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STUDY ON CATALYTIC ROLES OF TUNGSTEN CARBIDE NANOSPHERES FOR CH_4/CO_2 REFORMING OVER NI BASED CATALYSTS

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ABSTRACT

In this paper, WO_3 nanospheres are used carriers and Ni-WC_x nanospheres are synthesized via the method of incipient impregnation and temperature programming carbonization with the content of Ni is 10%. The presence of Ni promotes the cracking of CH_4, while the activation of CO_2 takes place on WC_x. Thus, the deactivation due to carbon accumulation or WC_x oxidation could be avoided.

KEYWORDS

Tungsten carbide nanospheres, Nickel, Methane, Carbon dioxide, Reforming.

1. INTRODUCTION

Dry reforming of methane with CO_2 (DRM) has become an interesting alternative for syngas production due to the fact that the greenhouse gases CO_2 and CH_4 can be utilized through the reaction [1,2]. At the same time, The DRM process produces syngas with a H_2/CO ratio of 1 that is suitable for Fischer–Tropsch (F–T) and carbony synthesis the process is a strong endothermic reaction, with a large reaction heat in the generated syngas, which can release stored energy by reversible reaction, and has multiple research values such as science and environmental protection [3]. Both noble and non-noble metals were found to show catalytic activity towards the reaction. But noble metal catalysts are expensive and non-noble metal catalysts (mainly nickel-based catalysts) have the problem of catalyst deactivation due to coking [4,5].

Transition metal carbides have attracted extensive attention over the recent years because their catalytic performances are similar to those of noble metals in reactions [6, 7]. This paper reports the WO_3 nanospheres as the carrier, using the method of volumetric impregnation with the load of Ni was 10% [8, 9]. Then Ni-WC_x nanospheres bifunctional catalysts are prepared through a series of temperature-programmed processes [10].

2. EXPERIMENTAL

2.1 Catalyst preparation

We prepared WO_3 nanospheres by stirring an aqueous solution of the pure sodium tungstate and citric acid for 0.5h. Then hydrochloric acid was added to it stirring for 10 min. The above mixture was then transferred into a Telfon-lined stainless-steel autoclave for hydrothermal treatment at 120◦C for 24 h. As the autoclave cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with distilled water and absolute ethanol three times, dried at 60◦C overnight and calcined at 600◦C for 4 h. The nickel nitrate solution was impregnated to the carrier of WO_3 nanospheres. Ni-WC_x nanospheres were prepared in CH_4/H_2 (20 vol.% CH_4) following a series of temperature-programmed processes: temperature was raised from room temperature (RT) to300 ◦C at a rate of 5 ◦C min^{-1}, then from 300 to 700 ◦C at a rate of 1 ◦C min^{-1}, and subsequently kept at 700 ◦C for 2 h. The above material was cooled down to RT in flowing CH_4/H_2 and passivated in flowing 1% O_2/Ar for 12 h.

2.2 Catalyst characterization

X-ray powder diffraction (XRD) analysis was conducted using anXRD-6000 (Shimadzu) equipment with Cu Kα radiation (λ= 0.1542 nm), operating at 40kV and 30 mA. BET surface area determinations were performed on a JW-BK-112 (Beijing JWGB Sci. & Tech. Co.,Ltd.).Carbon dioxide temperature-programmed oxidation (CO_2-TPO) studies were performed using a mass spectrometer (OmniStarTM Pfeiffer Vacuum,Germany). With the sample (0.1 g) placed in a quartz tubular reactor, CO_2-TPO was performed by introducing 10% CO_2/Ar into the system while the sample temperature was raised from RT to a specific temperature. The signal intensities of CO (m/e = 28) and CO_2 (m/e = 44) were detected. Methane temperature-programmed surface reduction (CH_4-TPSR) studies were performed using a mass spectrometer. With the sample placed in a quartz tubular reactor, CH_4-TPSR was carried out by introducing 10% CH_4/Ar into the system while the sample temperature was raised from RT to a specific temperature. The signal intensities of CH_4 (m/z= 15), H_2 (m/z = 2), H_2O (m/z = 18), CO (m/z = 28), and CO_2 (m/z = 44) were detected.

2.3 Activity measurements

Catalytic tests were performed in a fixed-bed micro-reactor at atmospheric pressure. Before the reaction, the catalyst was activated with a hydrogen flow at 500◦C for 1h. Then, the CH_4 and CO_2 (CH_4/CO_2=1:1) were introduced into the catalyst bed at a flow rate of 30 mL/min (F/W = 18,000 mL/g h).

3. RESULTS

3.1 BET

BET analysis on WO_3 and WO_3 nanospheres was shown in Table 1. Compared with the WO_3 (15 m^2/g), the surface area of WO_3 nanospheres was slightly larger and was 63 m^2/g. Ni supported on the WO_3 and WO_3 nanospheres, the surface area showed WO_3 nanospheres can better disperse metal nickel.

Table 1: The BET surface analysis data

Sample	$S_{BET}/(m^2.g^{-1})$
WO_3	15
WO_3 nanospheres	63

3.2 SEM

Figure 1 (a) and (b) shows the SEM images of WO_3 and WO_3 nanospheres catalysts. It can be seen that WO_3 nanospheres have a higher specific surface area because of its spherical shape. When Ni is loaded on WO_3 nanospheres, it can better disperse the active metal Ni, promote the cracking of methane and improve the activity of catalyst, which is consistent with the BET characterization results and the activity evaluation results.

