

저온 일산화탄소의 산화반응속도론적 연구

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Kinetics of the Oxidation of Carbon Monoxide on NiO at Low Temperature

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요 약. 반응온도 40°~95°에서 일산화탄소를 여러가지 온도에서 처리한 산화니켈을 촉매로 하여 산화시켰다. 일산화탄소의 산화 속도는 낮은 온도에서 진공속에서 처리한 산화니켈상에서 제일 빠르다. 이때 반응속도는 일차 반응에 따르며 활성화 에너지는 이 반응온도 범위에서 4kcal 정도이다. 공기중에서 NiCO₃를 분해하여 얻은 산화니켈촉매는 반응 온도가 95° 이상에서도 활성이 없다. 그러나 이산화 니켈을 진공에서 처리했을 경우 이 반응온도 범위에서 활성이 있다. 이때 산화니켈의 비화학 양론적인 과량의 산소가 일산화탄소의 산화속도를 지배하는 것 같다.

Abstract. The catalytic reaction between carbon monoxide and oxygen was investigated in the presence of catalysts which were specially treated by applying an annealing method at different partial pressures of carbon monoxide and oxygen and at reaction temperatures in the region of 40 °C to 95 °C. The oxidation rate is highest on NiO annealed at low temperature in vacuum. The data has been correlated with the first order kinetics, and the activation energies from the Arrhenius equation are found to be 4Kcal/mole in the region of the experimental temperatures. The excess oxygen in NiO obtained from the decomposition of NiCO₃ does not cause activation at 95 °C. But NiO catalysts annealed again in vacuum display activation even at 40 °C. The quantity of the excess oxygen in NiO surfaces seems to be the controlling factor in determining the rates of oxidation of carbon monoxide

Introduction

Some metal oxides are found to include oxygen in excess of the stoichiometric quantity, depending on the conditions of their formation. In *p*-type metal oxide, like nickel oxide, the

excess oxygen, referred to as active oxygen, exerts influence on a large number of catalytic activities on this oxide. The part performed by active oxygen in oxidation catalysis has been studied by Wagner and Hauffe¹ who were able to show that the typical behavior of oxide

semiconductors was mainly dependent on the oxygen content of the solid phase and independent of the type of oxide catalyst used.

On *n*-type oxide, as ZnO, CO is reversibly chemisorbed even below 0 °C with a heat of chemisorption of 15–20 Kcal/mole². For the highly active CuO, if the concentration of anionic vacancies becomes high, the catalysis can then proceed by an interface reaction³. Hole conducting oxides, on the other hand, are active below 150 °C. With these oxides, it is well known fact that in this temperature range, the whole catalysis can take place without the need for ionic movement among the ions of the catalyst surface with the aid of excess oxygen on *p*-type oxides external to the lattice, and in this state carbon monoxide is very reactive towards oxygen even at low temperature.

But about the activities of *p*-type oxide catalyst, as NiO, Dell and Stone⁴ have shown that although even at a low temperature, 20 °C, CO₃ complex forms readily, it is not an intermediate in the catalytic oxidation of carbon monoxide. Room-temperature catalysis on NiO was also studied by Roginsky and Tselinskaya⁵ who were able to show that the catalysis is slowly poisoned by the chemisorption of CO₂, in fact, and the reaction which proceeds with an activation energy of 2~3 Kcal/mole appears to involve a few very active sites, and changes in the electronic structure of NiO are without effect on the activation energy. Previously, Schwab and coworkers⁶, studying the same reaction on nickel oxide doped with lithium oxide and chromium trioxide, found that the rate-determining step of the oxidation process was related to the adsorption of the oxygen atom on the catalyst in the solid-gas reaction. They concluded that the oxidation occurs through the active oxygen formed on the catalyst surfaces, and this oxidizes the adsorbed carbon

monoxide in turn.

Based on our experimental data and previous results on process changes in oxidation reactions, it can be concluded that an oxidation reaction in the presence of catalysts annealed in vacuum does not proceed through alternate oxidation and reduction steps, but rather is based upon the active excess oxygen present on the catalyst surface, and that catalysis is dependent on the partial pressure of the oxygen in the gas phase. Therefore it is of use in studies of catalytic oxidation reactions to inquire how the active oxygen, in excess on the surface of the solid, influences the over all catalytic oxidation process. In consideration of the above, the present study makes an attempt to determine the kinetics for the oxidation of carbon monoxide on nickel oxide annealed in high vacuum.

