

Kinetics and Mechanism of the Oxidation of Carbon Monoxide on H₂-Reduced NiO-Doped α -Fe₂O₃

Don Kim, Keu Hong Kim*, and Jae Shi Choi

Department of Chemistry, Yonsei University, Seoul 120-749. Received September 28, 1987

The CO oxidation was performed on H₂-reduced NiO- α -Fe₂O₃ in the temperature range 150-250 °C. The kinetic study and the conductivity measurements indicate the oxidation reaction follows Langmuir-Rideal type process that is uncommon in heterogeneous catalyst¹. No active site is found on the catalyst surface for CO adsorption, but an oxygen vacancy adsorbs an oxygen, and this step is rate initiation. The partial orders are half for O₂ and first for CO, respectively. Apparent activation energy for over-all reaction is 9.05 kcal/mol.

Introduction

Several works have been reported for the catalytic oxidation of carbon monoxide^{2,4}. Some of them have been concentrated on the system including α -Fe₂O₃ or other transition metals, and focused to determine the adsorption sites on the surface of catalyst, the charge transfer in the adsorption process, and the identification of the rate determining step. Various experimental methods have been used to understand the phenomena of interphase between gas and solid. One of them is the measurement of electrical conductivity.

There are some difficulties in the measurement of electrical conductivity such as the ambiguity for the value of the surface barrier, the participation of intergranular resistance, etc. However, measurement of conductivity change for the time period gives special informations about the direction of charge transfer, adsorption sites and adsorption rates^{5,6}. When the catalyst is n-type semiconductor, the bare conductivity decreases with increasing oxygen adsorption. This decrement is due to localizing of conduction electron on the surface of catalyst. On the other hand, the electrical conductivity increases with the adsorption degree of the carbon monoxide, because of donated conduction electron to the catalyst. These transfers of conduction electron in adsorption process had been found in many transition metal oxides such as, ZnO⁷, TiO₂⁸, LiNbO₃⁹, etc.

There is no rule for the adsorption site, but it has been known that an oxygen vacancy is the adsorption site in TiO₂ while Zn²⁺ is in ZnO. In α -Fe₂O₃, it has been suggested that an oxygen vacancy acts as an adsorption site for oxygen², and the lattice oxygen does as that for CO¹⁰. According to the fact that the electrical conductivities are abruptly increased by trace impurity of Ni in α -Fe₂O₃¹¹, Ni on the surface is also thought to give an adsorption site.

In this study, we used 10 mol% NiO doped α -Fe₂O₃ as a catalyst which was reduced under hydrogen flow at 400 °C. The change of adsorption sites for reactant gases was observed by the conductivity measurements, and the oxidation mechanism was suggested from the kinetic and conductivity data on the oxygen vacancy-excess n-type semiconductor catalyst.

Experimental

1. Material Preparation

(a) The 10 mol% NiO- α -Fe₂O₃ powder and pellet.

NiO was prepared from chemically pure Ni(NO₃)₂·6H₂O by the wet method, and α -Fe₂O₃ was from FeCl₂¹². NiO and α -Fe₂O₃ were weighed precisely, ball-milled for 2 hr, and sintered for 50 hr at 1200 °C under air. The powder mixture was identified by X-ray diffraction and impurities of the sample were analyzed by AAS. Total impurity concentration is less than 150 ppm. The heat-treated sample was ball-milled for fine powder (100-160 mesh) and the surface area of the sample was measured by BET test (10.2 m²/g). The powder mixture was made into a pellet under a pressure of 9 ton/cm² and then cut into a cube 2 × 4 × 10 mm³ by an abrasive. The pellets and the powder were reduced at 400 °C in Pyrex tube under flowing hydrogen (20 ml/min) for 3 hr¹³. The reduced samples were stored in hydrogen atmosphere (1 atm), and kept in dynamic vacuum for 1 hr just before using.

