Effect of Zirconia and Nickel Doping on the Reduction Behavior of Tungsten Oxide in Carbon Monoxide Atmosphere

Fairous Salleh, Tengku Shafazila Tengku Saharuddin, Alinda Samsuri, Rizafizah Othaman, and Mohd. Ambar Yarmo

Abstract—The reduction of undoped tungsten oxide (WO_3) and doped tungsten oxide has been studied by using temperature programmed reduction (TPR) and characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and transmission electron microscope (TEM) analysis. Zirconia (Zr) and nickel (Ni) doped tungsten powder were prepared by impregnation method. The effect of Zr and Ni doping on reduction of WO_3 and the effect of holding time on reduction were also studied. The reduction behavior were examined by nonisothermal reduction up to 900 ℃ then continued with isothermal reduction at 900 ℃ for 45 min under (40 %v/v) carbon monoxide in nitrogen (CO in N_2) atmosphere. The results show that, TPR spectra of doped powder slightly shift to a lower temperature (℃) as compared to the undoped WO_3. The reduction steps involved in the undoped WO_3, 10 mol% Zr and 10 mol% Ni to WO_3 were found $WO_3 \rightarrow WO_2$ and W, $WO_3 \rightarrow WO_2$, W and W_2C and $WO_3 \rightarrow WC$ and $Ni_{0.98}C_{0.02}$ respectively. The carbide formation from reduction WO_3 in this study revealed that WO_2 and W could transform to carbide in excess of CO introduction. The ability to enhance the reducibility involved in WO_3 may associate to the presence of zirconium tungsten ($Zr(WO_4)_2$) compound and nickel tungsten oxide ($NiWO_4$).

Index Terms—Carbon monoxide, nickel, tungsten, tungsten oxide, zirconia.

I. INTRODUCTION

Tungsten can form as hard steel-grey metal that is often brittle and hard to work. Among other metal in pure form, tungsten has high melting point (3422 ℃), high hardness (3.43 GPa), high boiling point, low evaporation rate at high temperature and low thermal expansion coefficient (4.5×10^{-6} K^{-1}) [1]. The demand for tungsten is increasing in industries due to its good mechanical, electrical, electro erosive properties. As a results, it is the most commonly used metal for high temperature applications such as filament in light bulbs, rocket nozzles in space craft [2].

However, about 60 % uses of tungsten in hard-metals industry as tungsten carbide (WC). It is due to their good in hardness which close to diamond and has great abrasion, low coefficient of thermal expansion and corrosion resistance. The properties is crucial in manufacturing industry for metal, forming tools and dies, mining and abrasive tools which can be employed in high pressure, temperature, and corrosion circumstances [3], [4].

Tungsten oxides are most frequently used as starting material for producing metal tungsten powder [5] whereas, tungsten carbide synthesized by a solid-state reaction between W metal and C at 1200 – 2000 ℃ under controlled atmosphere [6].

Several of method for reduction of WO_3 has widely been studied. Reduction of WO_3 powders by hydrogen is one of the widely used methods to obtain metallic tungsten of high purity. Reference [7] reported that WO_3 is completely reduced to metallic at 800 ℃ in hydrogen atmosphere via formation of intermediate phases $WO_{2.72}$ (~ 520 ℃) and WO_2 (~ 600 ℃).

Moreover, carbon monoxide also can be used as a reducing agent [8] was studied the reduction of WO_3 with carbon monoxide by using TGA. The intermediate phases $W_{20}O_{58}$, $W_{18}O_{49}$ and WO_2 were observed in the reduction, and the final product is WC. Generally hydrogen reduction of tungsten oxide divided into two stages: (i) a low-temperature stage (< 777 ℃) which can reduce $WO_3 \rightarrow WO_2$ involving formation and reduction of three intermediate suboxide of ($WO_{2.96}$, $WO_{2.9}$ and $WO_{2.72}$, and (ii) high temperature stage (> 777 ℃) which reduce WO_2 to W [9].

Other than reducing agent, a foreign element could also influence WO_3 reduction by altering the reaction sequence and/or by changing nucleation and growth [10]. Reference [11] explored the zirconia-supported tungsten oxide reduction by methane reforming. The reduction divided into three stages namely: the reduction of WO_3 to WO_2, reduction of WO_2 to W and then significant methane decomposition. The optimal operating temperature range was 900 to 1000 ℃ [11]. Addition of ZrO_2 to WO_3 can enhance their catalytic activity and stability by improving their oxygen storage capacity, reducibility, and resistance to sintering effect [12].