Experimental Section

Preparation of Materials. Nickel oxide samples were prepared in the following ways under strictly controlled conditions. Sample 1: Extra-pure nickel carbonate powder from E. Merck AG. Darmstadt was decomposed for five hours at 450 °C in air, annealed in a quartz tube surrounded by an electrical heating furnace in vacuum, 1.12×10^{-4} mmHg, at 450 °C for an additional four hours, and then slowly cooled to room temperature. Samples 2 and 3 of nickel oxide were prepared under the same conditions as sample 1, except that the annealing of the nickel oxide was executed at 350 °C for sample 2, and 250 °C for sample 3. The resulting green-black oxides were found to show an X-ray diffraction pattern of pure nickel oxide and to have a BET surface area of 4.27 m² per gram for each sample. All the samples of nickel oxide were etched in dilute nitric acid and ammonium peroxydisulfate, washed with distilled water and dried in a vacuum desiccator.

Oxygen gas obtained from heating potassium chlorate at about 600°C was purified by passing it over glass wool, phosphorus pentoxide and calcium chloride. This method of purification was found to give a gas sufficiently free of catalytic poisons when used in catalytic reactions and it was identified as pure oxygen by gas chromatography. Carbon monoxide was prepared through a reaction of formic acid with concentrated sulfuric acid. The reaction was carried out by passing formic acid through concentrated sulfuric acid in an evacuated pyrex flask connected to a vacuum system. It was purified with glass wool, sodium hydroxide and calcium chloride. Gas chromatographs showed it to be pure gas.

Apparatus and Procedure. The experimental apparatus used is as follows. The system was connected to a Cenco Hyvac fore pump through an EC GF-20 A oil diffusion pump. The pressure was measurable down to 10^{-5} ~ 10^{-6} mmHg. After the temperature and the oxygen pressure in the sample container for annealing of NiO as low pressure as 1.52×10^{-4} mmHg were adjusted to the desired values, the sample container was inserted into the sintering furnace and the stopcock, which connects the vacuum system and sample container, was closed. After four hours of annealing, the temperature was lowered to room temperature. A weighed amount of the catalyst (0.5 g, 100~120 mesh) was placed in the reaction chamber which was then evacuated to 2.56×10^{-5} mmHg. Then premixed carbon monoxide and oxygen gases from the gas storage were admitted and the reaction chamber was placed in a water bath whose temperature was adjusted to the desired value.

The rates of oxidation were observed in the all-glass, completely closed reaction chamber, which has a total volume of 252 cc, by noting

the rate of change in pressure due to the oxidation of carbon monoxide as measured by means of a mercury capillary manometer. The reaction temperature was controlled (± 0.5 °C) by a Beckmann temperature controller and the manometer readings were taken with the aid of a magnifier. Most runs were not carried out to completion, however the initial ratio of carbon monoxide and oxygen was not different from the stoichiometric final pressure calculated from the initial pressure by gas analysis.

Experimental Results

According to the experimental results obtained by Prasad and Tendulkar⁸, nickel oxide prepared from the decomposition of nickel nitrate for three hours at 300 °C, fired in air at 640 °C contains a large excess of oxygen. But the samples of nickel oxide in this research were prepared by the decomposition of nickel carbonate at 450 °C in air and then annealed in vacuum. From the start of this experiment it was clear that the catalyst was involved in an irreversible process⁹ during the oxidation of carbon monoxide. It is, however, a well-known fact that the activity of catalysts reaches a minimum value after being used for a long time. For this reason the samples of nickel oxide were prepared at different annealing temperatures in vacuum so they would each have different catalytic activity in the oxidation of carbon monoxide.

