室蘭工業大学
学術資源アーカイブ
Muroran Institute of Technology Academic Resources Archive

# Pulsed oxidation reaction of CO over WO3 catalyst



| メタデータ | 言語: English<br>出版者: 室蘭工業大学<br>公開日: 2014-07-28<br>キーワード (Ja):<br>キーワード (En):<br>作成者: 金木, 則明, UNNO, Tatsuo, 原, 弘, 島田, 浩次, 城本, 義光<br>メールアドレス:<br>所属: |
| --- | --- |
| URL | http://hdl.handle.net/10258/3698 |

# PULSED OXIDATION REACTION OF CO OVER $WO_3$ CATALYST

Noriaki Kaneki, Tatsuo Unno, Hiroshi Hara,
Koozi Shimada, and Yoshiteru Jomoto

**Abstract**

The pretreatment of $WO_3$ catalyst used for the CO oxidation reaction was shown to require that it should be degassed under vacuum ($10^{-6}$torr), for 8 hours at room temperature. An unsteady state pulsed reaction rate, having a decay fraction for CO oxidation over $WO_3$, was also proposed.

## Introduction

$WO_3$ has been extensively studied as a catalyst and co-catalyst. The most important properties are antiferroelectricity and n-type semiconductor. It is used extensively as a catalyst in hydrogenation, polymerization, isomerization of olefins, hydrolysis and esterification of alchols, and pyrolysis of other compounds. It was reported that the temperature coefficient of electrical resistance of $WO_3$ ceramics, change from negative to positive by oxygen gas adsorbed on the surface of $WO_3$ at about 400°C.[1]

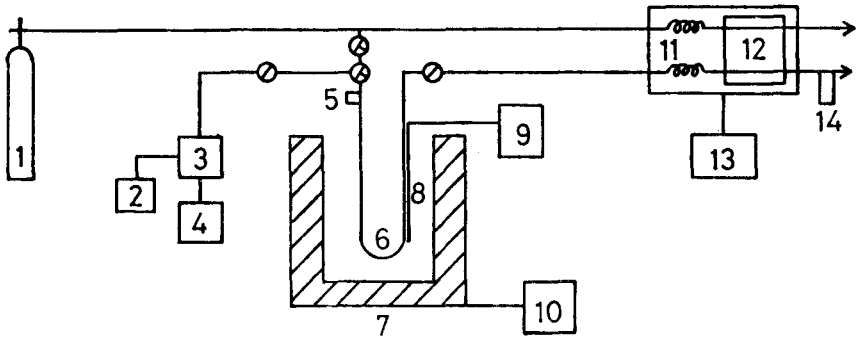
This paper reports a preparation conditions producing a catalyst having high activity for oxidation of CO and an unsteady reaction rate equation for CO oxidation over $WO_3$ by a convenient pulse technique. This reaction simultaneously involves a catalytic reaction and a decreased activity reaction because the two types of sites on the catalytic surface show different adsorption rates.

## Methods

$WO_3$ catalyst samples were prepared from a high purity p-tungsten ammonium powder. The powder was mixed in a ball mill for 2 hours, pressed into pellets at 1000Kg/cm$^2$, calcined in air at 300°C and screened at 24~60 Tyler mesh range.

The fixed reaction apparatus included a convenient gaschromatograph, a reactor and a vacuum manifold as shown in Fig. 1. A pure He gas(99.99999%) was flowed through the reactor as a carrier gas. Both the reactant gases, CO, and $O_2$, were also purified by a usual technique. Gases were analyzed by gaschromatography using a squalancesilicagel and an activated charcoal column.

