Kinetic Structure Change of the Oxidation of Carbon Monoxide on Differently Prepared Zinc Oxides

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Abstract

The fine kinetic structure of CO oxidation over zinc oxides, which were differently prepared from Kadox ZnO (K25-ZnO) and Kanto Chemical Co. ZnO (Kan-ZnO), has been compared in detail by using both the steady state and the transient response methods. The apparent reaction rate surface of K25-ZnO has been visualized in the form of three dimensional surface as a function of Pco and Po_2 at 130-170°C, which gives both maximum and minimum points on the surface. In the case of Kan-ZnO, the rate simply shows the first order with respect to Pco and the zero order with respect to Po_2. This extraordinary difference in kinetic structure can be considered as a result of the difference of crystal surface of original ZnO.

1. INTRODUCTION

Recently Bolis, Fubini and Giamello[1] have demonstrated that reaction activity of zinc oxide surface, such as the adsorption CO and H_2, strongly depends on form of the crystallites. Three polycrystalline ZnO samples have been studied : one obtained by ignition of zinc metal (Kadox) and the others obtained by decomposition of zinc carbonate (c-ZnO) and oxalate (o-ZnO). Kadox ZnO gives the higher surface reactivity rather than the others. The adsorption enthalpy of CO is evaluated to be 46 kJ/mol on the reduced surface of Kadox whereas 8 kJ/mol on c-ZnO. The authors explained difference in adsorption capacity by taking into consideration the presence of better defined crystallites with sharp edges on the Kadox ZnO.

Based on these results, it has been proposed that catalytic activity and kinetic structure of reaction may drastically be changed depending on preparation routes of ZnO samples. The aim of this paper is to compare the kinetic structure of CO oxidation over two differently prepared ZnO, one of which is from Kadox 25 New Jersey Zinc Co. (K25-ZnO) and the other from Kanto Chemical Co. (Kan-ZnO).

Carbon monoxide oxidation on zinc oxide has been used for the subject of a large number of reaction mechanism and kinetic studies[2-4] as a model reaction in heterogeneous catalysis. They have roughly been classified into two groups based on: (1) Langmuir-Hinshelwood (L-H) mechanism, concerning chemisorbed CO and oxygen and (2) Eley-Rideal (E-R) mechanism with reaction between gaseous CO (or weakly adsorbed CO) and adsorbed oxygen. Also the two reaction pathways mechanism (one is L-H and the other is E-R pathways) may be proposed[4,5], because different active species are located on the surface

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such as O (neutral) and O^-[6]. Recently many works involving multi-pathway reactions have been reported[7]. When this idea is accepted, the overall region of the variations in reaction conditions such as gas composition and reaction temperatures may be subdivided into three different regions, each of which has an advantageous pathway: (1) L-H pathway, (2) E-R pathway and (3) mixed pathway.

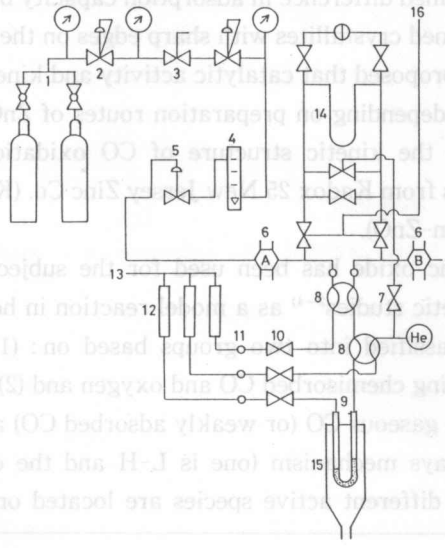
Generally, it is not so easy to clarify simultaneously the detail of comprehensive complex kinetic structure. The transient response method (TRM)[8,9] is a powerful tool to elucidate the mechanism of single pathway reaction. Let us apply TRM to the three regions and call this new method the patterned transient response method (PTRM). In the present study PTRM will be proved to be a useful tool for the analysis of multi-reaction pathways.

