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Reaction Rate Pulsation during Liquid-Phase Oxidation of Hydrocarbons

A number of detailed experimental studies of catalytic reaction systems in the past years have verified the existence of oscillatory states (*1*, *2*). Self-oscillations have been mainly observed in solid-catalyzed reactions of various types, including oxidation of carbon monoxide (*3*), ammonia (*4*), hydrogen (*5*), and hydrocarbons (*6*, *7*). Several kinetic models involving surface processes have been proposed to describe these oscillating catalytic oxidations. They are based on such assumptions as a strong dependence of the reaction activation energy on surface coverage (*1*, *2*) or surface temperature oscillations (*8*).

Reaction rate oscillation has also been observed in homogeneous systems where surface rate processes are absent (*9*, *10*). The problem is to understand how a uniformly mixed solution at constant temperature and pressure can oscillate. It is well accepted that oscillations can occur in media having nonhomogeneous constituents and gradients of density in the molecular species undergoing diffusion (*11*).

In the present work the oscillatory (pulsation) behaviours during the isothermal oxidation of hydrocarbons in the liquid phase has been studied in a 250-ml titanium reactor. The reactor was magnetically stirred and fitted with an air inlet at the bottom and an outlet through a condenser equipped with separator, pressure and temperature regulator, electric heating mantle, air or water cooler, and an outlet for product samples. The reaction was studied for an impeller speed of 2600 rpm and was not influenced by transport phenomena. The reactor was charged with reactants and its temperature was gradually increased under an applied air pressure and introduction of air whilst stirring over a period of 8–10 min. Outlet gases after passing through the electric gas cooler were continually monitored for oxygen using a Permolyt 2 oxygen analyser (VEB Junkalor Dessau, GDR) and for carbon dioxide using a gas chromatograph with thermocouple detectors. p-Xylene, dodecane, and acetic acid were purified by distillation. *p*-Toluic acid was prepared by cobalt-catalyzed oxidation of *p*-xylene at 130°C with oxygen. The complex $CoBr_2Py_2$ was prepared by the method of King *et al.* (*12*). Metal catalysts and activators were obtained commercially.

Oxidation reactions of hydrocarbons in the liquid phase are characterized by reaction velocities which shortly after the start of oxidation reach a certain "stationary" value. When no fresh hydrocarbon is fed to the reactor this rate gradually decreases. Therefore, at a constant rate of air inlet, the content of oxygen in the off-gas usually rises continually.

In our results, however, we have observed liquid-phase oxidations of hydrocarbons leading to time variations of the oxygen content of the off-gas that indicate a reaction rate pulsation. Such pulsatory states appeared when the mixture of *p*-xylene and *p*-toluic acid was oxidized in the presence of metal catalysts at 205°C, pressure 2.0 MPa, and constant air flow (*13*, *14*). Pulsations were aperiodic in nature and as will be shown later their behaviour depends on the type of the catalyst, solvent, and concentration of components in the reaction system. From Fig. 1 it is evident that the shape of the "oxygen curve" changes in the presence of water as

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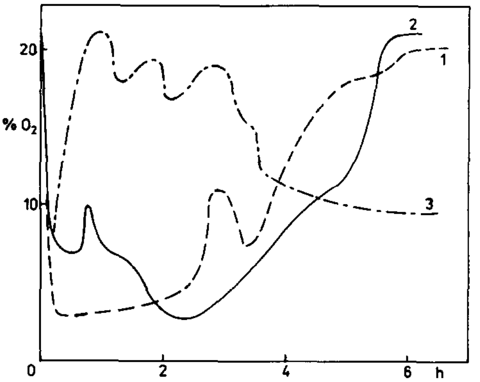

FIG. 1. Effect of water and type of catalyst on pulsation behaviour of oxygen in off-gas during oxidation of a mixture of *p*-xylene (0.44 mol) and *p*-toluic acid (0.147 mol) at 205°C and a pressure of 2.0 MPa catalyzed by 4.3 mmol of $CoBr_2Py_2$ complex. Air flow: 30 dm^3 h^{-1}. (1) In the absence of water; (2) 0.55 mol H_2O; (3) same as (2) but with $CoBr_2 \cdot 6H_2O$ catalyst.

solvent and is different in the case of cobalt dibromide and the complex $CoBr_2Py_2$ as catalyst.

