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NOTE

The Influence of Sulphur Compounds on β-Cu-Phthalocyanine Used as an Oxidation Catalyst

The well-known catalytic activity of metal phthalocyanines (*1–6*) has led to several attempts to use phthalocyanine catalysts in the presence of sulphur compounds in liquid phase reactions (*7–12*). In the gas phase, however, one may study in greater detail both the reactions of a sulphur compound added to a reacting substance and its adsorption and contamination of the phthalocyanine catalyst.

In the present work, the stability of monomeric β-Cu-phthalocyanine (sublimed at 10^{-5} Torr, BET surface 2.5 m^2/g) against poisoning by suphur compounds has been investigated with respect to the catalytic oxidation of 2-propanol vapor to acetone and water. A gas-chromatographic pulse technique has been used. Oxygen was passed at 22°C through either 2-propanol, 2-propanthiol, or mixtures of both. Pulses of 0.62 ml containing 720 Torr oxygen and 40 Torr 2-propanol or 580 Torr oxygen and 180 Torr 2-propanthiol or 630 Torr oxygen, 30 Torr 2-propanol and 100 Torr 2-propanthiol were passed in a helium flow (99.999%, Linde) of 40 ml/min velocity over 200 mg (4×10^{-4} mole) of the catalyst (catalyst temperature 350°C). Reaction products were analyzed by a Varian 1720 gas chromatograph (5-ft columns of Carbowax or molecular sieve 5A, column temperature 105°C, hot wire detector, 175 mA). Single reactants were injected by means of Hamilton microliter syringes.

1. 2-propanol underwent three reactions:

$$CH_3CHOHCH_3 + \tfrac{1}{2}O_2 \rightarrow CH_3COCH_3 + H_2O \quad (1)$$

$$CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + H_2 \quad (2)$$

$$CH_3CHOHCH_3 \rightarrow CH_2{=}CHCH_3 + H_2O \quad (3)$$

The degree of conversion according to Reaction (1) was about 40%; in addition, minor amounts of 2-propanol were converted according to Reactions (2 and 3). When oxygen was absent, the sum of the degrees of conversion according to Reactions (2 and 3) was about 5%.

2. 2-propanthiol underwent two main reactions:

$$2CH_3CHSHCH_3 + \tfrac{1}{2}O_2 \rightarrow (CH_3)_2CHS{-}SCH(CH_3)_2 + H_2O \quad (4)$$

$$CH_3CHSHCH_3 \rightarrow CH_2{=}CHCH_3 + H_2S \quad (5)$$

Reaction (5) also occurred in the absence of oxygen. The disulfide was observed only when oxygen was present. The sum of the degrees of conversion according to Reactions (4 and 5) was close to 100%. In the presence of oxygen a third reaction also occurred:

$$H_2S + \tfrac{3}{2}O_2 \rightarrow SO_2 + H_2O. \quad (6)$$

H_2S, generated in the absence of oxygen according to Reaction (5), was only detected when the surface of the catalyst had been saturated with H_2S by first passing several pulses of H_2S. Otherwise the amount of H_2S generated in Reaction (5) was adsorbed completely by Cu–Pc. This was observed for more than 10 successive pulses of 2-propanthiol. H_2S was desorbed very slowly. Even after a continuous He flow over the catalyst during more than 12 hr, SO_2 could be detected when pulses of oxygen were passed over the catalyst.

3. H_2S blocks the active sites of the Cu–Pc which in oxidation reactions are the central metal atoms (*13–15*). The conver-

sion of propanthiol to propene according to Reaction (5) was decreased to zero after 5 successive pulses. When oxygen was present, part of the poison was oxidized; therefore, unlike Reaction (5) in the absence of oxygen, Reaction (4) was not blocked completely but the degree of conversion of propanthiol to di-isopropyl-disulfide was decreased only to about one half of the original value. When mixtures of 2-propanol and 2-propanthiol were oxidized, Reaction (1) was also partly inhibited. The resulting steady state degree of conversion of 2-propanol to acetone was about 60% of the initial value.

4. Even a completely inactive catalyst could be regenerated by passing several pulses of oxygen over it, thereby oxidizing the adsorbed H_2S. The complete poisoning and regeneration could be repeated very often without a significant loss of catalytic activity.

Thus, Cu–Pc proves to be an active catalyst for oxidation reactions even under rough conditions, though the steady state degrees of conversion are smaller in the presence of sulphur compounds than in their absence.

The kinetics and temperature dependence of the six reactions are now being studied, together with an ir investigation of the adsorbed species.

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