Data for samples 1, 2, and 3 of nickel oxide were found to obey closely a first order equation with respect to the total pressure in the temperature region of 40 °C to 95 °C. The comparative rates of oxidation of carbon monoxide with nickel oxide for samples 1, 2, and 3 plotted in the form of the integrated first order equation, are shown in Figs. 1, 2, 3, and 4. The values of the rate constants (Table 1) of Samples 1, 2,

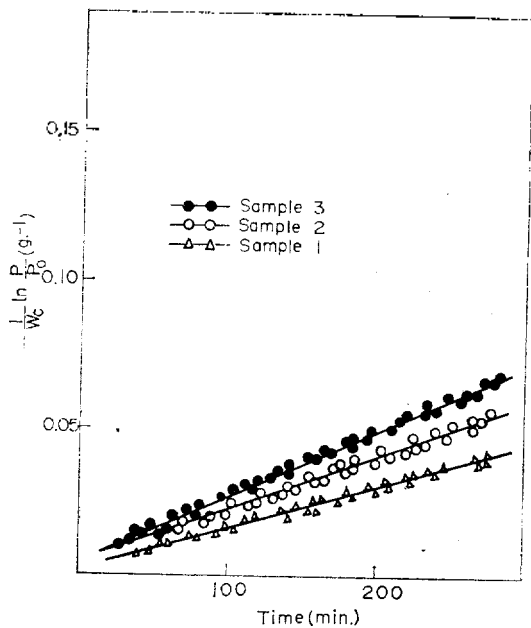


Fig. 1. The rates of oxidation of carbon monoxide on NiO, samples 1, 2 and 3 at 40°C, $P_{CO}=150$ mmHg, $P_{O_2}=75$ mmHg, W_C =weight of catalyst in grams, NiO(0.5 g).

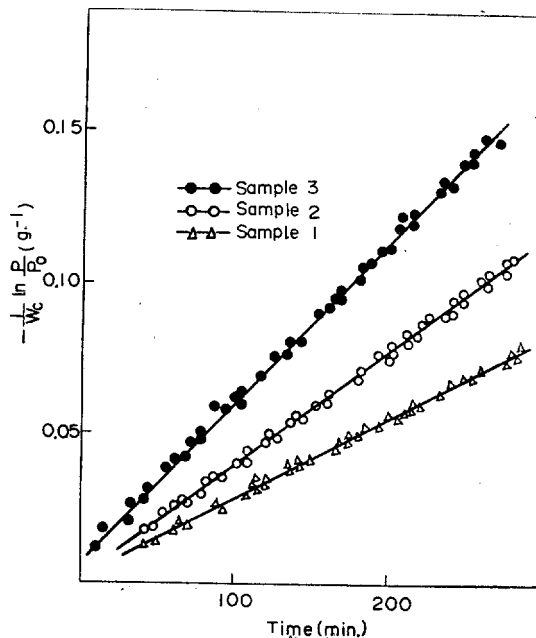


Fig. 3. The rates of oxidation of carbon monoxide on NiO, samples 1, 2 and 3 at 80°C, $P_{CO}=150$ mmHg, $P_{O_2}=75$ mmHg, W_C =weight of catalyst in grams, NiO (0.5 g).

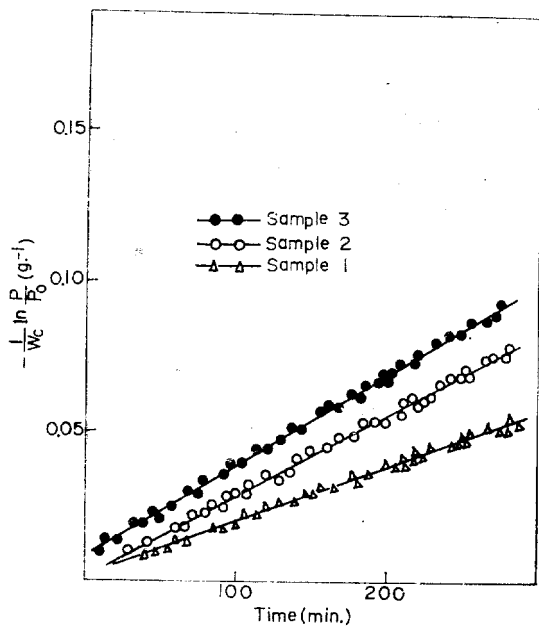


Fig. 2. The rates of oxidation of carbon monoxide on NiO, samples 1, 2 and 3 at 60°C, $P_{CO}=150$ mmHg, $P_{O_2}=75$ mmHg. W_C =weight of catalyst in grams, NiO(0.5 g).