2. EXPERIMENTAL PROCEDURE

A schematic layout of the equipment used for transient response experiments is shown in Fig. 1. The gases employed were supplied by Takachiho Chemical Co. (all > 99.7 pure). Flowrates were controlled using Okura mass flow valves with an accuracy of ± 3 %.

In the present study, three gas streams could be set up, each containing a mixture of CO/O_2 /He and He of any desired composition. These were directed to two four way valves that have three inlet ports, one for each feed stream, and three outlet ports, two to two bypass lines and the other to the reactor. The pressure in the bypass lines was adjusted using a needle valve to ensure that the pressure in the three streams was equal. It has been shown that the switching of the four port valve gave a good approximation to a step change in feed composition.

The reactor used was a Pyrex glass tube in which a electrical conductivity cell was located at the end of catalyst bed. Step changes using He/N_2 mixture showed that the



1. Manifold
2. Pressure Regulator
3. Three Way Valve
4. Flowmeter
5. Flow Control Valve
6. Mixing Chamber
7. Stop Valve
8. Four Way Valve
9. Reactor
10. Needle Valve
11. Sampling Hole
12. Soap Meter
13. Effluent
14. Mercury Manometer
15. Furnace
16. Vacuum Pump

Fig. 1. Schematic layout of the experimental equipment used in the present study

reactor approximated very well to a piston flow reactor, in which the residence time was less than 15 sec.

The analysis was carried out using three Hitachi-164 chromatographs with a thermal conductivity detector. A Porapack Q column (1 or 2 m) was used for the analysis of CO_2 and a molecular sieve 5A column (0.5, 1 or 2m) was used to analyses CO, N_2 and O_2.

The catalysts used in this study are commercially available zinc oxide supplied from New Jersey Zinc Co. Kadox 25 and from Kanto Chemical Co. K25-ZnO was obtained from $ZnCO_3$ as a starting material, which is successively treated by the reduction, ignition, evaporation and oxidation in air, and Kan-ZnO was obtained from the oxidation of melted zinc metal. The X-ray diffraction analysis showed the same wurtzite-type crystalline structure of the two samples, whereas BET surface area was measured in a big difference as 4.0 m^2/g for Kan-ZnO and 20 m^2/g for K25-ZnO.

The electrical conductivity of the catalysts was measured by the same procedure as previously reported[10]. The catalyst (0.2 g) was sandwiched between two platinum electrode plates (0.97 mm i.d. and 0.5 mm thickness) pierced with 50 small holes. The d.c. conductivity was followed by measuring the voltage change of the standard resistor (100σ) using a microvoltmeter (Ohkura AM-1001 A).

All experiments were carried out at 1 atm pressure and a total flowrate range of 100 - 200 cm^3/min. Steady state experiments were performed to measure the effects of temperature, feed composition and space velocity on the activity of the catalysts. It has been shown by both experiment and calculation that under the experimental conditions chosen, both external and internal transport resistance are negligible.

NEC PC-9801DS was used to simulate the transient response curves. The reactor parameters used for the simulation are summarized in Table 1.

Table 1. List of Reactor Parameters

Catalyst	Reaction temperature (^0C) T	Catalyst surface area (m^2/g) S	Catalyst weight (g) W	Reactor length (cm) L	Superficial gas velocity (cm/min) U	Total amount of active sites (mol/g) 10^6 S_I	Total amount of active sites (mol/g) 10^6 S_{II}	Porosity (-) ε	Catalyst bed density (g/cm^3) ρ_c
K25-ZnO	130 - 170	20	78.3 (20-40 mesh)	58.7	204	1.1	1.1	0.56	1.7
Kan-ZnO	190 - 250	4.0	189.6 (20-40 mesh)	154 (190-250^{0}C) 55.4 (250^{0}C)	221.3	1.6	2.7	0.56	1.7

3. RESULTS AND DISCUSSION

3-1. Adsorption of Oxygen

A previous study[4] showed that oxygen was adsorbed on the surface of Kan-ZnO to form both neutral and O^- species. The amounts of the two species were evaluated, from the O_2-O_2 response curve and the O_2-σ response curve, to be $0.8*10^{-6}$ ($1.6*10^{-6}$ mole/g for active sites) and $1.35*10^{-6}$ ($2.7*10^{-6}$ mole/g for active sites) mole O_2 /g, respectively[4]. For K25-ZnO, by using the same techniques, they were given the same value $0.55*10^{-6}$ mole O_2 /g ($1.1*10^{-6}$ mole/g for active sites). The total amounts of the two active species were regarded as ones for the two active sites S_I and S_{II}. They were presented in Table 1.