The reduction and carburization of $NiO-WO_3$ mixture was performed to prepare homogenous Ni-WC composite powders. Reduction of WO_3 occurred at temperatures higher than 650 ℃. It has been reported at temperatures above 900 ℃, the carburization to WC take place, otherwise W_2C would be the primary carbide [3].

The reduction of WO_3 was investigated under 40 % CO in N_2 as a reducing agent by using the temperature programmed

reduction (TPR) and characterized by XRD. The objectives of this work are to enhance the reduction behavior by study the influence of different type of doping agents on reduction behavior and investigated the reduction product produced by varying holding reaction time.

II. MATERIALS AND METHODS

A. Chemical and Raw Materials

Powder of model (commercial) tungsten metal (IV) oxides $WO_3 \geq 99\%$, zirconyl chloride octahydrate, $Cl_2OZr.8H_2O$ (98+%) from Acros Organics, nickel nitrate, $Ni(NO_3)_2.6H_2O$ from Merck and ethanol, C_2H_6O (99.5%) from Systerm® are pure and used as supplied.

B. Catalyst Preparation

Two different doped tungsten oxides: zirconia and nickel were prepared by impregnation method. The impregnation was prepared by using a zirconyl chloride octahydrate $(Cl_2OZr.8H_2O)$ and tungsten trioxide (WO_3) powder. The amount of zirconia added was 10 mol% of total metal cation. Moreover, for 10 mol% of $Ni-WO_3$ was prepared by using nickel nitrate $(Ni(NO_3)_2.6H_2O)$ and WO_3. The compounds were dissolved in water with additional of ethanol at 60 ℃ with stirring for 4 hours, producing a viscous mixture. The solution was evaporated to dryness while stirring for 4 hours, then dried at 120 ℃ overnight followed by calcination in air at 600 ℃ for 4 hours. The calcined solid was crushed and stored in a vial.

C. Temperature Programmed Reduction (TPR)

Reduction of the undoped WO_3, zirconia doped WO_3 and nickel doped WO_3 were performed by using a Micromritics Autochem 2920 Chemisorption Analyzer apparatus. The completeness of the reduction of the powder was analysed using a temperature programmed reduction (TPR) method. 5 – 7 mg of the samples were carried out in nonisothermal mode up to 900 ℃ under streaming gas mixture of 40 % of CO in N_2 with a heating rate of 10 ℃/min with flow gas carrier rates 20 ml/min. Then, the experiment continued for isothermal mode hold for 15, 30 and 45 min at 900 ℃.

D. Characterization

XRD analysis of test samples was performed by using XRD's Bruker AXS D8 Advance type with X-ray radiation source of Cu Kα (40kV, 40 mA) to record the 2θ diffraction angle from 10 ° to 80 ° at wavelength ($\lambda = 0.154$ nm) of 1 g sample. For identification purposes of crystalline phase composition, diffraction pattern obtained were matched with standard diffraction data (JCPDS) files.

Nitrogen adsorption at 77 K (liquid nitrogen) was conducted using a Micromeritics ASAP 2010 instrument to obtain the adsorption isotherm of each sample. The Brunauer–Emmett–Teller (BET) surface area, micropores volume and micropores area were also calculated from the isotherms plot. Before analyses were done, samples were degassed at 200 ℃ for 4 hours.

The TEM analysis was performed using a Philips CM12 transmission electron microscope with an electron gun at 200 kV. Samples were dispersed in ethanol using supersonic waves and then placed on Cu grids under atmospheric condition.

III. RESULTS AND DISCUSSION

A. Characterization of Undoped and Doped WO₃ Using XRD

XRD spectra of as prepared undoped and doped WO_3 obtained after calcination at 600 ℃ are shown in Fig. 1. All peaks in the diffraction pattern of undoped WO_3 were assigned to the stoichiometric monoclinic phase (JCPDS 1-072-0677). Addition of 10 mol% of Zr to WO_3 there is minimal change observed with respect to displays of zirconium oxide (ZrO_2) and zirconium tungsten $(Zr(WO_4)_2)$ phase appear, indicating in a primarily WO_3 based structure. Moreover, addition of 10 mol% Ni there was a changes observed with respect to presence of complex oxide of nickel tungsten oxide $(NiWO_4)$.
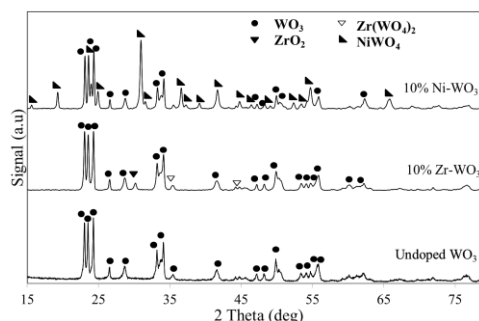