(b) CO and O₂. Carbon monoxide was made from the reaction of CaCO₃ and Zn powder in mole ratio of 1:2. The reaction was carried out by heating (about 650 °C) in quartz tube. CO was purified with glass wool, KOH and CaCl₂. Oxygen was made from heating KClO₃ with MnO₂ at 250 °C, and then purified with glass wool and P₂O₅. The analyses of the reactant gases CO and O₂ were performed with gas chromatograph using Porapak Q column. The purities of O₂ and CO were greater than 99.2% and 99.5%, respectively.

2. Kinetic Tests and Conductivity Measurements

The kinetic tests were carried out by measurements of pressure changes using a static reactor with fixed amount of powder catalyst (0.5g). The total initial pressure of stoichiometric reactant mixtures (2 CO + O₂) was 240 torr. The conductivity was measured by standard dc four probe method, and all distances between adjacent probes were same (2.0 mm).

The conductivity changes for gas adsorptions were measured by electrometer (Keithley 610C), potentiometer (Leed & Northrup 7555 K-5) and multi recorder. Since we could predict that there were no migrations of gases adsorbed as ion species at the interphase, it was possible to use standard dc four probe method.

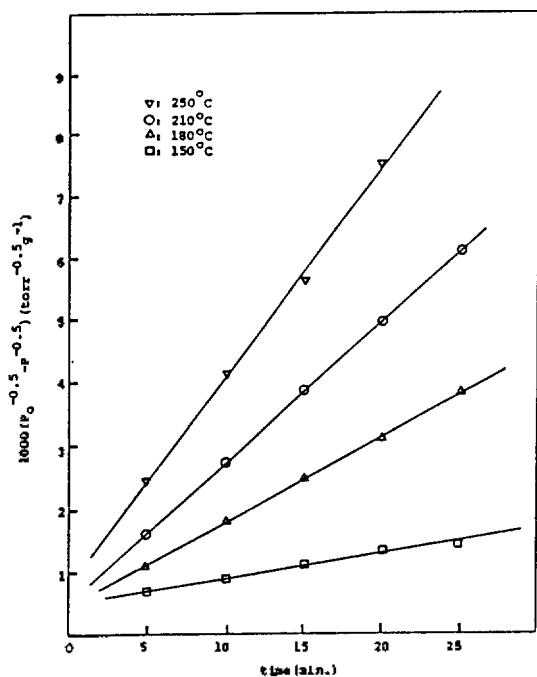
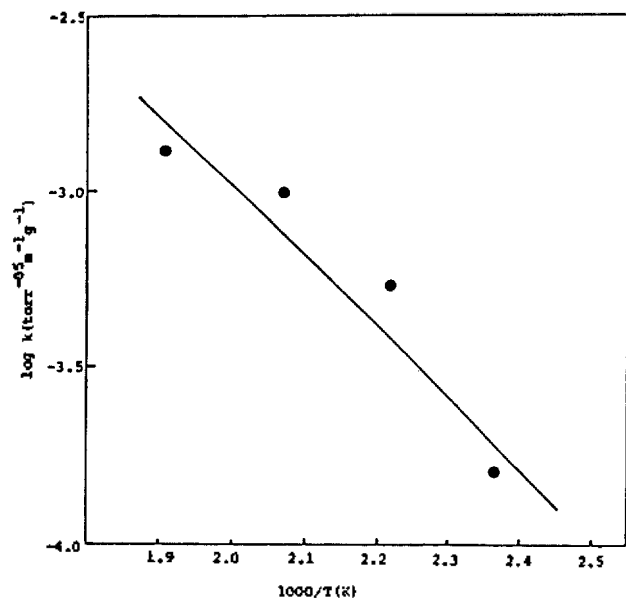
The experimental apparatus used in this work were similar to those used in previous works^{14,15}.