Experimentally it was found by this study that the relations between catalyst amount or pulse volume and product gas volume were directly proportional under the operating conditions chosen. The following sets of operating conditions were specified: pulsed volume: 0.5ml, catalytic amount: 0.5g, reaction temperature: 500°C and flow volume of carrier gas in the reactor: 40ml/min. The pulse length was less than 1% of the tube length of the reactor. The pulsed reaction was carried out as follows: after the catalyst was placed in the reactor,




| | | |
|---|---|---|
| 1. Gas supply | 6. Reactor | 11. Colum |
| 2. Vacuum gauge | 7. Furnace | 12. Cell |
| 3. Vacuum pump | 8. Thermocouple | 13. Recorder |
| 4. Diffusion pump | 9. Thermometer | 14. Flow meter |
| 5. Injection | 10. Power regulator | |

**Fig. 1**

the atmosphere inside the reactor was changed from air to the following alternative conditioning treatments : (1) Helium at room temperature for approximately 1 hour, followed by heating for a 3 hour period until a temperature of 500°C was reached. (2) Air at room temperature for approximately 1 hour, followed by heating for a 3 hour period until a temperature of 500°C was reached. (3) vacuum ($10^{-6}$torr) at room temperature for 8 hours, followed by heating for a 3 hour period until a temperature of 500°C was reached. (4) Hydrogen at room temperature for approximately 1 hour, followed by heating for a 3 hour period until a temperature of 500°C was reached. At the end of the conditioning period, the carrier gas is flowed through the reactor at a flow rate of 40 ml/min. and a mixed gas 0.5 ml is pulsed into the reactor with a millilitersyrige. The pulsed reactant gas was a mixture of carrier gas combined with CO and $O_2$. A 2:1 ratio of CO to $O_2$ was used in the gas mixture. The conversion ratio of product gas $CO_2$ obtained by a pulsed test is defined by the following relation:

$$\text{conversion ratio } [\%] = \frac{\text{product } CO_2 \text{ in pulse}}{\text{reactant CO in pulse}} \times 100$$

## Result

The first conversion of product $CO_2$ by the first pulse depends on the pretreatment of the sample under the variable atmosphere. The first conversion results obtained by the first pulse were given in Table 1. Vacuum pretreatment was thus chosen as the reference

Table 2 Effect of contaminative gas

| contaminative gas | conversion (%) |
|---|---|
| no contamination | 5.2 |
| $CO_2$ | 5.2 |
| CO | 5.0 |
| $O_2$ | 0.8 |

pulse gas ; $CO:O_2 = 2:1$
reaction temp. ; 500 (°C)

Table 1 Conversion vs. atmosphere

| atmosphere | conversion (%) |
|---|---|
| He | 3.4 |
| Air | 0.8 |
| Vacuum | 5.2 |
| $H_2$ | 0.3 |

calcining temp. ; 300 (°C)
reaction temp. ; 500 (°C)
calcining temp. atmos. ; air
pulse gas ; $CO:O_2 = 2:1$

condition for effect of contaminant gas. After pretreatment of the sample under vacuum, the sample was fully contaminated with each gas(CO, $CO_2$ and $O_2$) by the pulse technique. The first conversion results obtained by the first pulse were listed in Table 2. However, it was found that contaminated samples degassed under vacuum completely recovered the catalytic activity. Fig. 2 shows the conversion of $CO_2$ as influenced by pulse time and oxygen molar fraction [$O_2$mol/(CO+$O_2$)mol].

