areas and catalyst charges were used in the experiments with Ni oxide.

In contrast to the formation of NH_3 observed with Cu oxide (*10, 15*), no formation of NH_3 was observed with CuPc. Comparison of the catalytic activity of metal oxides with respect to hydrogenation of NO leads to the sequence Cu oxide $\gg$ Ni oxide $>$ Fe oxide. This sequence is different from the activity order of MPc's: NiPc $\gg$ CuPc $>$ FePc. Hence, the catalytic activity of MPc's is not caused by traces of oxides formed during the reaction.

In another study of hydrogenation of NO on 3*d* MPc's a somewhat different sequence in catalytic activity has been found. The most striking difference lies in the reported high activity of CuPc with respect to formation of NH_3, which has not been observed in the present study. A reason for this might be that MPc's were not purified before use as catalyst (*7*).

Considering decomposition of NO, the sequence of catalytic activity of 3*d* metal oxides is Co oxide $>$ Cu oxide $>$ Ni oxide $>$ Fe oxide (*13, 16*), distinctly different from the sequence found for the MPc's. The most striking result of the present study is to be seen in the high catalytic activity of MnPc. This is to be compared with the inactivity of MnO_2 in the temperature region up to 300°C (*13*) or well above 350°C (*14*). Indeed, on MnPc the activity is decreased by inhibition from the nonstationary degree of conversion in the first pulse to a lower degree of conversion in subsequent pulses. A similar though more pronounced decrease in activity with respect to NO decomposition is observed with Co_3O_4, the most active among 3*d* oxides (*16*).

CONCLUSION

It is seen that, depending on the central metal atom, MPc's are good catalysts either in decomposition or in hydrogenation of NO, whereas metal oxides catalyze both reactions equally. Furthermore, it is seen that (i) the catalytic activity of MPc's is not due to traces of oxides formed during the reaction in the presence of NO and O_2, and (ii) the ligand field of the phthalocyanine exerts a strong influence on the catalytic activity of the central ions. This justifies a self-consistent theoretical interpretation of the catalytic interaction of MPc's, as treated elsewhere (*8*).

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