3-2. Adsorption of CO and CO_2

The CO-CO response evaluated the amounts of adsorbed CO to be negligibly small on Kan-ZnO and $1.0*10^{-6}$ mol/g on K25-ZnO without depending on the concentration of CO. Fig. 2 illustrates the change in the electrical conductivity of catalyst during the reaction at steady state on K25-ZnO as a function of Pco, indicating no charge transfer between adsorbed CO and catalyst.

On the adsorption of CO_2, it obeys a Langmuir isotherm with the saturated amount of $2.7*10^{-6}$ mol/g on Kan-ZnO. A little amount of adsorption less than $3*10^{-6}$ mol/g, on the other hand, is observed on K25-ZnO, and one may assume that the adsorbed CO_2 has no serious effect on the reaction rate at present reaction conditions.

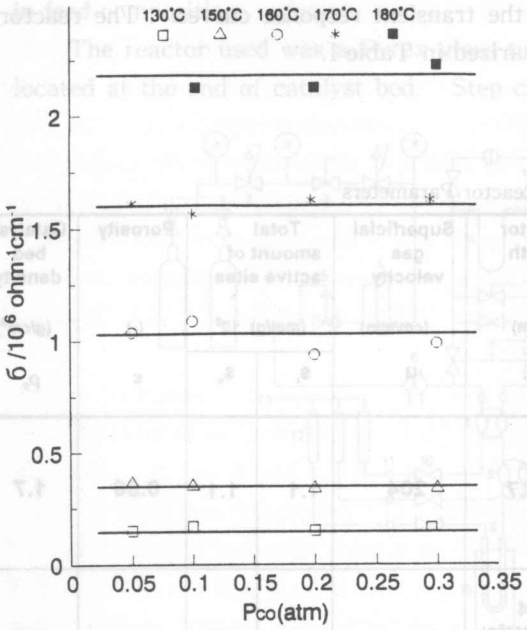


Fig. 2. Plots of σ as a function of Pco on K25-ZnO; Po_2=0.2 atm.

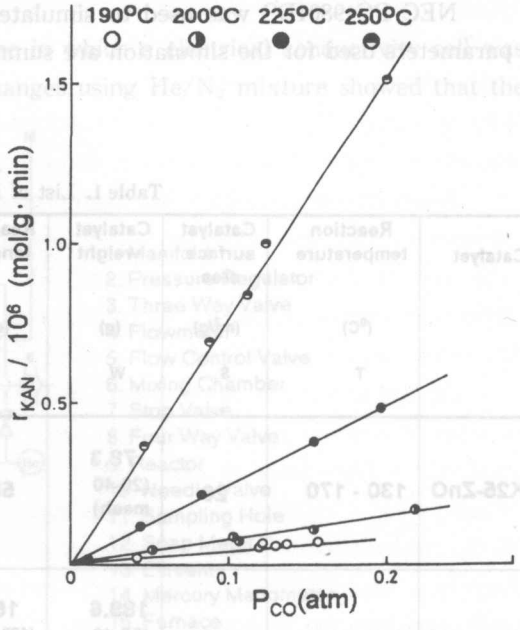


Fig. 3. Steady state rate r_{KAN} vs. Pco on Kan-ZnO; Po_2 =0.2 atm.

3-3. Reaction Model on Kan-ZnO

Fig. 3 illustrates the steady state rate as a function of P_{CO}. From this apparent linearity of the data, one can not recognize a two reaction pathway model. For the discrimination of the two pathway model, the transient response method can conveniently be applied.

