

Low-Temperature Periodical Activation of a Catalyst in Liquid-Phase Oxidation Reactions

L. A. Tavadyan, G. Z. Sedrakyan, and A. K. Tonikyan

Institute of Chemical Physics, National Academy of Sciences of Armenia, Erevan, Armenia

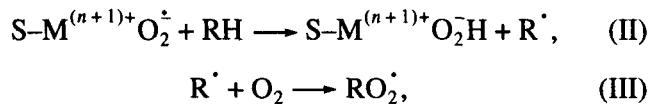
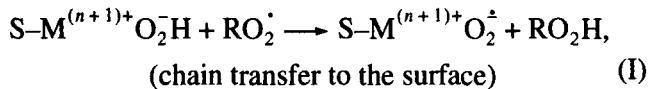
Received November 14, 1998

Abstract—The low-temperature periodical activation of the catalysts based on the metal complexes of nitrogen-containing carbon is observed in the course of isopropylbenzene oxidation. The concentration of the surface hydroperoxide groups responsible for the chain process affects both catalyst deactivation and reactivation. Possible reactions responsible for the deactivation and periodical activation of the catalyst are considered.

INTRODUCTION

Earlier [1–3], we proposed to use the synthesized metal complexes of nitrogen-containing carbon simulating the active centers of redox enzymes. These catalysts showed high activity and selectivity in the liquid-phase oxidation of alkylbenzenes.

In [1, 2], we conjectured that the high selectivity of these catalysts in alkylbenzene transformations into corresponding alkylhydroperoxides should largely be attributed to the chain transfer to the catalyst surface involving the surface oxygen-containing groups



where RH is a hydrocarbon, S is the surface, $RO_2 \cdot$ is the peroxy radical, and $M^{(n+1)+}$ is the surface metal.

The catalyst activity usually decreases in the course of the reaction.

Our goal was (i) to refine the proposed mechanism of the action of the catalysts based on the metal complexes of nitrogen-containing carbon and (ii) to elucidate the reasons for a decrease in their activity and the methods of their recovery.

The catalytic liquid-phase oxidation of isopropylbenzene with molecular oxygen was chosen as a model reaction.

EXPERIMENTAL

Kinetic Measurements

Isopropylbenzene oxidation was conducted in a special constant-temperature glass reactor with a magnetic stirrer [2]. The reaction was kinetics-controlled (the

oxidation rate was independent of the rate of rotation) at a stirring velocity of ≥ 20 rps. The products of isopropylbenzene oxidation were analyzed by gas–liquid chromatography.

The rate of oxygen consumption in the course of the reaction was measured with a pressure gauge setup.

The rate of radical generation in the chain oxidation of isopropylbenzene was measured using the inhibitor method with 2,6-di-*tert*-butyl-4-methylphenol (ionol) [4]. As found by gas-liquid chromatography, ionol (in the concentrations used) was not adsorbed on the surface of metal complexes of nitrogen-containing carbon. The correctness of this method of measurement of the radical generation rate was supported by a linear change in the induction period with the ionol concentration, which ranged from 1×10^{-4} to 5×10^{-4} mol/l.

Study of the Catalyst Surface

Hydroperoxide groups on the surface of the metal complexes of nitrogen-containing carbon were detected by iodometry upon its preliminary washing with the solvents (isopropylbenzene, acetone, benzene, and chloroform).

X-ray photoelectron spectra of the heterogeneous catalysts were recorded using a VIEE-15 instrument with a magnesium anode ($h\nu = 1253.6$ eV). The C1s (285.0 eV) line was used for calibration. To determine the ratios of the elements on the sample surface, the ratio of the integral intensities of the lines of these elements, corrected with due regard to their atomic sensitivities [5], were measured.

Auger electron spectra of the heterogeneous contacts were recorded with a PHJ-551 instrument (reference vacuum, 2×10^{-10} torr). Auger spectra were excited by the electron beam with an energy of 3 eV and a modulating voltage of 6 V.