Results

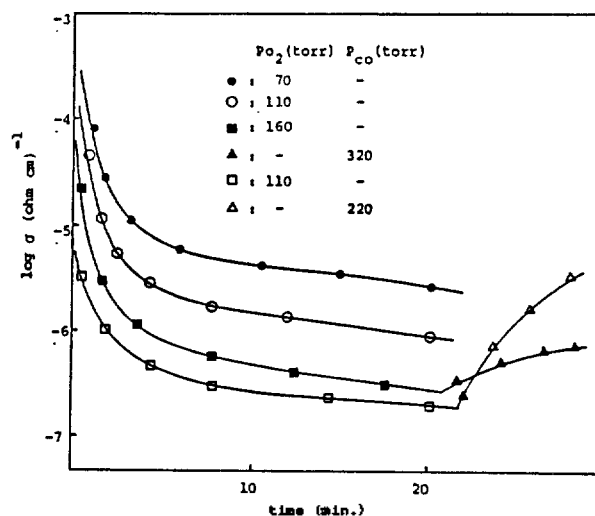
The kinetic data for CO oxidation on Ni-doped α -Fe₂O₃ reduced by hydrogen are found to obey closely the expression $-dp/dt = kP^{1.5}$ about the initial stoichiometric pressure ($P_0 =$

Table 1. Effect of temperature on the rate constants of CO oxidation on H₂ reduced NiO- α -Fe₂O₃

T °C	1000/T(K)	k (min ⁻¹ , g ⁻¹ , torr ^{-0.5})
150	2.36	1.6×10^{-4}
180	2.21	5.3×10^{-3}
210	2.07	9.1×10^{-3}
250	1.91	1.3×10^{-2}

**Figure 1.** Oxidation rates of CO on H₂-reduced 10 mol % NiO-doped α -Fe₂O₃; 150-250°C; P_{CO} = 160 torr; P_{O₂} = 80 torr; P₀ = total initial pressure; P = total pressure.**Figure 2.** Arrhenius plot for the oxidation of CO on H₂-reduced 10 mol % NiO-doped α -Fe₂O₃.**Table 2.** Effect of P_{O₂} and P_{CO} on the rate of CO oxidation on H₂-reduced NiO- α -Fe₂O₃

T °C	P _{O₂}	P _{CO}	2V (min ⁻¹ , g ⁻¹ , torr)
150	80	161	0.42
150	82	80	0.22
150	161	80	0.30
250	80	160	3.77
250	81	80	1.82
250	160	80	2.50

**Figure 3.** Different conductivity changes of the H₂-reduced 10 mol % NiO- α -Fe₂O₃ (●, ○, ■, ▲) and unreduced α -Fe₂O₃ (□, △) with P_{O₂}, and then with P_{CO} on time base; 250°C.

P_{CO} + P_{O₂} = 240 torr) in the reaction temperature interval 150-250°C.

Figure 1 shows oxidation rates at various temperatures, using an integrated rate expression. Arrhenius plot (Figure 2) gives an activation energy of 9.05 kcal/mol. Table 2 reveals the reaction rate variations for the change of P_{CO} and P_{O₂}. From Table 2 the partial orders are easily calculated, 0.5 for O₂ and 1 for CO.

Figure 3 shows that conductivity changes with variation of P_{O₂}, and that an adsorption of oxygen on the catalyst surface attains the equilibrium very fast, just as α -Fe₂O₃. But conductivity changes for the catalyst are greater than that for α -Fe₂O₃. From this result O₂ is thought to be adsorbed on oxygen vacancy easily. When the decreasing of the electrical conductivity trend reaches an equilibrium value under specified P_{O₂}, successively introduced stoichiometric P_{CO} increases the conductivity. Unlike α -Fe₂O₃, in Figure 4, no conductivity change is observed with variation of P_{CO}. Therefore it is considered that there is not any transition of conduction electron between the catalyst and introduced gas, that is, the adsorption site for CO does not exist on the catalyst surface. These phenomena imply Langmuir-Rideal process.

