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Fouling Mechanism in Liquid Phase Oxidation of Carbon Monoxide Catalyzed by Palladium(II) Salts in Acetic Acid Solvents

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Synopsis. The fouling mechanism during catalytic activity in the liquid phase oxidation of carbon monoxide has been investigated using catalytic acetic acid solutions containing palladium(II) salts and lithium nitrate as oxidants. The fouling phenomenon becomes understandable upon the recognition that the active palladium catalysts react with the nitrite ion formed during the oxidation reaction to produce inactive-stable complexes.

The liquid phase oxidations of carbon monoxide have been investigated as an extension of the Wacker process[1–4] in water and several reactions catalyzed by palladium salts have also been studied using acetic acid as a solvent.[5–8] Many of these studies were done with respect to the steady state reactions, but only a few have been made on the fouling process during the reaction. The present authors have previously investigated the mechanism of the CO-oxidation reaction using palladium salts in acetic acid solvents[9] and it was shown that the catalytic activity in $Pd(NO_3)_2$ and $Pd(OAc)_2$ systems decrease more rapidly than in the $PdCl_2$ system.

In the present work, the fouling mechanism of the CO-oxidation reaction was studied kinetically using a stirred reactor. It can be considered that the NO_2^- produced by reduction in the catalytic solutions during the reaction reacts with palladium complexes to give inactive-stable complexes.

Experimental

The palladium chloride solutions used were prepared by refluxing palladium chloride(II) and lithium chloride in acetic acid solvents dehydrated by phosphorus pentoxide. These solutions, which were 100 ml in volume, were diluted with 400 ml of dehydrated acetic acid after the addition of lithium nitrate. The catalytic solutions of $Pd(NO_3)_2$ and $Pd(OAc)_2$ were prepared by adding lithium nitrate to the solution of $Pd(NO_3)_2$ or $Pd(OAc)_2$ dissolved in dehydrated acetic acid (100 ml). Carbon monoxide and carbon dioxide were prepared by dehydrating with calcium chloride. Air, oxygen, and nitrogen gases used were dried over silicagel after removing a small amount of carbon dioxide and water with concd sulfuric acid and rod-like sodium hydroxide. The materials used for the preparation of these mixtures were those commercially available. The amount of NO_2^- was determined by measuring the absorbance of light (530 nm) emitted using Griess (G.R.) reagent.

The reactor,[3,4] which was made of glass with a 75 mm inside diameter and a height of 145 mm, was used for bubbling the mixtures of gases with a downward glass filter. The stirrer had a two bladed impeller at a position 40 mm from the bottom of the reactor and the reactions were carried out at 30 °C. The reaction mixtures of the gasses were analyzed by gas chromatography after condensation of acetic acid.

Results and Discussion

In the $Pd(OAc)_2$ system with the highest catalytic activity, the relation between the reaction rate in the steady state and the feed rate or the stirring rate was investigated using the reactor described above. It was shown that the mass transfer rates were unchanged for feed rates of 10—20 cm³/s and for a stirring rate of 900 rpm., therefore, under these conditions, the rate-determining step is the chemical-reaction processes. Accordingly, all the experiments were carried out under the conditions of $F \geq 10$ cm³/s and $N = 900$ rpm. In the case of $PdCl_2$ or $Pd(NO_3)_2$ systems, it was confirmed that the rate-determining step was the chemical-reaction processes under these conditions.

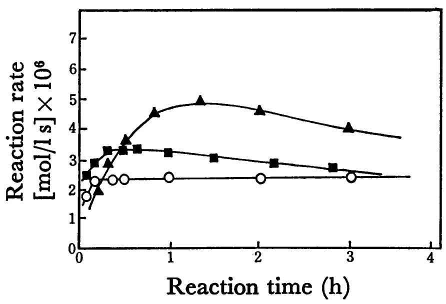
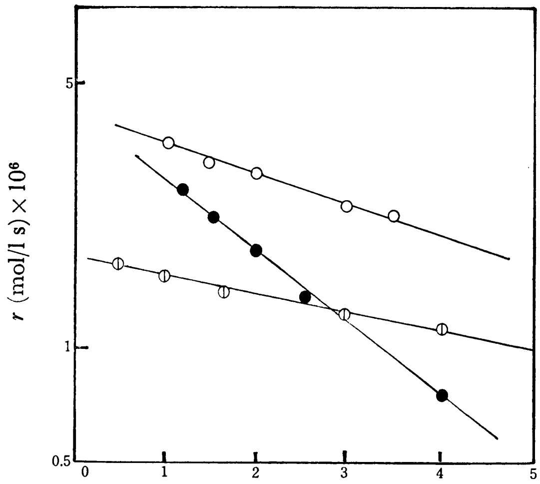


Fig. 1. The dependence of the reaction rate on the reaction time.
○: $PdCl_2$ C_{pd}: 3.59×10^{-4} (mol/l), ■: $Pd(NO_3)_2$ C_{pd}: 2.00×10^{-4} (mol/l), ▲: $Pd(OAc)_2$ C_{pd}: 2.00×10^{-4} (mol/l). C_{co}: 3.30×10^{-4} (mol/l), C_{NO_3} 0.290 (mol/l).