The effect of catalyst composition on pulsation behaviour was studied in more detail using cobalt bromide catalysts activated by nitrogen compounds and with mixed-metal catalysts in the absence of bromine or other activators. For cobalt bromide catalysts the concentration of bromine and certain types of nitrogen compounds, both of which function as activators (*14*), has a strong influence on the pulsation behaviour (Fig. 2). A sharp transition from the high to the low reaction rate repeated several times in the system containing α,α′-bipyridyl or β-picoline activators (Fig. 3) was also observed with other nitrogen compounds, e.g., acridine, hexamethylenediamine, diphenylamine, 2,6-lutidine, isochinoline, and triethanolamine. The largest oscillations were registered in the early period of oxidation (first 2 h), after which a stable state of reaction rate was obtained. The carbon dioxide content of the reactor off-gas behaved similarly to that of oxygen during oscillations.

In the reaction system consisting of *p*-xylene, *p*-toluic acid, and water, aperiodic oscillatory behaviour occurs also in the absence of bromine or amine activators, using mixed-metal catalysts only (Fig. 4). Such states were registered with many bimetallic mixtures, e.g., a mixture of cobalt salts with Mo, Zr, Co, U, Pb, Mn, Fe or a mixture of manganese salts with Ni, Ce, Pb, Cu salts under the same conditions as shown in Fig. 4.

The transition from an oscillatory to a stable state which occurred with the above-mentioned metal mixtures was similar to that in the case of the nitrogen activators (Fig. 3).

Oscillatory states appeared also in the oxidation of *n*-dodecane in acetic acid as

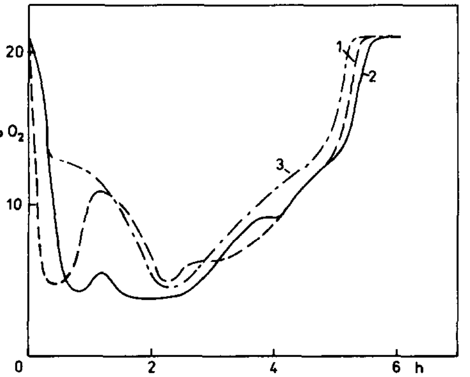

FIG. 2. Dependence of oxygen pulsation on concentration of bromine. Catalyst: 4.32 mmol $Co(OAc)_2 \cdot 4H_2O$, 8.64 mmol pyridine, 1.11 mol H_2O, HBr (47%): (1) 8.64 mmol, (2) 17.28 mmol, (3) 34.56 mmol; for other conditions, see Fig. 1.

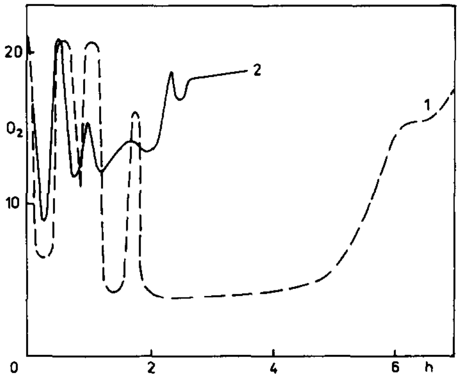

FIG. 3. Effect of the type of amine activator on pulsation. Catalyst: 4.32 mmol $CoBr_2 \cdot 6H_2O$; activator: 8.64 mmol; water: 1.11 mol; for other conditions, see Fig. 1; (1) β-picoline, (2) α,α′-bipyridyl.