Discussion

From Figure 1, it is shown that the present catalyst has ca-

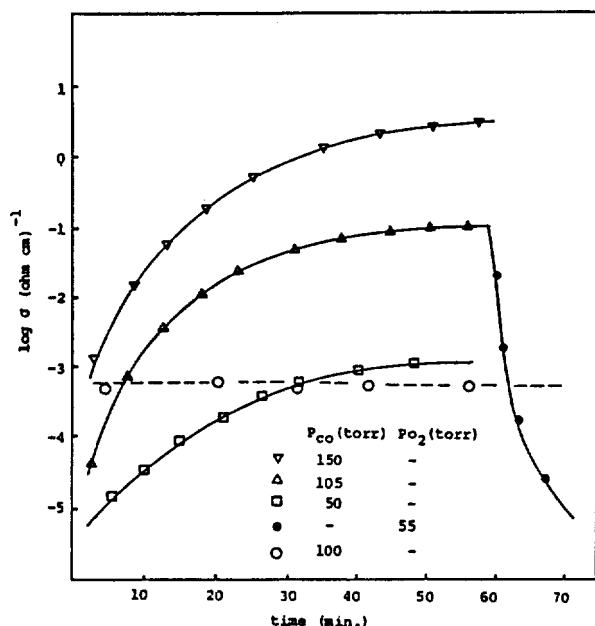


Figure 4. Different conductivity changes the H₂-reduced 10 mol % NiO- α -Fe₂O₃ (○) and unreduced α -Fe₂O₃ (▽, △, □, ●) with P_{CO} on time base: 250°C.

talytic activity above 150°C. This is lower temperature than that of previous works (NiO- α -Fe₂O₃(10) and CdO- α -Fe₂O₃ (3): 300°C). And this fact also indicates the oxidation rate of CO significantly depends on the concentration of oxygen vacancy in the catalyst, the amount of conduction electron.

1. Possible Adsorption Sites. On the surface of reduced catalyst there are many kinds of sites Fe²⁺, Fe³⁺, Ni²⁺, oxygen vacancy, etc. These would be the active sites of the reaction gases. Generally, carbon monoxide adsorbed on the n-type semiconductor surface donates electron to catalytic surface (CO(g) - CO⁺(ads) + e), increases the amount of conduction electron on the catalyst, and surprisingly increases the electrical conductivity. The electrical conductivity obeys following equation

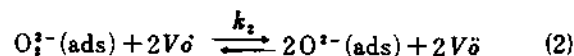
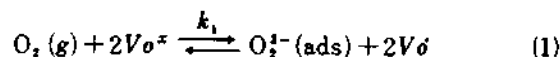
$$\sigma = ne\mu$$

where σ , n , e , and μ are electrical conductivity, concentration of charge carrier, charge, mobility of charge carrier. Because the values of μ and e are fixed at constant temperature, the electrical conductivity depends only on the value of n . But, as shown in Figure 4, there is no prominent change of conductivity measured after introducing CO gas into the H₂-reduced NiO- α -Fe₂O₃ catalyst, different from that of unreduced NiO- α -Fe₂O₃¹⁰.

Experimental observation description obviously indicates that any types of charge transition does not exist between CO gas and active sites on the catalyst surface. The electrical conductivity, however, highly increases as CO gas is introduced into unreduced catalyst¹⁰. This consequence is attributed to the relatively large amount of lattice oxygen. From this fact, it is expected that the adsorption of CO is not affected on the oxygen vacancy and metal site but lattice oxygen

Secondly we can look into the possible adsorption site of oxygen from Figure 3. When the oxygen gas is introduced into the sample, the electrical conductivity sharply decreases in short interval (-3 minutes). But, the decreased electrical con-

ductivities regain the original values under dynamic vacuum below 10 torr. This represents the adsorption of oxygen is reversible ($1/2O_2(g) + e \rightleftharpoons O^{2-}(ads)$)¹⁶. In the reduced sample, the adsorption site of oxygen is a site where electrons can be donated to the gas, same as other n-type catalyst. Then the possible site of donating electrons is Fe²⁺ or oxygen vacancy, which is produced by H₂-reduction. Although glass system of Fe₂O₃-B₂O₃ has large amount of Fe²⁺ sites, the electrical conductivity does not change through the adsorption of oxygen¹⁷. It is possibly concluded that the adsorption site should be oxygen vacancy. The site of Ni can be also possible for adsorption of oxygen but for the relatively small concentration, this site does not largely affect the overall reaction. By the adsorption of oxygen, the electrons in the oxygen vacancies are transported to the oxygen and then delocalized. And the strength of double bonds in oxygen molecule will be enfeebled³. Considering that the molecular oxygen is decomposed into atomic oxygen by the following reactions,



equilibria (1) and (2) are well coincided with the kinetic data that the partial order for oxygen is 0.5, which clearly shows an oxygen molecule being adsorbed as an atomic state.