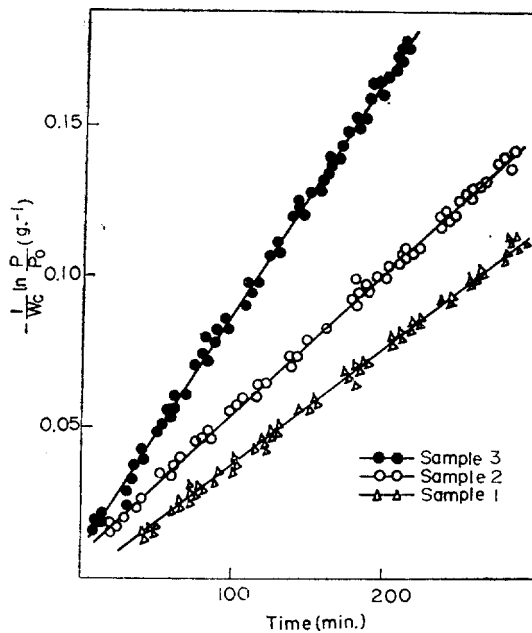


Fig. 4. The rates of oxidation of carbon monoxide on NiO, samples 1, 2 and 3 at 95°C, $P_{CO}=150$ mmHg, $P_{O_2}=75$ mmHg. W_C =weight of catalyst in grams, NiO(0.5 g).

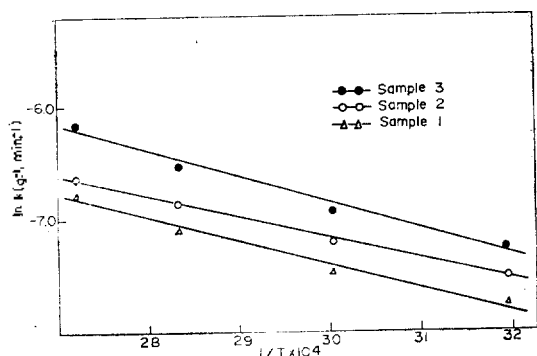


Fig. 5. Arrhenius plots for the rates of the oxidation of carbon monoxide on NiO, samples 1, 2 and 3; temperature range, 40~95 °C.

Table 1. Effect of catalysts on the rate constants of the oxidation of carbon monoxide on NiO. $P_{CO}=150$ mmHg; $P_{O_2}=75$ mmHg; NiO, 0.5 g.

T, °C	$k(\text{min}^{-1}, \text{g}^{-1}) \times 10^4$		
	Sample 1	Sample 2	Sample 3
40	1.400	1.778	2.286
60	1.875	2.588	3.258
80	2.667	3.667	5.286
95	4.000	4.727	8.000

and 3 in all reaction temperature regions were found to be compatible with the Arrhenius equation. From the Arrhenius plots (Fig. 5), the slopes of the lines were calculated and the activation energies were found to be 4.1 Kcal/mole for sample 1, 3.6 Kcal/mole for sample 2, and 4.5 Kcal/mole for sample 3. In Table 2 are listed the data for the average rates of oxidation of carbon monoxide under different partial pressures of oxygen and carbon monoxide. From the data in Table 2 the partial orders of oxygen and carbon monoxide could be calculated according to Parravano's approach¹⁰. In cases where the different partial orders of oxygen and carbon monoxide with respect to the total pressure could be written as

$$-dP/dt = k(P_{CO})^n(P_{O_2})^m$$

the values found for n and m are shown in Table 3. From the values of partial orders calculated in Table 3, an equation which represents experimental data is as follows at temperatures in the region of 40 °C to 95 °C with nickel oxide samples 1, 2, and 3.