Before recording X-ray photoelectron and Auger spectra, the samples were pressed into an aluminum foil.

Materials

The metal complexes of nitrogen-containing carbon were synthesized by the programmed pyrolysis of a mixture of polyacrylonitrile and corresponding metal chloride powders in argon. The final temperature of the thermal treatment was 650°C.

The metal complexes of nitrogen-containing carbon were used as powders with a particle size of 5×10^{-3} – 5×10^{-2} cm. The specific surface areas of the cobalt, magnesium, copper, nickel, zinc, and chromium complexes of nitrogen-containing carbon were 10, 11, 14, 9, 12, and 9 m²/g, respectively, as measured by nitrogen adsorption.

Isopropylbenzene and the solvents were purified using the conventional procedures [6]. Azo-bis(isobutyronitrile) (AIBN) and ionol were repeatedly recrystallized from ethanol and hexane, respectively.

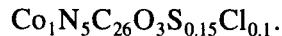
RESULTS AND DISCUSSION

Composition of the Metal Complexes of Nitrogen-Containing Carbon

X-ray phase analysis showed that the metal complexes of nitrogen-containing carbon were amorphous compounds free of the metal chloride traces.

Figure 1 depicts a general Auger spectrum of the cobalt complex of nitrogen-containing carbon. As can be seen, the sample contains substantial amounts of nitrogen (380 eV) and oxygen (510 eV), along with the main element, carbon (with a kinetic energy of 272 eV). The low intensity of the cobalt lines (670, 720, and 780 eV) may be attributed to the bulky units of metallic cobalt in its complex with nitrogen-containing carbon. The admixtures of sulfur (150 eV) and chlorine (180 eV) were also identified on the sample surface.

The composition of the cobalt complex of nitrogen-containing carbon, determined from the Auger spectrum, satisfactorily agrees with the elemental analysis:



The state of the metal in its complex with nitrogen-containing carbon was studied in detail for the copper complexes of nitrogen-containing carbon by X-ray photoelectron spectroscopy. As Fig. 2 shows, the maximum of the main $\text{Cu}2p_{3/2}$ line shifts towards low energies as compared to the maximum of the same line for metallic copper. This indicates a strong effect of the electron density transfer from the support (nitrogen-containing carbon) to the active metallic component. The low intensity of the "shake-up" satellite suggests that the number of the Cu^{2+} atoms in the analysis zone is 20–30% of the overall number of the copper atoms. The rest of copper analyzed is in the form of Cu^{1+} and Cu^0 . The broad main line of the metal complex of nitrogen-containing carbon indicates a substantial scatter in both the unit sizes and the atom positions in these units.

Low-Temperature Periodical Activation of the Catalyst

In the course of the liquid-phase oxidation of isopropylbenzene in the presence of the metal complexes of nitrogen-containing carbon, their catalytic activity was always restored upon a temporal (10–20 min) decrease in the temperature of the reaction mixture to 10–25°C. The selectivity of the formation of isopropylbenzene hydroperoxide also changed. Figure 3 illustrates the low-temperature periodical activation of the cobalt complex of nitrogen-containing carbon. Under certain conditions, a similar pattern was also observed for other catalysts based on the nickel, sodium, and magnesium complexes of nitrogen-containing carbon.

We found earlier that the mechanism of the chain oxidation of alkylbenzenes in the presence of the metal complexes of nitrogen-containing carbon is heterogeneous–homogeneous, and it takes into account a longer chain length in this reaction than in the reaction initiated by AIBN [1–3]. For example, for isopropylbenzene oxidation in the presence of the nickel complex of