The CO-CO_2 response curve indicated a characteristic mode which was derived into two parts: one was an instantaneous increase or decrease part at the initial stage of the response curve, and the other was a gradual change part approaching to a steady state level[4]. To explain this mode, the two path reaction model was proposed as follows.

Reaction path I which corresponds to the instantaneous response part

$$CO(g) + O^-S_I \xrightarrow{k_I} CO_2S_I + e \quad (1)$$

$$O_2(g) + 2S_I + 2e \rightleftarrows 2O^-S_I \quad (2)$$

$$CO_2S_I \rightleftarrows CO_2(g) + S_I \quad (3)$$

Reaction path II which corresponds to the slow response part

$$CO(g) + OS_{II} \xrightarrow{k_{II}} CO_2S_{II} \quad (4)$$

$$O_2(g) + 2S_{II} \rightleftarrows 2OS_{II} \quad (5)$$

$$CO_2S_{II} \underset{K_{CO_2}}{\overset{k_{IICO_2}}{\rightleftarrows}} CO_2(g) + S_{II} \quad (6)$$

Since both the rates of oxygen adsorption and carbon dioxide desorption are very fast (because the reaction rate is the zero order with respect to P_{O_2} and the transient response of CO_2 shows the instantaneous mode) in the reaction path I, k_I is easily calculated from the graphical analysis of the response curve of CO_2 formed. In reaction path II, k_{II}, k_{IICO_2} and K_{CO_2} are also calculated from the linear plot of P_{CO}/r_{II} vs. P_{CO_2} because r_I can separately be evaluated. All the kinetic parameters obtained are summarized in Table 2.

Table 2. Summary of the calculated parameters (Kan-ZnO).

Temp.	k_I /10^{-6}	k_{II} /10^{-6}	k_{IICO_2} /10^{-7}	K_{CO_2}
190°C	0.26	0.39	0.219	991
200°C	0.50	0.5	0.435	650
225°C	2.1	0.69	2.14	112
250°C	6.6	1.1	9.07	27.5

3-4. Reaction Model on K25-ZnO

In our previous paper[5], it has been demonstrated that the steady state rate has both a maximum and a minimum points, which can not be explained by a single reaction pathway model. The following two reaction pathway model is proposed.

Reaction path I

$$CO(g) + S_1 \underset{K_1}{\overset{k_1}{\rightleftharpoons}} CO\,S_1 \quad (7)$$

$$O_2(g) + 2S_1 \underset{K_2}{\overset{k_2}{\rightleftharpoons}} 2O\,S_1 \quad (8)$$

$$CO\,S_1 + OS_1 \xrightarrow{k_3} CO_2(g) + 2S_1 \quad (9)$$

Reaction path II

$$O_2(g) + 2S_2 \underset{K_4}{\overset{k_4}{\rightleftharpoons}} 2O\,S_2 \quad (10)$$

$$CO(g) + OS_2 \xrightarrow{k_5} CO_2(g) + S_2 \quad (11)$$

All the kinetic parameters are evaluated by the steady state rate analysis using a linear estimation technique as shown in Fig. 4 for Po_2 and in Fig. 5 for Pco. The values of kinetic parameters are presented in Table 3.

For reaction path II, k_5 can easily be evaluated from the initial height (Δr_{E-R}) of the instantaneous response curve at Pco higher than Pco = 0.40 atm, in which reaction path II is advantage[11]. Δr_{E-R} is plotted as a function of the values of CO-concentration jump (ΔPco) employed in the transient response and it is shown in Fig. 6. From the slope of the straight lines obtained, one can calculate k_5 at all temperatures and they are presented in Table 3.