## Discussion

According to the results shown in Table 1 and 2, the first conversion of $CO_2$ of the samples pretreated under He and vacuum was higher than the $CO_2$ conversion of the samples under Air and $H_2$. Furthermore, no inhibition of the first conversion of $CO_2$ was observed by the addition of CO and $CO_2$, but $O_2$ gas had the inhibition effect. It seems that CO and $CO_2$ gases are seldom adsorbed on the surface of $WO_3$, but $O_2$ gas is easily adsorbed. On the other hand, in the pretreatment with a reducing gas such as $H_2$, the first conversion of $CO_2$ is noticeably reduced. This may due to the fact that reduced $WO_3$ has less catalytic activity because the $H_2$ may have changed $WO_3$ into other compounds such as $W_2O_3$ and $WO_2$ that don't show catalytic activity for the CO oxidation reaction. The results for Fig. 2 reveal that the first conversion of $CO_2$ increased with a increasing oxygen partial pressure in the first pulse, but, also, on the second and later pulses, the conversion of $CO_2$ decreased with increasing pulse time. Thus it would seem that the $WO_3$ sample from which a part of oxygen is degassed, shows enhanced catalytic activity of CO oxidation. The reaction is enhanced with increasing oxygen partial pressure of the pulse. The discrepancy between surface with pretreating under vacuum and without was not observed by X-ray diffraction. It appears that the surface on the catalyst $WO_3$ was reduced under vacuum because the color of the surface on the catalyst pretreated under vacuum changed from yellow to dark green. It is a necessary operation that a $WO_3$ oxidation catalyst be partially degassed under vacuum or inert gas. Our experiment found that $WO_3$ has higher activity under vacuum than under He.

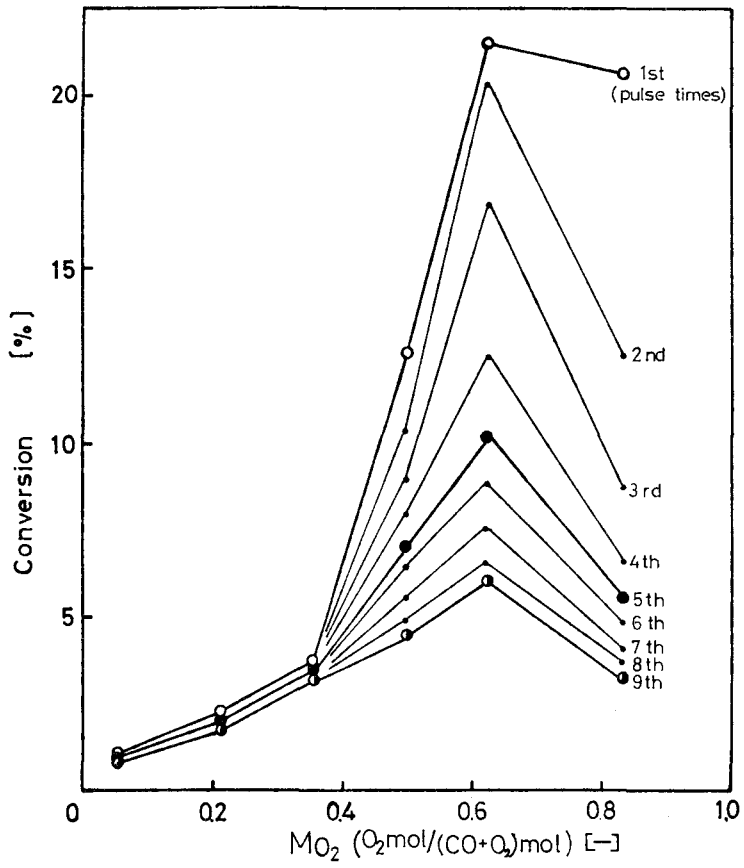

Conversion [%]
20
15
10
5
0
0.2
0.4
0.6
0.8
1.0
$MO_2$ ($O_2$mol/(CO+$O_2$)mol) [—]
1st
(pulse times)
2nd
3rd
4th
5th
6th
7th
8th
9th