2. Kinetics. From Figure 1, H₂-reduced NiO- α -Fe₂O₃ sample is a useful catalyst in oxidation reaction for CO above 150°C. Since the reaction rate depends on 0.5 order with respect to O₂ and 1 order with respect to CO above 150°C, CO participates in the reaction as a molecular type while O₂ does as an atomic type. From eq.(1) and (2), the equilibrium equation can be written as follows

$$k_1 = [O_2^{\cdot-}(ads)] [V_o^{\cdot}]^2 / [O_2(g)] [V_o^{\cdot}]^2 \quad (3)$$

$$k_2 = [O^{\cdot-}(ads)]^2 [V_o^{\cdot}]^2 / [O_2^{\cdot-}(ads)] [V_o^{\cdot}]^2 \quad (4)$$

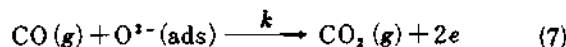
$$k = k_1 \cdot k_2 = [O^{\cdot-}(ads)]^2 [V_o^{\cdot}]^2 / [O_2(g)] [V_o^{\cdot}]^2 \quad (5)$$

where $[V_o^{\cdot}]/[V_o^{\cdot}]^2$ term linearly depends on electron concentration, therefore the concentration of oxygen ion adsorbed as an atomic type is

$$[O^{\cdot-}(ads)] = k' [O_2(g)]^{1/2} \quad (6)$$

where the concentration of adsorbed oxygen ion is proportion to $P_{O_2}^{1/2}$.

There is no change of electrical conductivity (Figure 4) when only CO is introduced into the sample. As shown in Figure 3, however, the reduced electrical conductivity with the introduction of oxygen increases with subsequent introduction of CO. It is predicted that CO reacts with O²(ads) directly. The reaction occurs through Langmuir-Rideal type elementary reaction that is uncommon in heterogeneous catalytic processes¹.



Carbon monoxide in gas phase diffuses to the surface of the solid where O²(ads) exists as saturated state, and then reacts with reactive O²(ads), increasing the concentration of conduction electron. But O₂(g) also diffuses to the surface,

decreasing the concentration of conduction electron by eq.(1) and (2). If O₂ adsorption is rate determining then total reaction order must be 0.5. But this order is not agree with kinetic data. Therefore we conclude that the adsorption of oxygen should be only the reaction initiation step, and eq.7 should be the rate determining step. From eq.7 production rate of CO₂ is

$$d[\text{CO}_2]/dt = k[\text{CO}][\text{O}_2^{2-}(\text{ads})] \quad (8)$$

and by eq.(6)

$$d[\text{CO}_2]/dt = k''[\text{CO}][\text{O}_2]^{1/2} \quad (9)$$

From this proposed rate law, we could get the partial orders of CO and O₂ that are first and 0.5, respectively, consistent with experimentally observed rate law.

Acknowledgement. We are grateful to the Korean Science and Engineering Foundation for financial support and Dr. S.H. Lee, Professor K.Y. Choo and Mr. C.K. Kang for helpful discussions.