Fig. 1. XRD patterns of the fresh undoped WO_3, 10 mol% $Zr-WO_3$ and 10 mol% $Ni-WO_3$ samples obtained after calcination at 600 ℃ for 4 hours.

B. Physical Surface Analysis (BET)

BET surface area (S_{BET}) of the undoped WO_3 and Zr and Ni doped WO_3 catalysts are summarized in TABLE I. Surface area of undoped WO_3 was 2.20 m^2/g. While, surface area of doped tungsten oxide for 10 mol% Zr and 10 mol% Ni doped tungsten oxide were 3.75 and 3.79 m^2/g respectively. It was found the surface area was increase with addition of Zr and Ni to WO_3. This could suggest that has more active sites that might be attributed to the lower temperature reduction of WO_3 after doping. Hence, the addition can significantly increase the surface area.

TABLE I: BET SURFACE AREAS OF PURE WO₃, NICKEL AND ZIRCONIUM DOPED WO₃

Compounds	Surface area (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)
Undoped WO_3	2.20	16.92	0.009
10% $Zr-WO_3$	3.75	12.89	0.012
10% $Ni-WO_3$	3.79	18.39	0.017

Pore size of undoped WO_3 was 16.92 nm, by addition of 10 mol% Zr and 10 mol% Ni Zr to WO_3 were 12.89 and 18.39 nm respectively. It was found that the pore size increasing by addition of Ni. Moreover the pore volume for undoped was 0.009 cm^3/g, by addition of Zr and Ni the pore volume were increased to 0.012 and 0.017 cm^3/g respectively. It could be due to more pore volume were filled with metal doping.

C. Surface Morphology by TEM

TEM analysis has shown the morphology of undoped and doped WO_3 shown in Fig. 2. By addition of Zr, the structure observed seems agglomerate and not clearly differentiating with TEM. However effect of addition of 10 mol% Zr resulted in presence of new peaks of zirconium tungsten oxide ($Zr(WO_4)_2$) and zirconium oxide (ZrO_2), whereas 10 mol% of Ni resulted in presence of complex oxide of nickel tungsten oxide, $NiWO_4$ which supported with XRD results shown in Fig. 1.
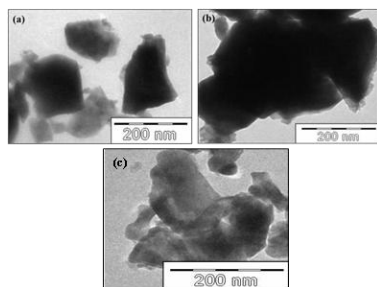

Fig. 2. TEM microstructures of (a)WO_3 powder (b) 10 mol% Zr-WO_3 and (c) 10 mol% Ni-WO_3 calcined at 600 °C for 4 hours.

D. Temperature Programmed Reduction (TPR)

Nonisothermal TPR profiles obtained in a carbon monoxide atmosphere (40% CO in N_2) for the WO_3, 10 mol% Ni-WO_3, and 10 mol% Zr-WO_3 were compared. The TPR profile of nonisothermal reduction until 900 °C then continued with isothermal reduction at 900 °C for 45 min shown in Fig. 3. Generation of carbon dioxide (CO_2) as product gas was observed and measured by TCD signal.

The TPR profile (a) of undoped WO_3 is observed as a broad shoulder indicates that reduction does not commence detectably due to low rate of reaction occurred lead to low TCD signal. However, small reduction to suboxide $WO_{2.9}$ of undoped WO_3 begins at temperature 600 °C. After holding the temperature constants at 900 °C (78 min) for approximately 45 min, a new peak which denoted as I observed at 80 min. This peak attributed to the formation of suboxide $W_{18}O_{49}$ (more) and WO_2 (less). However reduction of WO_2 thus produced might be that responsible for the following incomplete peak commencing near at holding time at 45 min. Reduction step $WO_3 \rightarrow WO_{2.92}$ in undoped WO_3 sample was not detected due to low signal. It is comparable to previous literature reported [9] reduction WO_3 by (5% H_2/N_2) which give two peaks at 696 °C and 867°C which represent reduction of WO_3 to suboxide $WO_{2.9}$ and $WO_{2.9}$ to WO_2 respectively.

