

layer and (2) the lower, "water-transparent" layer. Distillation yielded the following fractions:

Upper oily layer	n_D^{20}	Lower water-transparent layer	n_D^{20}
I 55–110°, 20 cm ³	1.4142	I 55–75°, 35 cm ³	1.3745
II 110–195°, 15 cm ³	1.4702	II 75–95°, 40 cm ³	1.3690
III 195–205°, 12 cm ³	1.5040	III 95–98°, 92 cm ³	1.3365
IV residue in flask	1.5500	IV no residue.	

During the distillation of the upper, oily portion of the catalytic reaction mixture the increase of temperature is accompanied by an increase of the refractive index, while the increase of the distillation temperature of the lower, water-transparent layer results in a fall of the refractive index. More detailed analysis of the upper, oily layer obtained on the KLB catalyst, gave the following results: $d_4^{20} = 0.8558$, iodine number 73.5 (content of unsaturated compounds 44%), capacity for sulphonation 100%, refractive index 1.5030. The upper, oily layer boils over a wide temperature range and the lower, water-transparent layer in the range 50–100°. The initial boiling point of this layer, formed as a result of the dehydration and extensive conversion of the initial product suggests that it contains, apart from the undecomposed alcohol, ethyl ether and lower aldehydes and ketones, which is confirmed by the differences in the refractive indices of the individual fractions and qualitative tests for the functional groups.

It is interesting to compare the data on the conversion of ethanol and on the cracking of cumene over positive, negative, and inert natural catalysts. The experiments were carried out at catalyst: starting materials ratios of 2:1 over a period of 30 min at 400–500° (Table 5).

The studies made constitute fresh proof that the formation of petroleum, gas, bitumen, etc., which exhibit an extremely wide variety of properties, depends directly on the composition, structure, and genesis of the surrounding medium, i.e. on the presence of natural sorbents, catalysts, and inert substances in the surrounding earth. The mineral specimens investigated can be divided into three groups with respect to their catalytic properties (Table 5): (1) catalysts with positive action; (2) catalysts with negative action; (3) inert catalysts. The coexistence of these groups in nature is a necessary condition for the formation of petroleum, gas, etc. deposits. Thus the role and importance of natural sorbents, catalysts, and inert substances in the formation of deposits of petroleum, gas, bitumen, etc. within the earth is very great and this factor can be used in prospecting.

SUMMARY

1. The catalytic properties of the natural minerals investigated depend on their composition, structure, and genesis.
2. In some chemical processes the natural minerals are not inferior and sometimes actually superior to the catalytic properties of many recognised natural and synthetic catalysts.
3. Natural materials such as clays, decomposed tuffs, bauxites, garnierite, pyrolusite, and the catalysts BSM, BSMA, KLB, KZHR, KGSM, and other mixtures of this type can serve, after thorough selection and tests, as catalysts for certain types of processing petrochemical and oil products.

4. The formation of petroleum and gas deposits, which have a very wide variety of properties, is directly related to the presence of natural sorbents, catalysts, and inert substances in the earth.

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CATALYTIC PROPERTIES OF SYSTEMS CONSISTING OF POWDERED METALS AND PHTHALOCYANINES

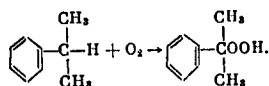
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The phthalocyanine complexes of various metals are of special interest as catalysts of oxidative and reductive processes¹ in connection with the similarity of their structure to that of biocatalysts as widespread as haemoglobin, chlorophyll (porphyrins), and others. Recently this interest increased because, as shown for the first time by Vartanyan

and subsequently confirmed by a number of other workers, the phthalocyanines exhibit semiconductor properties². This permitted a new approach to the study of the catalytic properties of these compounds³.

The present paper deals with systems consisting of powdered metals covered by a thin film of the phthalocyanine complex of the same metal. The electrical and physical properties of such systems have been investigated already⁴ for nickel, cobalt, iron, and copper. The systems were prepared by allowing phthalonitrile vapour to act upon the metal powder. The reaction with the surface of the metal yields a film of the phthalocyanine complex of the metal and the system acquires semiconductor properties. Experiments showed that, depending on the temperature of the formation of these systems (250–400°), it is possible to vary the thickness of the surface metal phthalocyanine film and the electrical conductivity, the activation energy for conductivity, and other properties associated with this thickness[†]. The systems described may be regarded as analogues of the model proposed by Roginskii⁵ for the case where a metal is covered by a "sheath" of oxide film exhibiting semiconductor properties.