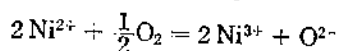
$$-dP/dt = k(P_{CO})^{0.5}(P_{O_2})^{0.5}$$

Discussion

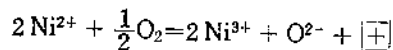
From the experimental results it is clear that the excess oxygen⁸, which is built into the catalyst during the decomposition of nickel carbonate, can not be removed by carbon monoxide at the temperatures in the region of 40 °C to 95 °C. But as shown in the data presented, the catalysts prepared by annealing the nickel oxide obtained from nickel carbonate are activated for the oxidation of carbon monoxide in this temperature range. This fact may be regarded as verifying that by the annealing of nickel oxide at the moderate temperatures (250~450 °C) excess oxygen in the nickel oxide surfaces oxidizes carbon monoxide in a temperature range where no lattice oxygen is readily removed, and yet rates of oxidation of carbon monoxide depend upon the annealing temperature of nickel oxide under the same oxygen pressure.

As shown in Figs. 1~4 the rates of oxidation of carbon monoxide are found to be less at the same reaction temperature on nickel oxide samples which were annealed at high temperatures as compared to a sample annealed at low temperature in vacuum. This result is presented as supporting evidence that nickel oxide catalysts annealed at high temperatures undoubtedly contain less excess oxygen in the nickel oxide surfaces than that annealed at low temperature.

Since the annealing of nickel oxide was performed under low oxygen pressure (10^{-4} mmHg) the Ni^{2+} ions, which were dissolved in the nickel oxide lattice, were not converted to Ni^{3+} ions so as to form positive holes. But because the decomposition of nickel carbonate was carried out in air, the excess oxygen might have been dissolved in the nickel oxide surfaces⁸ here and the released electrons from Ni^{2+} reduced the excess oxygen to excess oxygen ions¹¹



As a result of this reduction of the excess oxygen, positive holes were created and this may be represented by



where $\boxed{\oplus}$ represents positive holes. Thus the positive holes might function as the carriers of carbon monoxide or oxygen molecules from the gas phase.

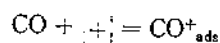
Also, as shown in Fig 5, the activation energies from the Arrhenius plots showed no change for the various samples though they were annealed at different temperatures. Therefore, the activity of the positive holes in each sample is much the same for this temperature range and constant partial pressures of carbon monoxide and oxygen. But as shown in Figs. 1, 2, 3, and 4 the rates of oxidation of carbon monoxide on nickel oxide samples increase with decrease in annealing temperature of nickel oxide at constant oxygen pressure for the same reaction temperature.

Assuming a positive hole mechanism, the oxidation rates would not be due to the activity of positive holes but to their quantity on the nickel oxide surfaces. And as the quantity of positive holes on nickel oxide surfaces may increase with decrease of annealing temperature, the oxidation rates increase due to the increased number of positive holes arising

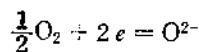
from the nickel oxide at different annealing temperatures in vacuum. In other words, positive holes due to the excess oxygen on the nickel oxide surfaces seem to be more activated by annealing in vacuum and less quantity in concentrations under high temperature annealing. As a result, the rate of oxidation of carbon monoxide increases with the decrease in annealing temperature range with nickel oxide catalysts.

With increasing reaction temperature, comparing Figs. 1, 2, 3, and 4, independent of positive holes, the oxidation rates show a tendency to increase. The reason, in general, is that increasing the reaction temperature on a sample makes a positive hole more active.

According to the vacancy mechanism, the oxidation process may be explained as follows. Carbon monoxide from the gas phase will first be reversibly removed and, once in close contact with the activated positive holes on nickel oxide surfaces, will pass to an irreversibly adsorbed state

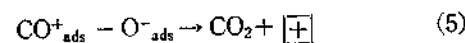
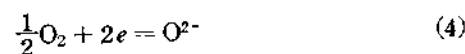
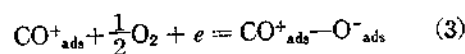


On the other hand, oxygen from the gas phase, which may accept electrons, may be reduced to O^{2-} ¹² and may cause the formation of a positive hole on the nickel oxide surface