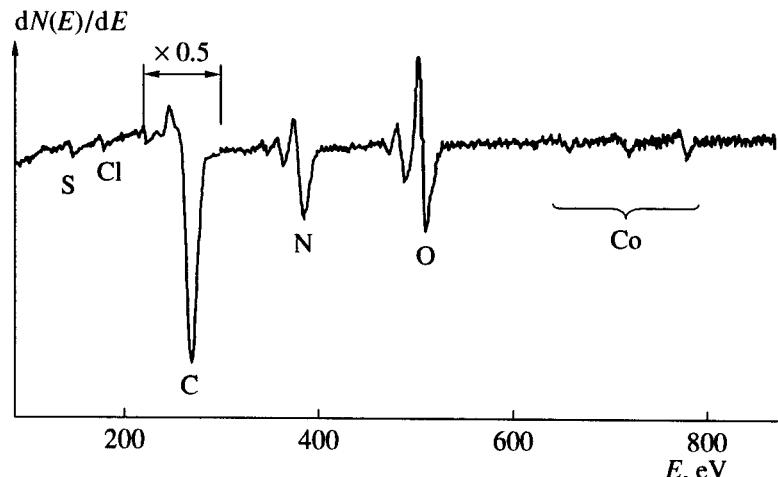


Fig. 1. General Auger spectrum of the cobalt complex of nitrogen-containing carbon.

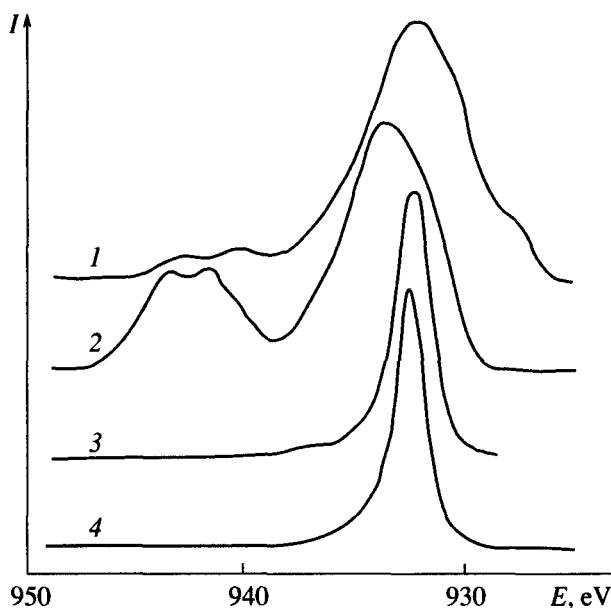


Fig. 2. X-ray photoelectron Cu $2p_{3/2}$ spectrum in (1) the copper complex of nitrogen-containing carbon, (2) CuO, (3) Cu 2 O, and (4) metallic Cu.

nitrogen-containing carbon (10 g/l) at 90°C, the chain length was 105. At the same time, for isopropylbenzene oxidation initiated by AIBN (2.8×10^{-4} mol/l) ensuring the same initiation rate ($W_i = 1.67 \times 10^{-7}$ mol l $^{-1}$ s $^{-1}$), the chain length was only 54. It was of interest to elucidate how the periodic activation of the catalyst affects the parameters of the chain process.

The rate of the long-chain oxidation processes (w_{O_2}) may be expressed as $w_{O_2} = W_i v$, where W_i is the rate of radical generation, and v is the chain length.

The fact that the reaction rate first decreases and then attains its initial value may largely be attributed to the variations in the chain length (see Fig. 3, curves 3 and 4). This is consistent with the hypothesis that the catalyst is mainly involved in the chain propagation.

Mechanism of the Chain Process Involving Metal Complexes of Nitrogen-Containing Carbon

A condition for an increase in the length of the oxidation chain in the presence of the metal complexes of nitrogen-containing carbon is that the rates of steps (I) and (II) must be higher than of the rate-limiting step of chain propagation in the absence of the catalyst