By using the kinetic parameters obtained, one can visualize a rate surface of total reaction as shown in Fig. 7. As can be seen, the predicted rate surface over the whole range of feed composition reflects the effects of carbon monoxide and oxygen partial pressures on the rate

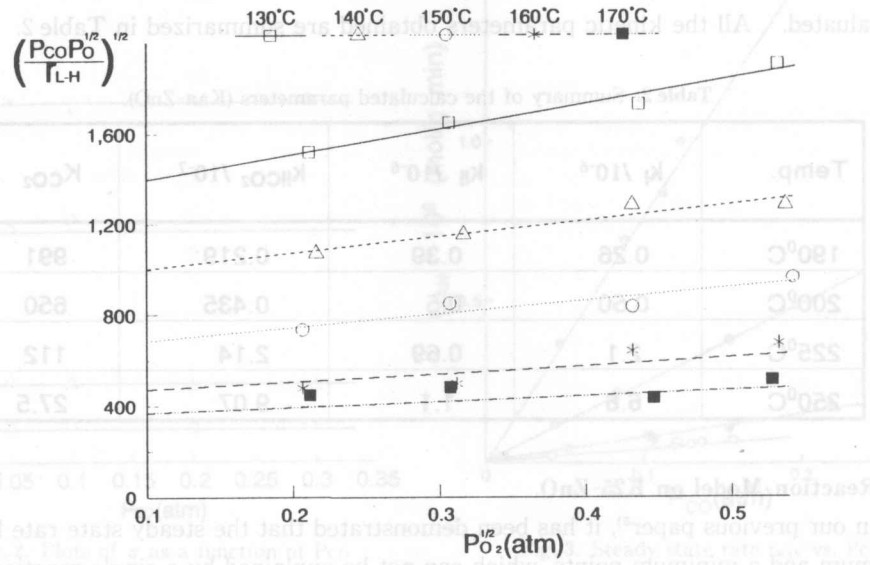


Fig. 4. Linear correlation of the steady state rate data as a function of Po_2 on K25-ZnO.

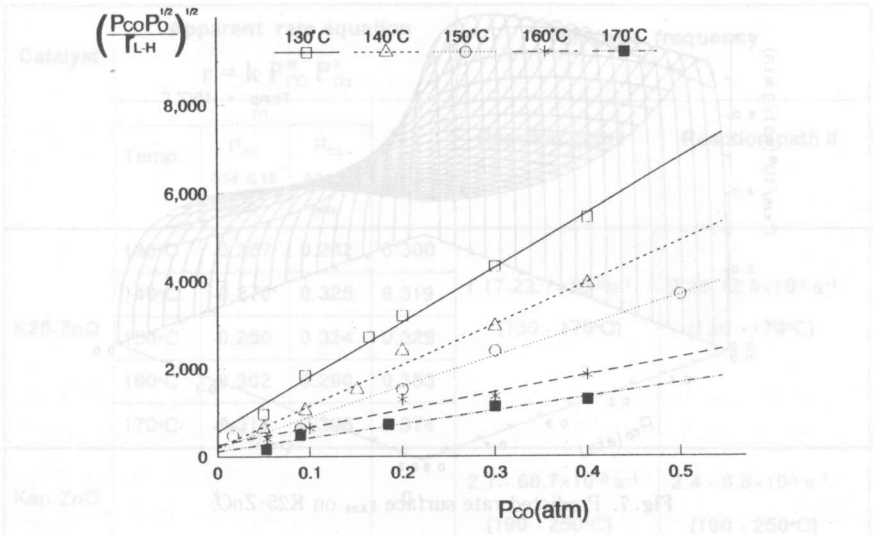


Fig. 5. Linear correlation of the steady state rate data as a function of Pco on K25-ZnO.