This is because at this low reaction temperature, no matter how activated the positive holes may be, oxygen, as we have seen, is not chemisorbed in any quantity in the normal way. Therefore, the positive holes will tend to disappear and the subsequent removal of oxygen from the gas phase into the oxygen ion site on the nickel oxide surface appears to facilitate desorption of carbon dioxide from the state of the carbonate ion. This oxidation process based on careful analyses of the literature¹³⁻¹⁵

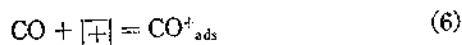
and our observations may be represented by



where CO^+_{ads} is the molecule of adsorbed carbon monoxide, O^-_{ads} is the atom of oxygen. In equation(1) the process in which the molecule of carbon monoxide is adsorbed to a positive hole on the nickel oxide surface is regarded as a carbon monoxide molecule combining with a positive hole. As shown in equations(1) and (5) the possible process of formation of positive holes may take place in two different ways. One is that the positive holes were formed on the nickel oxide surfaces by the excess oxygen arising from the decomposition of nickel carbonate to produce an oxygen ion, O^{2-} , and the other is that if this oxygen ion donates two electrons to oxygen from the gas phase, only the oxygen atom of the adsorbed state will react with adsorbed carbon monoxide molecule and produce another ion of oxygen. Among the oxidation steps, as shown in equations(1)~(5), if the process, $\text{O}^{2-} = \frac{1}{2}\text{O}_2 + 2e$, is fast followed by the process, $\text{CO} + \boxed{+} = \text{CO}^+_{\text{ads}}$, the rate-determining step of the over-all reaction of the oxidation of carbon monoxide on nickel oxide catalysts will become the process, $\text{CO} + \boxed{+} = \text{CO}^+_{\text{ads}}$ or $\frac{1}{2}\text{O}_2 + 2e = \text{O}^{2-}$.

As shown in Table 2, at constant reaction temperature, the rates of oxidation depend upon the partial pressure of oxygen and carbon monoxide, and in Table 3, the calculated partial

order of reaction is 0.5 for oxygen and carbon monoxide. From the experimental data it can be seen that both the carbon monoxide and oxygen affect the overall reaction rate and it is reasonable to consider that the over-all oxidation process is represented by the steps



where the positive hole is not wholly covered by any one of the reactants. In the pretest of adsorbed state of reactants, the oxygen molecule in the gas phase was not adsorbed in the catalyst surface at any temperatures in the region of 40 °C to 95 °C. But carbon monoxide molecule was adsorbed even at 40 °C and this experimental result of the pretest is characterized by the process (6) which occurs faster than(7) due to the large initial excess of oxygen in the catalyst surface. And therefore it is reasonable to say that the rate-determining step is not the adsorption of carbon monoxide, $\text{CO} + \boxed{+} = \text{CO}^+_{\text{ads}}$, by the positive holes of the nickel oxide surface. The adsorption of oxygen, $\frac{1}{2}\text{O}_2 + 2e = \text{O}^{2-}$, is rate controlling one. The above interpretation of the rate-determining step is a contrast to the results of Cour¹⁶ who concluded that in the oxidation of carbon monoxide on NiO, doping of NiO with Li^+ increased the adsorption of O_2 , whereas doping with Ga^{3+} had the opposite effect. Doping apparently has no effect on the rate of oxidation of CO, the rate-determining step being the desorption of carbon dioxide. But a coincident result, in the stationary reaction between CO and $\text{O}_2(1:2)$ on NiO at 240 °C, has been described by Kuechler and Schlosser¹⁷ who found that the desorption of CO_2 is not the rate-determining factor. More recently for the rate-determining it was studied that O_2 chemisorption ($\text{O}_2 \rightarrow 2\text{O}^-$

Table 2. Effect of partial pressures of oxygen and carbon monoxide on the rate, v , of carbon monoxide oxidation on NiO.