The principal reaction chosen for investigation is the oxidation of cumene (isopropylbenzene) with formation of hydroperoxide:



This process was studied earlier on copper phthalocyanine as catalyst³ and on the phthalocyanine complexes of other metals⁶. In a previous study³ an attempt was made to relate the differences in the catalytic activities of the monomer and polymer of copper phthalocyanine to their electrical and physical properties.

EXPERIMENTAL

The apparatus consisted of a reactor with a jacket which was vigorously shaken (about 500 agitations per minute) in a precision thermostat. The experiments were made at about 100°. The cumene used was thoroughly purified; after washing with water it was dried over metallic sodium and vacuum-distilled at 50–70°. The homogeneous oxidation of the cumene was absent or slight and was always allowed for by blank experiments. A study was made of the catalytic properties of systems consisting of a metal covered by a film of its phthalocyanine complex: iron, cobalt, copper, and nickel were used. For comparison, experiments were made on the phthalocyanine complexes of the metals alone and on the powdered metals themselves. The catalytic activity was evaluated in all cases per unit surface area determined from the low-temperature adsorption of krypton or argon. The selectivity of the process was determined by comparing the volume of absorbed oxygen with the amount of cumenyl hydroperoxide formed, which was calculated from analytical data.

[†] The systems used in this work, consisting of metal covered by a film of the metal phthalocyanine, were prepared at 400°. The average thickness of the nickel phthalocyanine film in the system obtained at 400° was 6×10^{-6} cm. In the paper describing the preparation of the system [Zhur. Fiz. Khim., 39, 1760 (1965) (Russ. J. Phys. Chem., 933 (1965))] there is an error: 6×10^{-5} cm is printed instead of 6×10^{-6} cm.

DISCUSSION

The kinetic curves in Fig. 1 show that the pure metals are catalytically inactive. In all cases the specific activity of the systems consisting of the metal covered by a film of its phthalocyanine complex is much greater than that of the metal phthalocyanines not containing free metal.

Despite certain general features, the formation of cumenyl hydroperoxide on systems with different metals exhibits specific features. The activity of the iron phthalocyanine specimen containing free metal is approximately twice as high as that of the specimen without metal. In both cases the process is non-selective, the reaction products containing only 1–3.5% of the hydroperoxide. Control experiments established that the non-selectivity is due to the rapid decomposition of cumenyl hydroperoxide under the action of iron phthalocyanine. The effect of temperature on the reaction rate is in both cases slight. The activation energy calculated approximately from the initial rates at two temperatures (79.6° and 98.6°) is 4.5–5.5 kcal mole⁻¹. The oxygen absorption kinetic curves have initial sections which are nearly linear but subsequently the slope decreases (at this instant the degree of conversion of the cumene is about 40%). The decrease of the rate of absorption of oxygen can probably be explained either by deactivation of the catalyst surface or by a change in the character of the side-reactions, accompanied by absorption of oxygen, which occurred during the oxidation.

The oxidation of cumene on cobalt phthalocyanine containing free metal also occurs at a higher rate than on the phthalocyanine complex without the free metal, although

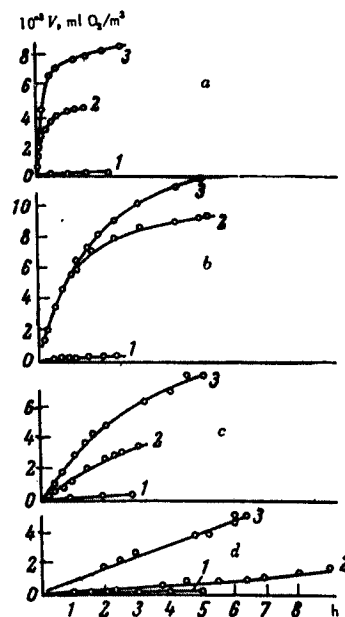


Fig. 1. Kinetic curves for the catalytic oxidation of cumene (V is the amount of oxygen absorbed per m^2 of the catalyst surface area): 1) powdered metal; 2) metal phthalocyanine; 3) metal covered by a film of the metal phthalocyanine; a) iron; b) cobalt; c) copper; d) nickel.

here the difference in specific activity is small. The process on cobalt phthalocyanine is non-selective, as in the case of iron phthalocyanine. The hydroperoxide content in the mixture amounts to only 0.5–3.7%. The reason for the non-selectivity is probably the same as for iron phthalocyanine.

The form of the kinetic curves for systems with copper is the same as for the cases described above. The selectivity of the process is 46.4–65.6%.