In fact, the analysis of the rates of steps (II) and (IV) suggests that the lower reactivity of the oxygen radical ion as compared to that of the peroxy radical (by a factor of $\sim 10^2$) [7–9] should be compensated by the higher O_2^\cdot concentration. One could potentially create such

conditions for the catalytic process when the concentration of the oxygen radical ions in the reaction system is higher than the concentration of peroxy radicals (according to our estimates, $[RO_2^\cdot] \approx 10^{-7}$ – 10^{-8} mol/l) by a factor of 10^3 – 10^4 . Because of their stabilization on the surface of metal complexes of nitrogen-containing carbon in both the gas and liquid [7] phases, the amount of oxygen radical ions in the reaction systems may be comparable to that of the surface adsorption sites. The amount of these sites was estimated as follows:

$$n = \frac{S_0 C_{\text{Cat}} n_0}{N_A} = \frac{10 \times (5-20) \times 10^{19}}{6.02 \times 10^{23}} \approx (0.83-3.32) \times 10^{-3} \text{ mol/l},$$

where S_0 is the specific surface area of the metal complex of nitrogen-containing carbon (m 2 /g), n_0 is the average number of the adsorption sites per 1 m 2 of the surface, C_{Cat} is the catalyst concentration in the reaction system (g/l), and N_A is Avogadro's number.

The concentration of peroxy radicals was calculated by the equation

$$[RO_2^\cdot] = (W_i/k_t)^{1/2},$$

where k_t is the rate constant of the recombination of the isopropylbenzene peroxy radicals.

When comparing the rates of steps (I) and (IV), note that the small amount of the surface hydroperoxide groups (which is lower than that of the hydrocarbon molecules by a factor of at least 10^3) may be compensated by the higher reactivity of the hydroperoxide group as compared to that of the C–H bond in isopropylbenzene. For example, the rate constant for hydrogen-atom abstraction from the C–H bond of isopropylbenzene by the peroxy radical [8] at 90°C is lower than the rate constant for the reactions of the *tert*-butylperoxy radical with alkylhydroperoxides [8, 10] and hydrogen peroxide by a factor of $\sim 10^3$ – 10^4 . Apparently, for the reaction involving the surface hydroperoxide group, this difference is much more pronounced because of the lower O–H bond energy. The lower reactivity of the oxygen radical ion as compared to that of the peroxy radical in the course of hydrogen-atom abstraction indicates the higher reactivity of the O–H bond of the surface hydroperoxide group.

The formation of the oxygen species on the surface of the metal complexes of nitrogen-containing carbon seems quite realistic. The electron-donor effect of the support on the active metal component discussed above stimulates the formation of the oxygen radical ion [11]. This is also confirmed by the calorimetric data [2] suggesting that the heats of oxygen adsorption on the surface of the metal complexes of nitrogen-containing carbon (30–85 kJ/mol) correspond to the heat of formation of the surface oxygen radical ion.

*Analysis of the Amount
of the Surface Hydroperoxide Groups*

The above kinetic analysis suggests that catalyst activation may be attributed to a change in the concentration of the surface hydroperoxide groups. Therefore, we attempted to measure their amount. The iodometric analysis showed that such groups were present in a considerable amount.

The kinetic measurements suggest that the number of the surface hydroperoxide groups changes with the chain length and reaction rate in a symbiotic manner (Fig. 3, curves 5).

The important role of the surface hydroperoxide groups in the course of oxidation was confirmed by the experimental data indicating that the thermal-vacuum treatment of the nickel complex of nitrogen-containing carbon used as a catalyst at 400°C for 1 h resulted in a 3–6-fold decrease in the number of these groups. In this case, the reaction rate at 100°C in the presence of the thermally pretreated catalyst is lower than that in the presence of the catalyst, which did not undergo thermal pretreatment, by the same factor (~4). The reactivation of the catalyst upon its treatment with oxidate at 20°C indicates that catalyst deactivation upon its thermal-vacuum treatment is insensitive to an irreversible change in the structure of the metal complex of nitrogen-containing carbon.

*Reactions Responsible for a Decrease
in the Catalyst Activity*

When oxygen is replaced with air, the catalyst loses its activity at much lower isopropylbenzene conversions (by a factor of ~10) (Fig. 4). This explains why the activity decreases with the consumption of the surface hydroperoxide groups in the reaction with alkyl radicals



In fact, with air in the place of oxygen, the alkyl radical concentration in the reaction mixture is considerably higher, which causes the acceleration of reaction (V). According to our estimates, the $[R \cdot]/[RO_2 \cdot]$ ratio in the reaction mixture in the course of the oxidation with air is higher than that observed during the oxidation with oxygen by a factor of ~5.