Sample 1			
$T, ^\circ\text{C}$	$P_{\text{CO}}(\text{mmHg})$	$P_{\text{O}_2}(\text{mmHg})$	$v(\text{mmHg} \cdot \text{min}^{-1} \cdot \text{g}^{-1})$
40	150	75	0.0289
40	75	35	0.0141
40	150	145	0.0409
40	75	75	0.0156
95	150	75	0.0803
95	75	40	0.0401
95	150	150	0.1052
95	75	75	0.0562
Sample 2			
40	150	75	0.0430
40	75	38	0.0215
40	150	145	0.0592
40	75	75	0.0258
95	150	75	0.1050
95	75	38	0.0530
95	150	145	0.1500
95	75	75	0.0598
Sample 3			
40	150	75	0.0500
40	75	40	0.0225
40	150	145	0.0725
40	76	75	0.0269
95	150	75	0.1700
95	75	40	0.0782
95	150	145	0.2516
95	75	75	0.0896

Table 3. Values of the partial orders, n and m , of carbon monoxide and oxygen in the oxidation of carbon monoxide on NiO.

Sample	$T, ^\circ\text{C}$	n	m
1	40	0.50	0.50
	95	0.52	0.48
2	40	0.49	0.51
	95	0.50	0.50
3	40	0.51	0.48
	95	0.50	0.50

of CO_2 , the rate controlling step²⁰. The same mechanism as (5) was proposed by Teichner and coworkers²¹ who reported that the slowest step is the interaction between CO and adsorbed oxygen ions. For the reaction order, Brooks²² and Vainshtok²³ reported that the oxidation rates are first order for CO at 75–150 °C and for the over-all reaction at higher than 150 °C respectively. No results have been appeared consistent with first for over-all reaction order at 40–95 °C.

On the basis of the present results it can be

ads) is the slowest step¹⁸⁻¹⁹ and the formation

concluded that the concentration of positive holes in solid phase is the factor in determining the rates of the oxidation reaction at low temperature.

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References

1. C. Wagner and K. Hauffe, *Z. Physik Chem.*, **B44**, 181(1938).
2. W. E. Garner and J. Haggs, *Trans. Faraday Soc.*, **32**, 1744(1936).
3. H. Jones and H. A. Taylor, *J. Phys. Chem.*, **27**, 623(1923).
4. R. M. Dell and F. S. Stone, *Trans. Faraday Soc.*, **50**, 501(1954).
5. S. Z. Roginsky and T. S. Tselinskaya, *Zhur, Fiz. Khim. SSSR*, **21**, 919(1947); **22**, 1360(1948).
6. G. M. Schwab and J. Block, *Z. Elektrochem.*, **58**, 756(1954).
7. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chem.", Vol. 1, P. 349, Longmans, New York, 1946.
8. M. Prasad and M. G. Tendulkar, *J. Chem. Soc.*, 1403(1931).
9. W. E. Garner, *J. Chem. Soc.*, 1239(1947).
10. G. Parravano, *J. Amer. Chem. Soc.*, **75**, 1452(1953).
11. W. J. Moore and J. S. Choi, *J. Phys. Chem.*, **66**, 1380(1962).
12. W. E. Garner, "Chemistry of the Solid State", P. 395 Academic Press, New York, 1955.
13. A. Bielanski and R. Dziembaj, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **16**(5), 269~74(1968).
14. M. I. Brittan, H. Bliss and C. A. Walker, *AIChE J.*, **16**(2), 305~14(1970).
15. A. A. Davydov, Y. M. Shchekochikhin and N. P. Keier, *Kinet. Katal.*, **11**(5), 1230~5(1970).
16. J. Cour, *Chim. Mod.*, **8**(57), 269~70(1963).
17. L. Kuechler and E. G. Schlosser, *Z. Naturforsch.*, **19a**, 54~58(1964).
18. L. A. Sazonov and E. V. Artamonov, *Kinet. Katal.*, **8**(3), 640~5(1967).
19. Syoichi Oki, Shokubai, **10**(3), 180~91(1968).
20. R. E. Ranc and S. J. Teichner, *Bull. Soc. Chim. Fr.*, (5), 1730~41(1967).
21. P. C. Gravelle, G. El Shobaky and S. J. Teichner, *J. Chim. Phys. Physicochim. Biol.*, **66**(10), 1760~9(1969).
22. C. S. Brooks, *J. Catal.*, **8**(3), 272~82(1967).
23. M. T. Vainshtok, P. Vergnon, F. Juillet and S. J. Teichner, *Bull. Soc. Chim.*, (8~9), 2812~24(1970).