References

1. Astumin, R. D., and Schelly, Z. A., *J. Am. Chem. Soc.*, **103**, 304 (1984).
2. Kim, K. H., Han, H. S., and Choi, J. S., *J. Phys. Chem.*, **83**, 1286 (1979).
3. Kim, K. H., Kim, D., and Choi, J. S., *J. Catal.*, **86**, 219 (1984).
4. Lee, S. H., Kim, Y. R., Kim, K. H., and Choi, J. S., *J.*

- Kor. Chem. Soc.*, **29**, 111 (1985).
5. Morrison, S. R. "The Chemical Physics of Surface", Chapter 2, Plenum Press, New York, 1978.
6. Van Oeffelen, D. A. G., Von Hooff, J. H. C., and Schuit, G. C. A., *J. Catal.*, **95**, 84 (1985).
7. Choi, J.S., and Kim, B.W., *Bull. Chem. Soc. Jpn.*, **46**, 21 (1973).
8. Choi, J. S., Kim, K. H., and Choi, S. R., *Inter. J. Chem. Kinetics*, **9**, 489 (1977).
9. Inoue, Y., Sato, K., and Suzuki, S., *J. Phy. Chem.*, **89**, 2827 (1985).
10. Kim, K. H., Jun, J. H., and Choi, J. S., *Bull. Kor. Chem. Soc.*, **5**, 41 (1984).
11. Benjelloun, D., Bonnet, J., Dordor, P., Launay, J., Onillon, M., and Hagenmuller, P., *Revue de Chimie Minérale*, **21**, 721 (1984).
12. Reymond, J. P., Meriaudeau, P., and Teichner S. J., *J. Catalysis* **75**, 39 (1982).
13. G. Bate, "Ferromagnetic Materials", vol 2, chapter 7, E. P. Wohlfarth ED., North-Holland Pub. Co., N. Y., 1980.
14. Lee, S. H., Heo, K., Kim, K. H., and Choi, J. S., *Inter. J. Chem. Kinetics* **19**, 1 (1987).
15. Yoon, K. H., and Choi, J. S., *J. Phys. Chem.*, **74**, 1095 (1969).
16. Iwamoto, M., Yoda, Y., Yamazoe, N., and Seyomu, T., *J. Phys. Chem.*, **82**, 2564 (1978).
17. Kim, Y. Y., Master Thesis, Yonsei University, 1986.

Transient Absorption Spectra of Phenothiazine Derivative in the Vesicle System Containing Ru²⁺ Complex as a Sensitizer

Yong-Tae Park and Young-Doo Kim

Kyungpook National University, Department of Chemistry, Taegu 702-701

Richard D. Burkhart and Norris J. Caldwell

University of Nevada, Department of Chemistry, Reno, Nevada 89557, U.S.A.

The Photophysical and photochemical properties of Ruthenium bipyridine with two long hydrocarbon chains, [Ru(bipy)₂(dhhbipy)]²⁺ and transient phenothiazine derivative cation radical (PTD^{•+}) in the cationic vesicle were studied. Transient absorption spectra of cation radical of phenothiazine derivative in the vesicle system containing the Ru²⁺ complex, [(Ru(bipy)₂(dhhbipy)]²⁺, (1) as sensitizer and phenothiazine derivative as electron donor was observed by XeCl excimer laser photolysis system. Thus the excited ruthenium complex would be quenched by phenothiazine derivative(PTD) reductively in the vesicle system. The quenching rate constant(K_q) of Ru²⁺ with two long hydrocarbon chains in the vesicle by PTD was 9.6 × 10⁸M⁻¹S⁻¹. The absorption decay kinetics showed that lifetime of phenothiazine derivative cation radical is a value in the 4-8m sec range.

Introduction

Within recent years, substantial research effort has been extended in photochemical conversion of solar energy. In a solar energy storage study, a vesicle system of Calvin(1978)⁽¹⁾ Tunuli (1981)⁽²⁾ and Fendler (1985)⁽³⁾ is of interest. The attachment of Ru catalyst on the well of a vesicle containing sensitizer, electron donor and electron acceptor was devised

by Park (1983).⁽⁴⁾ Hydrogen was produced when the vesicle solution containing phenothiazine derivative and Ru²⁺ bipyridine complex with two long tails was irradiated with blue light. However, the reaction mechanism of the vesicle system was not clear. In a study of the vesicle system containing [Ru(bipy)₂(dhhbipy)]²⁺ the transient absorption of phenothiazine derivative in the sysem was observed. The absorption decay kinetics was also studied.