The rate of oxidation of cumene over the nickel–nickel phthalocyanine system is much higher than on nickel phthalocyanine alone. In contrast to iron phthalocyanine, the process occurs at a lower rate but with satisfactory selectivity with respect to the formation of cumenyl hydroperoxide (84.7–87.3%). Probably as a result of the low catalytic activity of the nickel system there is little or no breakdown of the hydroperoxide formed. For the same reason, the selectivity of copper phthalocyanine is higher than that of the iron and cobalt compounds but lower than that of the nickel compound. The metallic powders used were thermally reduced in hydrogen and stabilised in benzene. However, since the reaction was carried out at a temperature close to 100° in the presence of oxygen the metals were oxidised and for this reason they lost their catalytic activity in the reaction. This was confirmed by control experiments on copper and nickel oxides. In our experiments the metal phthalocyanines also catalysed the oxidation of cumene to the hydroperoxide, but their activity fell with time, as already described⁶.

Particular interest attaches to the fact that among all the metals investigated the catalytic activity of the metal–metal phthalocyanine systems is higher than that of the metal phthalocyanines alone. To explain this, it is desirable to examine certain properties of the metal–metal phthalocyanine systems.

Using nickel and cobalt as examples, we showed earlier⁴ that in the formation of the phthalocyanine film there is also a marked increase in the area of the metal when the latter reacts with phthalonitrile vapour, the effect being greater the higher the reaction temperature. This affects the thickness and possibly the structure of the phthalocyanine film formed which in turn may influence a number of the electrical and physical properties of the system. For example, in the case of nickel at a reaction temperature of 400° the average thickness of the resulting film is of the order of 10^{-6} cm, while at 250° a film whose thickness is of the order of 10^{-5} cm is formed. Compared with the pure metal phthalocyanine the electrical conductivity (σ , $\Omega^{-1}\text{cm}^{-1}$) is higher in the first case by six powers of ten while the activation energy for conductivity ΔE is reduced from 0.7 to 0.2 eV. In the second case σ is higher by a factor of ten, while ΔE is reduced to 0.5 eV. Both *p*-type and *n*-type conductivity is observed.

Since the metal phthalocyanine film is very closely bound to the metal, when its thickness is smaller than the screening length the electrons from the metal can be injected into the film and thereby increase both its electrical conductivity and its catalytic activity. From this point of view, in order to explain the difference in the catalytic activity of metal–metal phthalocyanine systems with different metals it would be desirable to compare the electron work functions of both the films themselves and the metals serving as substrates⁷. In view of the complexity of the systems, there is a possibility that other factors also operate, in addition to the injection of current carriers.

In the decomposition of hydrogen peroxide† the properties of the metal–metal phthalocyanine systems described above are shown only by the iron–iron phthalocyanine system. Fig.2 shows that the catalytic activity of powdered iron and iron phthalocyanine differ little from one another. On the other hand, the activity of the metal phthalocyanine with the free metal is several times higher. This finding suggests that in the decomposition of hydrogen peroxide, as in the oxidation of cumene, the injection of electrons from the metal into the phthalocyanine film can increase the activity of the latter.

Cobalt phthalocyanine does not catalyse this reaction, while cobalt phthalocyanine containing the metal phase does actively catalyse the decomposition of hydrogen peroxide but its activity is inferior to that of metallic cobalt itself (Fig.2).

The nickel and copper phthalocyanines do not catalyse the decomposition of hydrogen peroxide, which is consistent with the data of other workers¹. The metal–metal phthalocyanine system containing nickel also fails to catalyse this reaction.

The lack of catalytic activity in nickel and copper phthalocyanines and the considerable activity of the systems containing iron and cobalt are features analogous to the finding that in the synthesis of cumenyl hydroperoxide the catalysts with iron and cobalt exhibit only slight selectivity, while the systems with copper and in particular with nickel show high selectivity.

Catalytic reactions in the gas phase were also investigated: the decomposition of formic acid and hydrazine in systems containing nickel phthalocyanine. The kinetics of these reactions were studied under static conditions at temperatures between 100° and 170° and vapour pressures between 0.3 and 0.9 mmHg. The catalytic decomposition of formic acid occurs practically to the extent of 100% on all the specimens investigated, the reaction being $\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$. Up to considerable extents of decomposition the

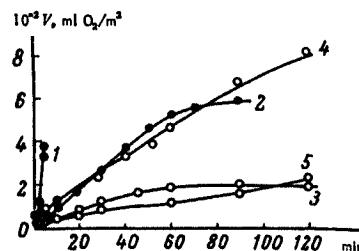
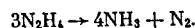


Fig. 2. Kinetic curves for the decomposition of hydrogen peroxide:
1) powdered cobalt; 2) cobalt covered by a film of cobalt phthalocyanine; 3) powdered iron; 4) iron covered by a film of iron phthalocyanine; 5) iron phthalocyanine.