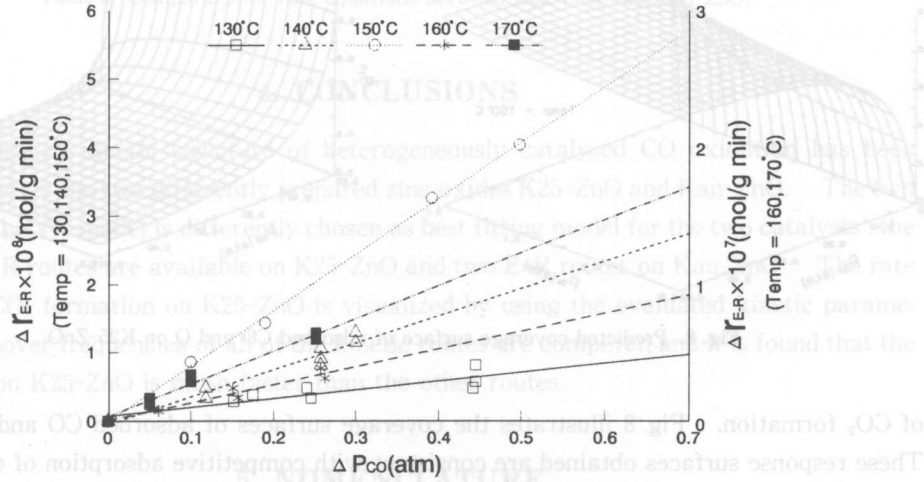


Fig. 6. Plots of Δr_{E-R} vs. ΔPco on K25-ZnO.

Table 3. Summary of the calculated parameters (K25-ZnO).

Temp.	k_1, k_2	K_1	K_2	k_3	k_4	K_4	k_5
130°C	3.88×10^{-5}	249	382	7.76×10^{-8}	9.25×10^{-6}	105	1.85×10^{-8}
140°C	8.10×10^{-5}	198	208	1.62×10^{-7}	2.63×10^{-5}	30.4	5.26×10^{-8}
150°C	1.73×10^{-4}	145	113	3.46×10^{-7}	6.85×10^{-5}	10.1	1.37×10^{-7}
160°C	4.01×10^{-4}	122	65.1	8.02×10^{-7}	1.63×10^{-4}	3.1	3.25×10^{-7}
170°C	7.50×10^{-4}	103	34.8	1.50×10^{-6}	4.25×10^{-4}	1.14	8.50×10^{-7}

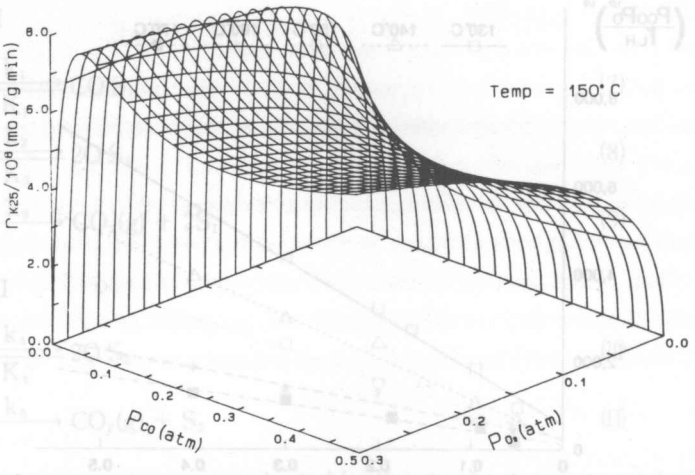


Fig. 7. Predicted rate surface r_{K25} on K25-ZnO.

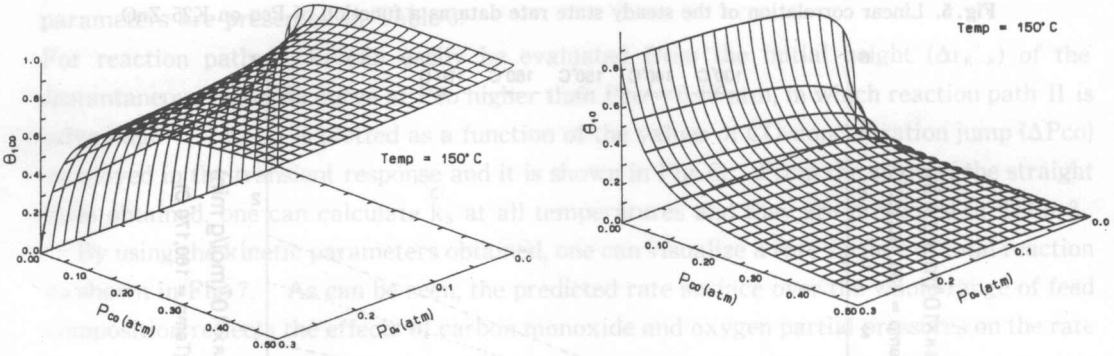


Fig. 8. Predicted coverage surface of adsorbed CO and O on K25-ZnO.

of CO_2 formation. Fig. 8 illustrates the coverage surfaces of adsorbed CO and oxygen. These response surfaces obtained are consistent with competitive adsorption of oxygen and carbon monoxide.