The shoulder and peak monitored in profile (b) were denoted as I and II at approximately 40 min and 87 min respectively for 10 mol% Zr-WO_3. The low peak I observed at 482 °C represents to reduction of WO_3 to $WO_{2.92}$ in agreement with previous study which small peak arising at ~ 600 °C which attributed to the $WO_3 \rightarrow WO_{2.92}$ reduction step [13]. WO_3 first reduce to $WO_{2.92}$, after reached temperature 900 °C, the reaction continued for 45 min, peak detoned as II appears which represent for $WO_{18}O_{49}$ (less) to WO_2 (more). The incomplete peak beginning near at holding time at 45 min might probably responsible for reduction of WO_2 to W. It is clearly show that addition of Zr to WO_3 could give

remarkable influence on the reduction process of the powder. TPR spectra of Zr doped powder had been shifted to a lower temperature, 482 °C compared to reduction of undoped WO_3 that reduce to $WO_{2.92}$ at temperature 600 °C.

The TPR profile (c) represents 10 wt% Ni-WO_3 assigned three reduction events (denoted I, II, and III). At early reduction time represent by event I owing to shoulder and small peak at 428 °C which may regarding to the reduction of WO_3 to $W_{18}O_{49}$. Event II and III were observed sharp peaks with high TCD signal compared to event I. Event II which belongs at peak 830 °C subsequent to reduction steps of $W_{18}O_{49}$ to partially WO_2 and W. After hold the reaction for 15 min, new peak appeared which denoted to peak III, which is attributed to the WO_3 reduce completely to WO_2 and start to form tungsten carbide, WC. The TPR results obviously show that the reduction peak of 10 mol% Ni doped WO_3 are slightly shifts to lower temperature (428 °C) by enhance the reduction to form $W_{18}O_{49}$ as compared with the pure WO_3. The interaction between Ni and W ions leads to this slightly decrease of the reduction temperature of Ni doped WO_3.
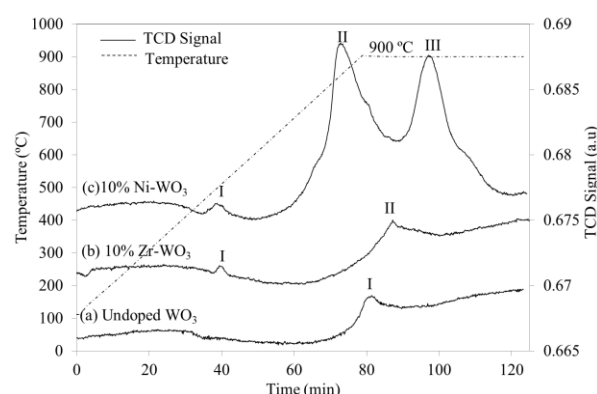

Fig. 3. TPR profile nonisothermal reduction of undoped WO_3, 10 mol% Zr-WO_3 and 10 mol%Ni-WO_3 at temperature 900 °C and maintained for 45 min under 40% (CO in N_2) atmosphere.

E. Reduction Based on Crystallinity

Final product of the reduction composition of doped WO_3 was compared to undoped WO_3. The final product was under go reduction at temperature 900 °C, and maintained at different holding time as 15, 30, and 45 min. The reduction products obtained in different holding time were collected to study the x-ray diffraction pattern of the product of reaction.

XRD analysis in sample collected after nonisothermal reduction under 40 % (CO in N_2) at 900 °C is shown in Fig 4. XRD analysis of reduced undoped WO_3 shows formation of suboxide $W_{18}O_{49}$ assigned (JCPDS 01-084-1516), small amount WO_2 (JCPDS 01-0871-0614), and some unreduced WO_3 (JCPDS 01-075-2072). As the addition 10 mol% of Zr to WO_3, the majority of WO_3 peaks reduced to suboxide $WO_{18}O_{49}$ and some WO_2 peak observed. Peaks of ZrO_2 were also detected but almost undetected. Whereas, addition of 10 mol% Ni, the WO_3 phase were totally disappeared, but $WO_{18}O_{49}$ was present as the dominant species, a few peak of WO_2 and new alloy peak of Ni_4W (JCPDS 03-065-2673) was detected. It was clearly can be concluded that addition of Zr and Ni enhanced the WO_3 reducibility. However reduction product by addition of Ni shown low intensity of crystalline phase of $W_{18}O_{49}$ due to further reduce to WO_2 in comparison