To prove the prevailing destructive role of step (V), we performed the following experiment. The catalyst (20 g/l) was stored in isopropylbenzene in argon for 3 h in a reactor equipped with a stirrer and containing

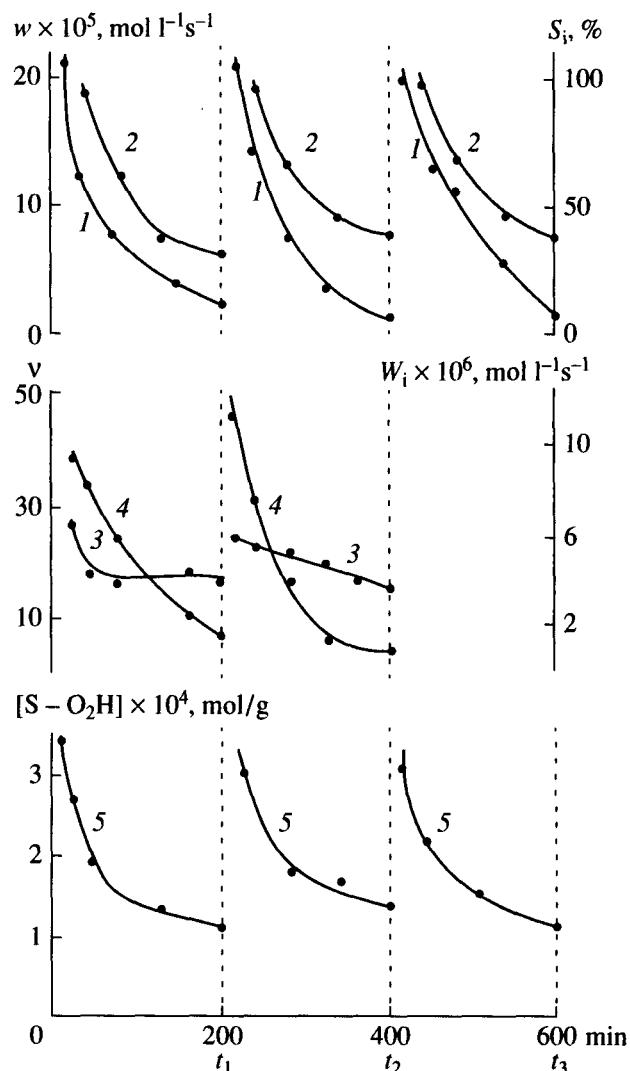
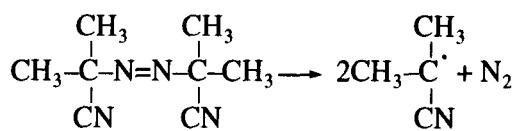


Fig. 3. Changes in the (1) rate, (2) instantaneous selectivity with respect to dimethylphenylhydroperoxide, (3) initiation rate, (4) chain length, and (5) concentrations of the surface hydroperoxide groups in the course of isopropylbenzene oxidation in the presence of the cobalt complex of nitrogen-containing carbon (CCNCC). The reaction temperature was 378 K, $P_{O_2} = 90.7$ kPa, and $[CCNCC] = 15$ g/l. t_1 , t_2 , and t_3 correspond to the cooling of the reaction mixture. The isopropylbenzene conversion in 200 min is 8–10%.