3-5. Surface Reactivity of K25 and Kan-ZnO

The two zinc oxides indicate almost same pattern of X-ray diffraction even though they give a big difference of surface area. Based on the surface area, the turnover frequency (T. F.) of CO_2 formation for the two catalysts can be compared by using an extrapolation at 190°C for K25-ZnO and the values are presented in Table 4. The L-H mechanism in reaction path I on K25-ZnO shows higher value of T.F. ($9.32*10^{-2}\ s^{-1}$) than ones of E-R mechanism ($6.24*10^{-2}\ s^{-1}$). In reaction path II, T. F. on K25-ZnO ($6.24*10^{-2}\ s^{-1}$) is also much higher than one on Kan-ZnO ($2.4*10^{-3}\ s^{-1}$). From these results, one may recognize that K25-ZnO has much reactive surface rather than Kan-ZnO. In the present study, one can not clarify the reason why the former is much active. One possible explanation will be considered to be the difference of the form of crystallites, as has been reported by Bolis et all[1].

Catalyst	Apparent rate equation $r = k P_{CO}^{m} P_{O_2}^{n}$				Turnover frequency	
	Temp.	m P_{CO} 0.04 -0.18 (atm)	m P_{CO} 0.34 -0.7 (atm)	n	Reaction path I	Reaction path II
K25-ZnO	130°C	-0.287	0.282	0.300	1.17-22.7×10^{-3} s^{-1} (130 - 170°C)	0.28-12.9×10^{-3} s^{-1} (130 - 170°C)
	140°C	-0.270	0.325	0.319		
	150°C	-0.250	0.334	0.329		
	160°C	-0.302	0.290	0.353		
	170°C	-0.317	0.336	0.374		
Kan-ZnO	1			0	2.7 - 68.7×10^{-3} s^{-1} (190 - 250°C)	2.4 - 6.8×10^{-3} s^{-1} (190 - 250°C)

Table 4. Comparison of rate equations between K25-ZnO and Kan-ZnO.

4. CONCLUSIONS

The detailed kinetic structure of heterogeneously catalysed CO oxidation has been demonstrated on the two differently prepared zinc oxides K25-ZnO and Kan-ZnO. The two reaction pathways model is differently chosen as best fitting model for the two catalysts : the L-H and E-R routes are available on K25-ZnO and two E-R routes on Kan-ZnO. The rate surface of CO_2 formation on K25-ZnO is visualized by using the evaluated kinetic parameters. Turnover frequencies of all of the kinetic routes are compared and it is found that the L-H route on K25-ZnO is mush faster than the other routes.

5. NOMENCLATURE

E-R : Eley-Ridel mechanism

K_{CO2}, K_1, K_2, K_4 : equilibrium constant for equations (6), (7), (8) and (10), respectively (atm^{-1})

k_{IICO2}, k_1, k_2,k_4 : forward rate constant for equations (6), (7), (8) and (10), respectively (mol/g min atm)

k_I, k_{II}, k_3 : rate constant for equation (1), (4) and (9) (mol/g min)

k_5 : rate constant for equation (11) (mol/g min atm)

L-H : Langmuir-Hinshelwood mechanism

Pco : partial pressure of CO (atm)

Po_2 : partial pressure of O_2 (atm)

r_{KAN}, r_{K-25} : steady state rates of CO formation on Kan-ZnO and K25-ZnO, respectively (mol/g min)

Δr_{E-R} : differential reaction rate of E-R part evaluated by the CO-CO response curve (mol/

g min)

S_I, S_{II} : active site for catalytic reaction path I and II, respectivelly (-)

T : temperature (K)

T. F. : turnover frequency (rate constant at rate determining step/total amount of active site S_I or S_{II}) (s^{-1})

W : weight of catalyst (g)

σ : electrical conductivity of the catalyst ($\Omega^{-1}\,cm^{-1}$).

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