Fig. 2

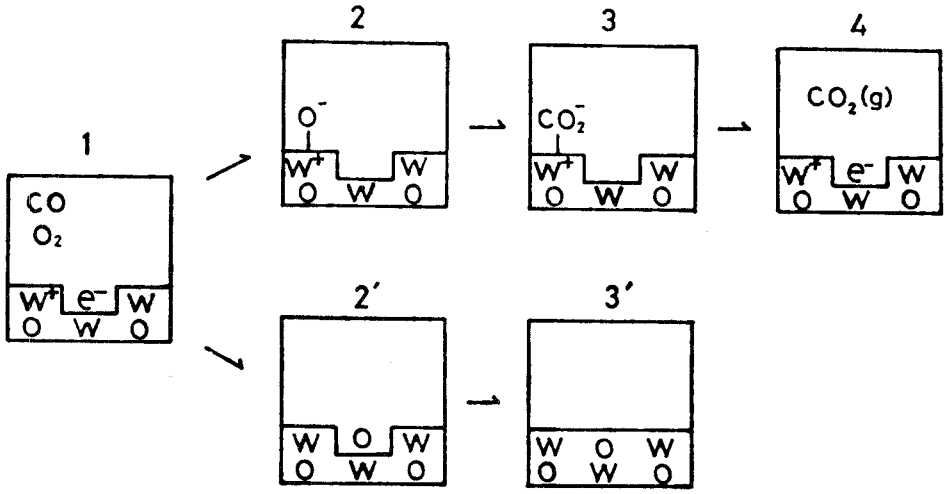

1
CO
$O_2$
$W^+$ $e^-$ W
O W O
2
$O^-$
$W^+$ W
O W O
3
$CO_2^-$
$W^+$ W
O W O
4
$CO_2$(g)
$W^+$ $e^-$ W
O W O
2′
W O W
O W O
3′
W O W
O W O

Fig. 3

From the above experimental results, although the reaction mechanism of CO oxidation over $WO_3$ has to be discussed in more detail, for this discussion, it is assumed that the oxidation reaction is proceeded as in Fig. 3. A picture of formation of oxygen defect on the surface of $WO_3$ that degassed under vacuum is shown in the block 1 of Fig. 3. When a gas mixture of CO and $O_2$ was introduced on the active catalyst $WO_3$ by a pulse, a donor molecular oxygen is first adsorbed on the surface of ionized metal, as shown on block 2. Block 3 reveals that the oxygen shown in the block 2 reacts with an electron accepter molecular CO. In block 4, a produced $CO_2$ releases from the surface of $WO_3$ and the resulting surface state for the catalytic reaction is similar to that of starting block 1. The results shown in Fig. 2 also reveal that the catalytic activity was decreased with an increase of pulse time. We offer that any reaction path other than the process shown in blocks 1 to 4 in Fig. 3 would occur in parallel. The parallel reaction ( blocks 2' and 3') reduced catalytic activity at the same time as the catalytic reaction took place as shown with blocks 1 to 3' in Fig. 3. The blocks in Fig. 3 showed that $O_2$ gas is again adsorobed on the same site of the oxygen defect formed under vacuum as shown in a block 2' and the state of $WO_3$ prior to the vacuum pretreatment is reduced in block 3'. The $WO_3$ shown in block 3' in Fig. 3 showed less catalytic activity. But the $WO_3$ will be again recovered by treatment by vacuum. A distinction of oxygen between 2 and 2' in Fig. 3 is believed to be due to different isomeric oxygen species. However, in this paper, the distinction is not clearly explained.

If the catalytic reaction proceeds according to the model discussed above, the model that was proposed to explain the reaction may be written in the following reaction form. The state on the surface of $WO_3$ pretreated under vacuum is

$$WO_3 \rightarrow WO_{3-x} + \frac{x}{2}O_2 \qquad (1)$$

where, $WO_{3-x}$ shows the state of $WO_3$ pretreated under vacuum, but the value x is small enough to be neglected.