AIBN (2×10^{-2} mol/l) at 85°C. In this case, AIBN acts as a source of alkyl radicals:



The surface of the catalyst thus treated contained a much smaller amount of hydroperoxide $S-O_2H$ groups. At the same time, this catalyst showed low activity in the course of isopropylbenzene oxidation. Nevertheless, we believe that some other reactions

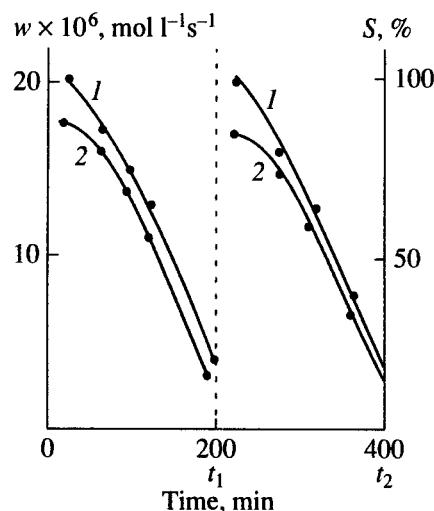


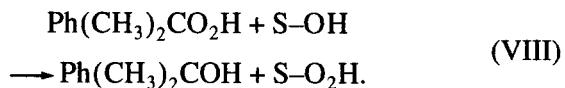
Fig. 4. Changes in the (1) rate and (2) instantaneous selectivity of dimethylphenylhydroperoxide formation in the course of isopropylbenzene oxidation in the presence of the cobalt complex of nitrogen-containing carbon (15 g/l). The reaction temperature was 378 K and $P_{O_2} = 18$ kPa. t_1 and t_2 correspond to the cooling of the reaction mixture.

resulting in a decrease in the $S-O_2^-H$ concentration can also take place, for example,



Reactions Responsible for Catalyst Reactivation

To elucidate the reasons for catalyst reactivation, we carried out the following experiment. The catalyst deactivated in the reaction was treated with cumene, containing acetophenone and dimethylphenylcarbinol, and then with cumene and chlorobenzene solutions of cumene hydroperoxide at 20°C. The catalytic activity of the metal complexes of nitrogen-containing carbon was restored only when the treating liquid contained cumene hydroperoxide. This suggests that catalyst reactivation is related to the formation of the surface hydroperoxide groups involving alkylhydroperoxide



The probability of reactions (V) and (VII), resulting in the decomposition of the $S-O_2^-H$ groups, decreases with temperature. This may be attributed to both a decrease in the ratio of the rate constants of steps (VII) and (VIII) (k_7/k_8) and a noticeable decrease in the alkyl radical concentration.

ACKNOWLEDGMENTS

The work was supported by INTAS-94-0771. We thank Yu.M. Shul'ga for recording the X-ray photoelectron and Auger spectra.

REFERENCES

1. Tavadyan, L.A. and Tonikyan, A.K., *Kinet. Katal.*, 1989, vol. 30, no. 1, p. 128.
2. Tavadyan, L.A. and Tonikyan, A.K., *Arm. Khim. Zh.*, 1987, vol. 40, no. 10, p. 610.
3. Tavadyan, L.A. and Tonikyan, A.K., *Kinet. Katal.*, 1988, vol. 29, no. 1, p. 48.
4. Emanuel', N.M., Denisov, E.T., and Maizus, Z.K., *Tsypnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (Chain Reactions of Liquid-Phase Oxidation of Hydrocarbons), Moscow: Nauka, 1965.
5. Nefedov, S.I., Sergushin, N.P., Band, I.M., *et al.*, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1975, no. 9, p. 72.
6. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972, p. 546.
7. Norikov, Yu.D., Salukvadze, L.V., Rozentuller, B.V., *et al.*, *Kinet. Katal.*, 1981, vol. 22, no. 1, p. 252.
8. Howard, J.A., *Adv. Free Radical Chem.*, 1972, vol. 4, p. 49.
9. Tavadyan, L.A., Mardoyan, B.A., and Musaelyan, M.V., *Int. J. Chem. Kinet.*, 1996, vol. 28, no. 8, p. 555.
10. Tavadyan, L.A., Mardoyan, V.A., and Nalbandyan, A.B., *Arm. Khim. Zh.*, 1986, vol. 39, no. 3, p. 137.
11. Nishinaga, A.N. and Tomita, H., *J. Mol. Catal.*, 1980, vol. 7, no. 2, p. 179.