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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Low-Temperature Oxidation of Carbon Monoxide by Aqueous Solutions of Palladium Salts

The practical tasks of purifying the exhaust gases of internal-combustion engines and the air of mines and pits have posed, as one of the most important problems, the problem of oxidizing small amounts of carbon monoxide ([1]). All known catalysts developed for this purpose are, as a rule, active in the temperature range 300—600° ([2—4]); therefore low-temperature liquid-phase oxidation of carbon monoxide is of great importance. In this case, along with oxidation of carbon monoxide, dust and nitrogen oxides will be captured.

When carbon monoxide acts on aqueous solutions of palladium salts, reduction of the latter occurs ([5]). The CO oxidation reaction probably proceeds through the formation and decomposition of the corresponding π-complexes of the type $[PdX_3CO]^-$. If the zero-valent palladium released as a result of the reaction is not reoxidized to the divalent state, the catalyst rapidly loses activity. Palladium can be readily oxidized ([6—9]). In the present work, the oxidation of 0.1—2% by vol. carbon monoxide in a flow system ([10]) was studied in the presence of aqueous solutions of palladium salts at 20 and 40°, with addition of oxidants: Cu^{2+}, Fe^{3+}, H_2O_2, $CrCl_3$, and $K_2Cr_2O_7$. In addition, the influence of the ligands Cl^-, Br^-, and CH_3COO^- on the rate and depth of CO oxidation was investigated. The gas flow rate was varied within 200—800 $l \cdot hr^{-1}$. The apparatus was equipped with a device for measuring the potential of the system. The reaction gas was continuously analyzed for carbon monoxide content by an automatic GIP-7 gas analyzer. The pH of the catalytic solution varied within 3.9—4.1 and is determined mainly by the acidic properties of the salts.

Fig. 1. Effect of the anions Cl^-, Br^-, and CH_3COO^- on the depth of oxidation of carbon monoxide (1%), $t = 20°$;
$V = 800\ l \cdot hr^{-1}$

Preliminary experiments showed that the most active and stable catalyst is a mixed palladium–copper–iron catalyst. The maximum depth of CO oxidation is observed at the ratio $[Pd^{2+}]/[Cu^{2+}] = 0.22$; in this case the nature of the ligands

Figure 2

Figure 2: Figure 2

has a large effect. Figure 1 gives the dependence of the depth of CO oxidation on the concentration of the ions Cl^-, Br^-, and CH_3COO^- at the optimal ratio of the ions Pd^{2+}, Fe^{3+}, and Cu^{2+}. The greatest activity is exhibited by a catalyst containing Cl^- 3.5 g/l, Br^- 20.6 g/l, and CH_3COO^- 13—15 g/l.

The effect of Cu^{2+} and Fe^{3+} on the depth of oxidation of carbon monoxide at 20° is shown in Fig. 2. As follows from the figure, small additions of Fe^{3+} (0.5—1.0 g/l) to a catalyst containing optimal amounts of Cu^{2+} sharply increase its activity. The depth of CO oxidation rises from 45—50 to 98—100%. Increasing Fe^{3+} to 1.5—2.5 g/l sharply inhibits the process.

In the absence of Cu^{2+}, at the optimum Fe^{3+} content in the catalyst, carbon monoxide is oxidized by 28-30%; addition of Cu^{2+} from 5 to 20 g/l gives a high degree of purification of the gas from CO (~100%).

The depth of CO oxidation with an increase in temperature from 20 to 40° decreases somewhat (by 3-4%). Within the investigated limits of the gas-flow rate (200-800 $l \cdot h^{-1}$), CO oxidation does not depend on the rate.

Fig. 2. Effect of additions of Cu^{2+} (1) and Fe^{3+} (2) on the process of oxidation of carbon monoxide by palladium salts: $t = 20°$, $V = 800\ l \cdot h^{-1}$.

It should be noted that the palladium-copper-iron catalyst is characterized by strong foaming, which increases with rising temperature.

A catalyst containing Pd^{2+} 2.5 g/l, Cu^{2+} 14.1 g/l, and Fe^{3+} 1.1 g/l practically does not decrease its activity during 6-7 h of continuous operation in the oxidation of small CO concentrations (0.3-0.5%) and at a flow rate of 400 $l \cdot h^{-1}$. When the gas feed rate to the catalyst is increased to 800 $l \cdot h^{-1}$ at a CO content of up to 1%, the high activity of the catalyst is retained only for 1.5-2 h (Fig. 3, 1).

Measurement of the potential of the system showed that the decrease in catalyst activity occurs as a result of a considerable decrease in the concentration of the oxidizing agent. The change in the catalyst begins with the appearance of monovalent copper and a gradual increase in its amount; then metallic palladium precipitates. In this case the potential of the system shifts toward more negative values. It follows from this that, in order to maintain high catalyst activity, complete reversibility of the oxidation-reduction system is necessary, in particular

$$Cu^{2+} \rightleftharpoons Cu^{+} + e.$$

To increase the stability of the catalyst, we tested several methods.

Figure 3

Figure 3: Figure 3

Fig. 3. Change in catalyst activity with time.
1 –Pd^{2+} 2.5; Cu^{2+} 14.1; Fe^{3+} 1.1 g/l; 2 –the same, with H_2O_2 feed; 3 –new regeneration method.

Additions of potassium bichromate and chromic chloride did not give the desired result; introduction of 5 g/l $K_2Cr_2O_7$ led to complete suppression of the process of oxidation of carbon monoxide. Earlier, in studying the dependence of catalyst activity on the concentration of Fe^{3+} ions, we found that even a slight increase in the amount of iron begins to sharply inhibit the oxidation process. Probably, an increase in the concentration of an oxidizing agent with a high redox potential prevents the destruction of the $[PdX_3CO]^-$ complex and the formation of reduced forms.

The stability of the catalyst increases with continuous feeding of diluted H_2O_2 (0.4%). Thus, without noticeable change in activity, the catalyst operated for 8 h at a feed rate of 1% CO of 800 $l \cdot h^{-1}$ (Fig. 3, 2).

However, the aqueous hydrogen peroxide solution gradually dilutes the catalytic solution, and its activity decreases.

To increase the stability of the catalyst, we have, for the first time for this process, applied a new method of regeneration. The use of this regeneration method makes it possible to render the process continuous and practically arbitrarily long (Fig. 3, 3). Thus, a homogeneous catalyst has been found which oxidizes low concentrations (0.2-4%) of carbon monoxide by 100% in a single pass at a flow rate of up to 800 $l \cdot h^{-1}$.

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Note: Figure translations are in progress. See original paper for figures.