The $WO_{3-x}$ that is electrically in equilibrium is

$$WO_{3-x} \rightleftarrows WO^{+}_{3-x} + e^{-} \qquad (2)$$

The ionized metal reacts with $O_2$ gas, and so, a complex compound is produced

$$\frac{1}{2}O_2(g) + WO^{+}_{3-x} + e^{-} \rightarrow O^{-}W^{+}O_{3-x} \qquad (3)$$

The complex also reacts with CO gas

$$O^{-}W_{3-x} + CO(g) \rightarrow CO^{-}_{2}W^{+}O_{3-x} \qquad (4)$$

After reaction, the produced gas $CO_2$ is released

$$CO^{-}_{2}W^{+}O_{3-x} \rightarrow CO_2(g) + W^{+}O_{3-x} + e^{-} \qquad (5)$$

Thus, the total catalytic reaction is

$$WO_{3-x} + \frac{1}{2}O_2(g) + CO(g) \rightarrow W^{+}O_{3-x} + e^{-} + CO_2(g) \qquad (6)$$

If the rate determing step is assumed to be the oxygen adsorption in equation 3 in our experimental results, then the first pulsed reaction can be:

$$V_1' = k_1'[W^+O_{3-x}][e^-]P_{O_2}^{1/2} \quad (7)$$

Equation 2 allows the derivation of equation:

$$[W^+O_{3-x}] = [e^-], \quad K = [W^+O_{3-x}][e^-] \quad (8)$$

Equation 8 can be rearranged to yields:

$$V_1' = k_1'KP_{O_2}^{1/2} \quad (9)$$

Where, k is a reaction rate constant, and k is an equilibrium constant.

Below, we now write the other poisoning reaction mechanism shown in blocks 1 to 3' of Fig. 3 for the above catalytic reaction. We can write:

$$\frac{1}{2}O_2 + W^+O_{3-x} + e^- \rightarrow WO_3 \quad (10)$$

Then the reaction rate is presented

$$V_1'' = k_1''[W^+O_{3-x}][e^-]P_{O_2}^{1/2} \quad (11)$$

thus, the reaction rate which is really observed by the first pulse will be the differences between the equation 9 and 11

$$V_1 = K(k_1' P_{O_2}^{1/2} - k_1'' P_{O_2}^{1/2}) \quad (12)$$

then, in the second pulse or much more, we must consider that the fraction of active sites decreased by the each pulse. Let term $\alpha$ be the fraction of active sites that disappeared by a pulse. Then, in the second pulse reaction, the catalytic reaction is

$$\frac{(1-\alpha)}{2}O_2 + (1-\alpha)W^+O_{3-x} + (1-\alpha)e^- \rightarrow (1-\alpha)O^-W^+O_{3-x} \quad (13)$$

where $1-\alpha$ is the fraction of active species. Similarly, the reaction occured between the surface of $WO_3$ and oxygen gas in the second pulse is

$$\frac{(1-\alpha)}{2}O_2 + (1-\alpha)W^+O_{3-x} + (1-\alpha)e^- \rightarrow (1-\alpha)WO_3 \quad (14)$$

then, in the second pulse, the net reaction rate observed is:

$$V_2 = K^{(1-\alpha)}(K_2' P_{O_2}^{\frac{1-\alpha}{2}} - K_2'' P_{O_2}^{\frac{(1-\alpha)x}{2}}) \quad (15)$$

Thus, in the n-th pulse, the reaction rate is:

$$V_n = K^{(1-\alpha)^{n-1}}(k_n' P_{O_2}^{\frac{(1-\alpha)^{n-1}}{2}} - k_n'' P_{O_2}^{\frac{(1-\alpha)^{n-1}x}{2}}) \quad (16)$$

If we put $x \ll 1$ and the second term is smaller than the first term in right side of the equation 16, that is, when the amount of degassed oxygen on the surface of $WO_3$ under vacuum is smaller, the equation 16 can simplify to:

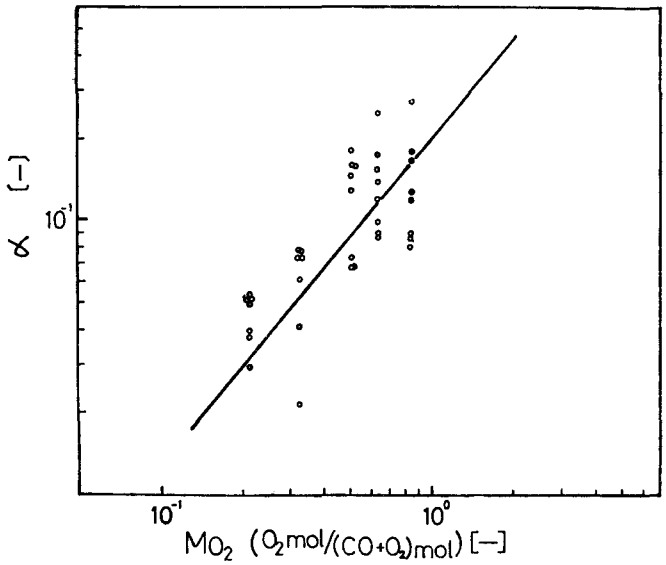



**Fig. 4**

$$V_n = K' P_{O_2}^{\frac{1-(n-1)\alpha}{2}} \tag{17}$$

where, $K' = k'_n K^{(1-\alpha)^{n-1}}$

Fig. 4 reveals the relation between the fraction of active sites disappeared $\alpha$ and oxygen molar fraction $Mo_2$ [$O_2$mol/($O_2$+CO)mol]. The correlation equation that was fitted to these data is about

$$\alpha = 0.2 M_{0.2}^{1.15} \tag{18}$$

where, $\alpha[-] = \dfrac{A_n - A_{n+1}}{A_n}$

$A_n$ and $A_{n+1}$ are present with $CO_2$ conversion of n th and (n+1)th pulse. According to equations 17 and 18 and Fig. 2, in the same pulse times, a pulse reaction increases with increasing oxygen partial pressure in a pulse. But, the fraction of decreased active sites, $\alpha$, also increases with increasing oxygen partial pressure, as shown in Fig. 4. Futhermore, the reaction for oxygen partial pressure will increase with increasing oxygen partial pressure up to a peak value, and then decrease thereafter as shown in Fig. 2. On the other hand, for a given pressure, increaing the pulse times causes the slope of the decay curve to increase.

From these experimental results as shown in Fig. 2, a quantitative comparison of the model developed in this paper with the results obtained experimentaly is extremely difficult because of the problems that arise in the precise evaluation of such parameters as k and K in an experimental reaction. However, the qualitative comparison of theoretical and experimental results is not difficult. Representative curves from these experimentals are shown in Fig. 2. These feature qualititavely the characteristic of model presented herein as indicated by the equation 16. In view of the model presented here, it seems that the rate-determing

step is a oxygen adsorption process on the surface of the $WO_3$ catalyst and the unsteady state reaction rate is given by an equation having a decay fraction because of the existence of two types of sites on the catalytic surface, may show different adsorption reaction rates.

## Conclusions

A technique for pretreating of $WO_3$ catalyst under vacuum ($10^{-6}$Torr), for 8 hours, at room temperature was shown. $WO_3$ preteated had a high catalytic activity and an unsteady state equation having a decay function for the CO-$O_2$ pulsed reaction over $WO_3$ was obtained.

(Received May.9.1979)

Nomenclature

| | |
|---|---|
| A=$CO_2$ conversion | [%] |
| k=rate constant of reaction | [mol・$cm^3$/sec・$atm^{1/2}$] |
| K=equilibrium constant | [$cm^{-6}$] |
| $M_{O_2}$=molar fraction of oxygen | [-] |
| $P_{O_2}$=partial pressure of oxygen | [atm] |
| V=rate of reaction | [mol/$cm^3$・sec] |
| $\alpha$=decay fraction | [-] |

subscripts

1, 2, n = pulse time

superscripts

'=active reaction

"=reaction of poisoning

### Literature Cited

1) Kaneki, N., H. Hara, K. Shimada and T. Shimizu : J. Amer. Ceramics Soc., 59, 368 (1976)