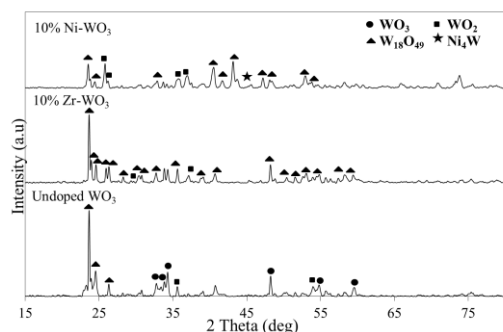of reduction product by addition of Zr which shown higher intensity.

Fig. 4. XRD patterns of non-isothermal reduction of undoped WO_3, 10 mol% Zr-WO_3 and 10 mol% Ni-WO_3 at temperature up to 900 ℃ under 40% (CO in N_2) atmosphere.

Isothermal reduction was applied to further reduce the samples. The reaction was conducted at temperature 900 ℃ and maintained at several holding time. Fig. 5 shows the XRD patterns of isothermal reduction for 15 min by comparing with undoped WO_3, 10 mol% Ni-WO_3, and 10 mol% Zr-WO_3. After hold for 15 min in reduction of undoped WO_3, remaining unreduced WO_3 in nonisothermal reduction was further reduce to $W_{18}O_{49}$, some of remaining $W_{18}O_{49}$ reduced to WO_2 and one peak with low intensity of W (JCPDS 04-0806) were observed. Moreover, reduction of 10 mol% Zr-WO_3 was completely reduced to WO_2 with one small peak of $W_{18}O_{49}$ observed by holding for 15 min at 900 ℃. Peaks of WO_2 were also observed in the XRD pattern for 10 mol% Ni-WO_3 as a result of further reduction for 15 min of remaining $WO_{18}O_{49}$. However, there a few new peaks appeared such Ni_2W_4C (JCPDS 20-0796), Ni_3W_3C (JCPDS 01-078-5006), Ni (JCPDS 1-077-9326), W (JCPDS 4-0806), and WC (JCPDS-051-093). After flowing with CO gas for 15 min lead to formation of tungsten carbide, WC. It is resulted from excess of CO supply to the samples, which converted WO_2 remained in nonisothermal to WC [14].
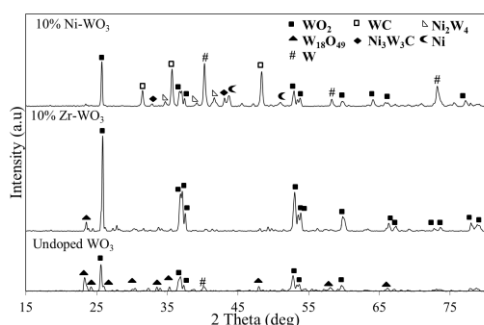

Fig. 5. XRD patterns of non-isothermal reduction of undoped WO_3, 10 mol% Zr-WO_3 and 10 mol% Ni-WO_3 at temperature up to 900 ℃ and maintained at 900 ℃ for 15 min under 40% (CO in N_2) atmosphere.

The reductions of samples were repeated with similar condition but increasing the holding reaction time to 30 min. From the XRD results in Fig. 6, it is shown that undoped WO_3 was further reduced by the presence of predominantly $W_{18}O_{49}$ phase, some WO_2 and one high intensity of W (JCPDS 4-0806) phase observed. Furthermore, one new small peak of semi carbide, W_2C (JCPDS 3-065-8829), three peaks W metal appeared from 10 mol% Zr-WO_3 after

holding the reduction for 30 min with WO_2 as a major peak. The extent of reaction to 30 min for 10 mol% Ni-WO_3, lead to disappearance of WO_2 peak due to the reaction with excess CO to form high intensity of WC (JCPDS 51-0939), small peak of Ni (JCPDS 1-077-939) and W metal. Formation of phase of WC in reduction of 10 mol% Zr-WO_3 is probably due to transformation of WO_2 to WC [7].
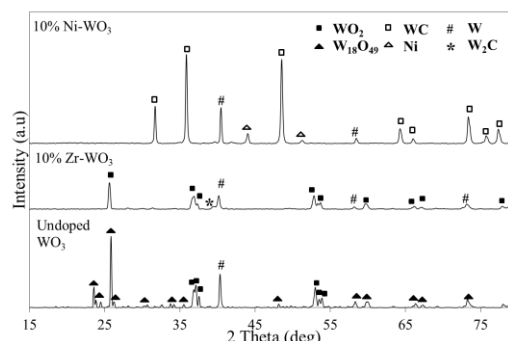

