LOW-TEMPERATURE OXIDATION OF CO TO CO$_2$ IN SOLUTIONS OF HALIDE COMPLEXES OF Pt AND HETEROPOLYACID (HPA)

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Received December 17, 1992
Accepted February 11, 1992

Kinetics of oxidation of CO to CO$_2$ in solutions of halide complexes of Pt(IV) and HPA at room temperature has been studied. A reaction mechanism is suggested. The catalyst Pt + HPA is stable at T = 0-50°C and 0.9 < pH < 2.5.

We have established that in solutions of halide complexes of Pt(IV) and HPA, CO is oxidized to CO$_2$ at room temperature. HPA acts as reversible oxidant. In this system CO oxidation can be described by the following two steps [1,2]:

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} + \text{HPA} & \xrightarrow{\text{Pt(IV)}} \text{CO}_2 + \text{H}_2\text{HPA} \quad (1) \\
\text{H}_2\text{HPA} + \frac{1}{2} \text{O}_2 & \rightarrow \text{HPA} + \text{H}_2\text{O} \quad (2) \\
\text{CO} + \frac{1}{2} \text{O}_2 & \xrightarrow{\text{Pt+HPA}} \text{CO}_2 \quad (3)
\end{align*}
\]

where H$_2$HPA is HPA reduced by two electrons.

Pt + HPA appears to be much more stable compared to our
previous catalyst Pd(II) + HPA [1,2], which was highly active but in the reaction course deactivated to precipitate Pd_{met}'.

The aim of the present study was to examine kinetic oxidation of CO by HPA in the presence of Pt complexes, i.e. step 1.

EXPERIMENTAL

Kinetics of the reaction was studied by a volumetric method [1]. P-Mo-V-heteropolyacid of the composition H_{7}PMo_{8}V_{4}O_{40} was used as a catalyst. HPA was prepared like in Ref. [3]. To stabilize the catalyst, halide ions in the form of sodium salts were added to the solution.

Reaction rate was measured on steady-state segments of the kinetic curves. All experiments (except W-T) were carried out at 25 °C.

CO oxidation over PT + HPA can be performed either, as a two-step or a one-step process. In the two-step process the sum of steps 1 and 2 is a cycle. In each cycle HPA is reduced by 3 electrons, then the catalyst is oxidized by air.

RESULTS AND DISCUSSION

The necessity to stabilize the oxidation catalyst has prompted us to replace Pd by Pt. Although the activity of halide complexes of Pt is approximately one order of magnitude lower than that of the corresponding complexes of Pd [4], its carbonyl complexes are much more stable compared to Pd carbonyls [5]. During the reduction of Pt(IV,II) complexes by CO at T < 50 °C, Pt does not precipitate as a metal, but forms a dark-cherry-colored water-insoluble polymeric compound Pt(O)_{2}[Pt(CO)_{2}]_{n} (n > 5), which is sufficiently stable in CO atmosphere. This dicarbonyl of Pt(O) (DCP) was obtained and described by two independent groups [6,7].

We have established that the active components in the reaction are the carbonyl complexes of reduced Pt. Since Pt(IV) compounds are low-active towards CO oxidation [4,7], a preliminary stage in studying step 1 was H_{2}PtX_{6} reduction to DCP in the absence of HPA.