The oxidation rates of carbon monoxide catalyzed by palladium salts are shown in Fig. 1. In the case of palladium chloride, the oxidation rate became linear with time after about 10 min and remained constant for several hours. However, the activity decreased gradually after a long reaction period and the color of the solutions varied from an initial brown to yellow at the end. In the cases of $Pd(NO_3)_2$ and $Pd(OAc)_2$ catalysts, the reaction rate reached a maximum after several minutes and its activity decreased gradually without any precipitate. This reaction rate is of first order with respect to the concentration of the palladium salts, and therefore, the overall rate expression can be represented by

$$r = r_\infty \exp(-k_d t),$$

where r_∞ represents the steady state reaction rate and k_d the rate constant of the fouling reaction. The logarithm of the rates for constant concentration of palladium *versus* reaction time in the $Pd(NO_3)_2$ system for the



Reaction time (h)

Fig. 2. The dependence of activity of $Pd(NO_3)_2$ catalyst on the reaction time.

	$[LiNO_3]$	CO%	O_2%	N_2%	$[NO_2^-]$
⦶	0.232 [M]	6	18.8	75.2	8800 [μg-N/l]
○	0.928 [M]	15	17.0	68.0	17800 [μg-N/l]
●	1.16 [M]	6	0	94.0	34300 [flg-N/l]

$C_{pd}=0.995—1.02\times10^{-4}$ (mol/l).

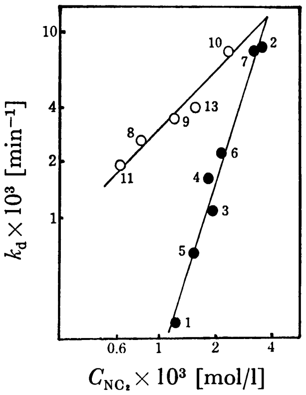
various concentrations of lithium nitrate and the various feed streams are linear, as is shown in Fig. 2, and the fouling rate constants were calculated from the slopes. The fouling rate constants increase with decreasing oxygen content in the feed streams and with increasing concentration of NO_2^- formed by the reduction of NO_3^-. In Fig. 3, the logarithm of k_d is plotted against the logarithm of the concentration of NO_2^- formed during the oxidation reaction under the various catalytic solutions and feed streams of carbon monoxide. The values of k_d in the $Pd(NO_3)_2$ system are greater than those in the $Pd(OAc)_2$ system, as is shown in Fig. 3 and were much greater than those ($k_d=0$) in the $PdCl_2$ system under similar conditions. The best fit to the data are seen to be straight lines with slopes of one, which corresponds to a first order reaction in the case of the $Pd(NO_3)_2$ system and of 3.3, in the $Pd(OAc)_2$ system. These results show that the fouling process in the case of the $Pd(NO_3)_2$ catalyst is associated with the concentration of NO_2^- equivalent to $Pd(NO_3)_2$ and in the case of the $Pd(OAc)_2$ catalyst, two moles of NO_2^- to one mole of $Pd(OAc)_2$.

It is well known that NO_2^- in solutions reacts with acetic acid to produce NO_3^- and NO, as is shown by:

$$HOAc + NO_2^- \longrightarrow OAc^- + HNO_2 \qquad (2)$$

$$3HNO_2 \longrightarrow H_3O^+ + NO_3^- + 2NO \qquad (3)$$

Tamura and Yasui[8] have reported that NO resulting from formula (3) does not form a stable palladium nitrosyl complex. No precipitate is produced with OAc^- formed by in formula (2) and the catalytic activity does not change with the addition of 10% of water in the solution. The fouling rate constants are independent of the concentrations of palladium salts, $LiNO_3$ and carbon monoxide, but do depend on the concentration of NO_2^- in the solutions.



$C_{NO_2}\times10^3$ [mol/l]

Fig. 3. The dependence of the rate constant of decay on the nitrite ion concentration.
○: $Pd(NO_3)_2$, ●: $Pd(OAc)_2$.

Catalysts		$C_{pd}\times10^4$ (mol/l)	$C_{NO_2}\times10^1$ (mol/l)	CO%	
$Pd(OAc)_2$	1	1.79	7.25	5	95 (O_2)
	2	1.19	10.0	25	75 (N_2)
	3	1.57	10.0	10	90 (air)
	4	3.18	7.25	10	90 (O_2)
	5	7.34	5.80	4	96 (air)
	6	3.43	7.25	10	90 (N_2)
	7	1.90	10.0	20	80 (N_2)
$Pd(NO_3)_2$	8	1.00	2.32	10	90 (air)
	9	1.01	9.28	15	85 (air)
	10	1.02	11.6	6	94 (N_2)
	11	1.01	2.32	6	94 (air)
	12	0.995	2.32	20	80 (N_2)
	13	1.01	4.64	20	80 (N_2)

It can be concluded that the fouling process causes the formation of inactive-stable palladium nitro complexes by the NO_2^- formed during the CO-oxidation reaction, and its fouling reaction rate decreases according to the following sequence:

$$Pd(NO_3)_3 > Pd(OAc)_2 \gg PdCl_2.$$

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