Fig. 6. XRD patterns of non-isothermal reduction of undoped WO_3, 10wt% Zr-WO_3 and 10wt% Ni-WO_3 at temperature up to 900 ℃ and maintained 900 ℃ for 30 min under 40% (CO in N_2) atmosphere.

The reduction of sample was repeated with similar condition but increasing the holding reaction time to 45 min. From the XRD results in Fig. 7, the reduction product of undoped WO_3 identifying peaks predominantly WO_2 phase and three peaks of W metal. Prolong the reduction time to 45 min of 10 mol% Zr-WO_3 lead to increasing the formation of W_2C peaks and increasing the intensity of W phase instead of remaining WO_2 peaks observed. Reference [3] have reported that carburization to WC takes place at temperatures above 900 ℃, otherwise W_2C would be the primary carbide formed.

The XRD pattern of reduced sample of 10 mol% Ni-WO_3 shows the structure comprised primarily of WC, two small peaks of $Ni_{0.98}C_{0.02}$ (JCPDS 1-074-5561) and no W phase observed. The formation of WC may also transform from W metal, it can be seen in the reduction of 10 mol% Ni-WO_3 where the intensity of W peak decrease sharply after hold for 45 min, compared to peak observed in reaction which hold for 30 min. It was in agreement with previous study [8], where the formation of WC may be either from WO_2 or W.

Furthermore, additions of Ni to WO_3 lead to a facilitated reduction and carburization which due to catalytic effect of Ni which enhances the CO adsorption [3]. However, addition of Zr to WO_3 enhanced the reducibility by lowering the reduction temperature.
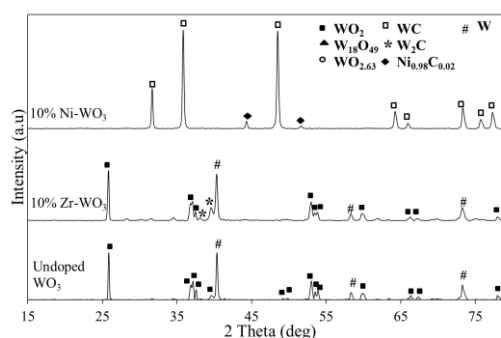

Fig. 7. XRD patterns of non-isothermal reduction of undoped WO_3, 10 mol% Zr-WO_3 and 10 mol% Ni-WO_3 at temperature up to 900 ℃ and maintained 900 ℃ for 45 min under 40% (CO in N_2) atmosphere.

It can be concluded that, increasing the reaction time in the reduction process could improve the reducibility of the WO_3 [15]. Different holding time will produce different reduction products due to different interaction with reducing agents towards changes in reduction phases. Reduction at temperature 900 °C and hold for 45 min in undoped WO_3 and 10 mol% Zr, were completely reduced to WO_2 with low intensity of W metal peak. W_2C also form in 10 mol % Zr. However, by addition of 10 % mol Ni, the WO_3 was completely reduced to WC and $Ni_{0.98}C_{0.02}$.

IV. CONCLUSION

The reduction behaviour of undoped WO_3 and different doped WO_3 were investigated. It can be concluded that reduction WO_3 obeys the consecutive steps namely: as $WO_3 \rightarrow WO_{2.92} \rightarrow W_{18}O_{49} \rightarrow WO_2 \rightarrow W \rightarrow W_2C \rightarrow WC$. The addition of Zr had a remarkable influence on the reduction process of the powder by improving their oxygen storage capacity and reducibility. Furthermore, addition of Ni for WO_3 reduction have tendency for the formation of WC due to the catalytic effect. Moreover by hold the reduction time could improve the reducibility of the sample oxide. The reducibility of unreduced WO_3 could be enhancing by increase the concentration of CO or increase the holding time of reduction.

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