† A 0.43% solution of hydrogen peroxide was used in the experiment. The reaction was carried out at 40°. The catalytic activity was determined from the volume of oxygen evolved per m^2 of the surface area.

reaction kinetics are described by a first-order equation. Hydrazine decomposes to an extent greater than 95% on the specimens studied:



The reaction is of first order up to a conversion of 30–50%, but at higher conversions the process is inhibited.

In the decomposition of formic acid the systems consisting of metal grains covered by a layer of the phthalocyanine are more than ten times more active than the corresponding phthalocyanines themselves, regardless of their conductivity types. This can be accounted for by the same causes as the enhanced activity of such systems in the decomposition of hydrogen peroxide and the oxidation of cumene. The finding of the maximum activity in metallic nickel does not exclude the explanation of the observed relation between the activities by the penetration of formic acid molecules to the metal surface via pores (going right through the film) or cracks in the phthalocyanine film. The latter hypothesis is supported also by the similarity of the activation energies for the decomposition of formic acid over metallic nickel and over the nickel–nickel phthalocyanine system (10.0 and 11.0–12.5 kcal mole⁻¹ respectively). The nickel–nickel phthalocyanine systems both in *n*-type and *p*-type, and nickel phthalocyanine itself do not differ appreciably in activity in the decomposition of hydrazine. A higher activity is shown by metallic nickel in this case too.

The hypotheses concerning the mechanism of the catalytic action of systems comprising a metal phthalocyanine and the metallic phase are so far only qualitative. In order to establish quantitative relations, it is necessary to extend the range of reactions investigated and to obtain more exact data for those which have already been studied.

We should like to thank S. Z. Roginskii, Corresponding Member of the USSR Academy of Sciences, for his interest in this work and discussion of the results.

SUMMARY

1. A study has been made of a number of reactions on catalysts consisting of powdered iron, copper, cobalt, and nickel covered with thin films of the corresponding phthalocyanine complexes. The rates of these reactions have been compared with those of the reactions on the metal powders and on the phthalocyanine complexes alone.
2. The mechanism of the effect of thin phthalocyanine films on the catalytic properties of the metal–metal phthalocyanine systems has been discussed.

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REDUCTION OF SOLID SOLUTIONS OF MAGNESIUM FERRITE AND CHROMITE

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Magnesium ferrochromites are important and promising materials in the technology of hyperhigh frequencies^{1,2}. They enter into the composition of chromium spinelides — the principal phase in chromium ores, used in the manufacture of refractory materials^{3,4}, ferrochromium⁵, and other metallurgical products⁶. The study of the behaviour of these solutions in a reducing atmosphere is important both for technological purposes in metallurgy and for the preparation of magnetic materials with specified properties.

EXPERIMENTAL

The solid solutions $\text{MgFe}_x\text{Cr}_{2-x}\text{O}_4$ were prepared by the following procedure. Mixtures of the oxides MgO , Fe_2O_3 , and Cr_2O_3 , of "analytical reagent" grade, were thoroughly mixed in a ball mill in the presence of added ethanol in amounts corresponding to the compositions $x = 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00$. They were then pelleted and sintered in air at 1200° for 15 h and then kept for 5 h at 1000° and quenched in water to maintain the degree of inversion of the crystal lattice characteristic of the given temperature. The degree of inversion and the lattice constant of magnesium ferrochromites depend on the temperature of synthesis⁷.

X-Ray diffraction analysis of the initial specimens and their reduction products was made by the powder (Debye) method in a camera 57.3 mm in diameter using $K\alpha$ chromium radiation and asymmetric film mounting. V_2O_5 was used as a filter for the radiation. The crystal lattice constant was found by graphical extrapolation⁸.

$\text{MgFe}_{0.75}\text{Cr}_{0.25}\text{O}_4$ was reduced at 900°, 1000°, and 1100°, and the equilibrium conditions were determined in a vacuum apparatus with a circulating $\text{H}_2 + \text{H}_2\text{O}$ mixture in a closed space. The vapour pressure of water was maintained constant during the experiment and equal to the pressure of saturated vapour at 0°, by immersing the trap of the vacuum apparatus in a Dewar vessel with melting ice. After attainment of equilibrium, which was done both from the reduction side and from the oxidation side, the weighed specimen was removed from the furnace by means of an electromagnet and quenched. The water vapour was frozen out by immersing the trap in a Dewar vessel with liquid nitrogen and the equilibrium pressure of hydrogen was measured. The degree of reduction was estimated from