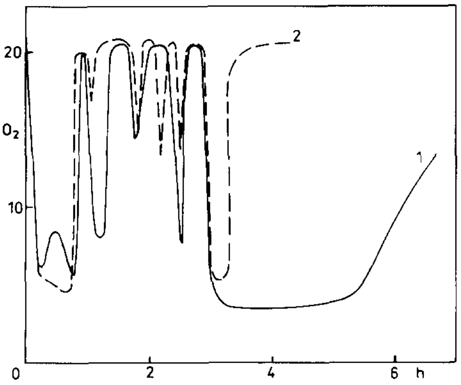

FIG. 4. Influence of mixed-metal catalysts on pulsation in the absence of activators. Catalyst: 2 mmol $Mn(OAc)_2 \cdot 4H_2O$ + 0.55 mmol: (1) Cr(III) acetate; (2) Fe(III) acetylacetonate. Conditions as in Fig. 1; water: 1.11 mol.

solvent at 140°C and a pressure of 2.0 MPa (Fig. 5). It should be emphasized that these oscillations are observed for a homogeneous one-phase system and in the absence of any metal catalyst.

The results may be discussed as follows. The majority of homogeneous liquid-phase oxidations of hydrocarbons proceed through steps which involve free-radical intermediates. Reaction rates usually reach a limiting value. This is attributed to the fact that hydroperoxides which initiate the reaction have reached a steady state (*15*). Sometimes, in the early stages of the metal-catalyzed oxidation of hydrocarbons, pulsation in the reaction rate is observed (*16–18*). For media of low polarity Black (*19*) proposed a mechanism which can explain the transition from catalysis to inhibition and pulsation behaviour. This mechanism which involves initiation through the formation of a metal–hydroperoxide catalyst complex is not expected to be applicable to oxidations in polar solvents. In this latter case highly polar molecules compete with hydroperoxides in complexing with transition metals.

Studies of the pulsation behaviour during the oxidation of a mixture of *p*-xylene and *p*-toluic acid in water at high temperatures and catalyzed either by cobalt or manganese salts only or with these salts activated with bromine and nitrogen compounds indicate that the instability is induced by the existence of some "inhibitory" components which are probably formed by decomposition of hydroperoxides. As we have shown earlier (*13, 14*), the investigated oxidation reaction is governed by a radical mechanism. Although the reaction system is composed of water and a hydrocarbon phase, both containing *p*-toluic acid and catalyst in various concentrations, the oxidation predominantly proceeds in the hydrocarbon phase and mass transfer does not play a significant role. Moreover, some of the above-mentioned pulsation phenomena occur in one-phase, water-free systems as well.

As observed in the results, the type and composition of the metal catalysts strongly affect the nature of the pulsation behaviour. Such features should be related to the part played by these catalysts in reactions with hydroperoxides or peroxidic species. However, it appears that the reaction of metal catalysts with hydroperoxides or other peroxidic species is not the unique cause of the instability behaviour of the oxidizing system. Indeed, the results depicted in Fig. 5 show pulsation states occurring in the absence of any metal catalyst. However, the role of the metal reactor wall in these reactions remains unclear.

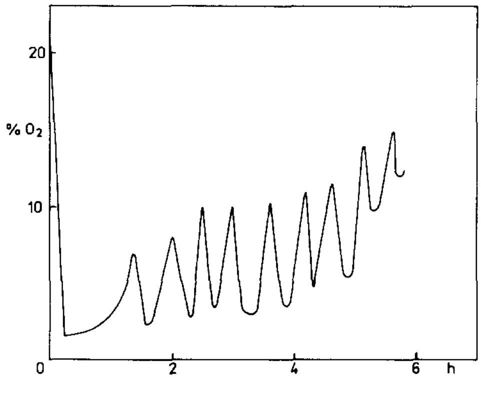

FIG. 5. Oscillation of the noncatalyzed oxidation of *n*-dodecane in acetic acid. Conditions: 140°C; 2.0 MPa; 29.4 mmol dodecane; 33.3 mmol acetic acid; air flow, 30 $dm^3\ h^{-1}$.

Further investigations on the characteristics of these pulsatory states are required to explain the abruptness of such autocatalysis–autoinhibitory conversions and to provide suitable kinetic models for these liquid-phase oxidations.

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