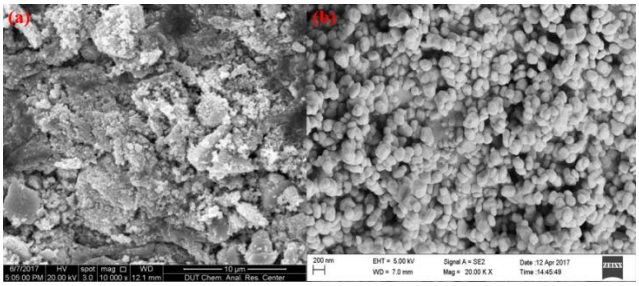

Figure 1: SEM images of the (a) WO_3 and (b) WO_3 nanospheres catalysts

3.3 XRD

Figure 2 shows the XRD patterns of Ni-WCx and Ni-WCx nanospheres. The diffraction peaks at 31.5◦、35.7◦、48.3◦、64.1◦、65.8◦、73.2◦、75.6◦、77.1◦ can be assigned to WC, while those at 34.5◦、38.1◦、39.6◦、52.4◦、61.9◦、69.8◦、75.1◦、76.1◦ assigned to W_2C. The diffraction peaks at 44.4o and 51.8◦ can be assigned to metallic Ni. As calculated by the Scherrer equation based on the metallic Ni diffraction peak at 44.4◦, the average particle size of - metallic Ni is 27 and 18.5 nm for Ni-WC_x and Ni-WC_x nanospheres, respectively, indicating better dispersion of metallic Ni on the latter. Compared with the Ni-WC_x , the peaks of Ni-WC_x nanospheres become much stronger . It is clear that Ni-WC_x nanospheres catalyst have a good crystal structure.

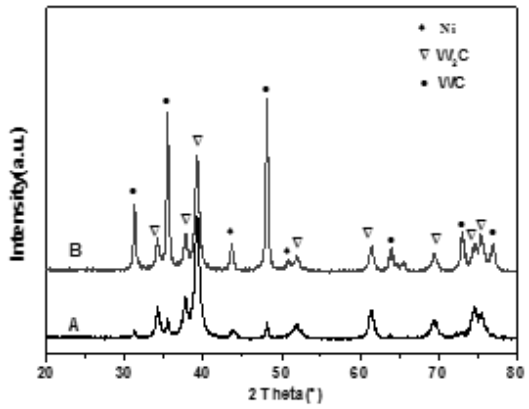

Figure 2: XRD patterns of (A) Ni-WC_x and (B) Ni-WC_x nanospheres

3.4 Activity measure

The effects of reaction temperature on catalytic activity of Ni-WC_x and Ni-WC_x nanospheres were compared and the results are showed in Figure 3. Over the two catalysts, CH_4 conversion increases with the rise of temperature. The conversions are lowest at 700◦C. With increasing temperature to 750◦C and 800◦C, CH_4 conversions are about 55% and 70% over Ni-WC_x nanospheres, which are both much higher than that over Ni-WC_x. We attribute this to the well dispersion of Ni on WO_3 nanospheres that results in promoting the cracking of methane.

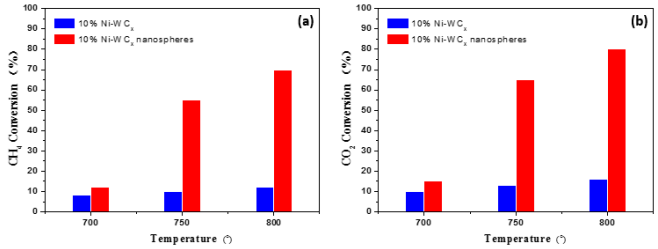

Figure 3: Effects of reaction temperature on (a) CH_4 conversion and (b) CO_2 conversion over Ni-WC_x and Ni-WC_x nanospheres catalysts (atmospheric pressure,F/W = 18000 mL/g h).

3.5 Stability measurement

A stability test was carried out at 800◦C for 29 h and the results are displayed in Figure 4. The conversions of CH_4 and CO_2 over Ni-WC_x nanospheres stay at ca.68% and 80%. On the other hand, the conversions of CH_4 and CO_2 over Ni-WC_x nanospheres remain rather stable across the period of 29 h under the conditions of CH_4/CO_2= 1 and WHSV =18000 mL/g h.

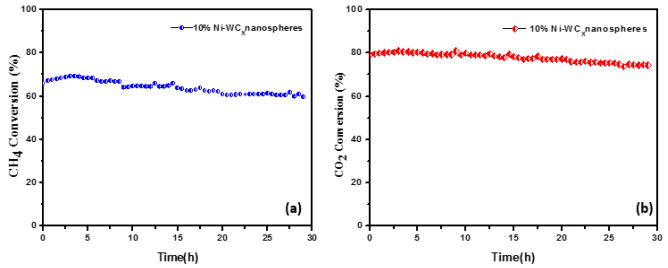

Figure 4: Catalytic performance over Ni-WC_x nanospheres catalyst: (a) Conversions of CH_4 and (b) conversions of CO_2 (F/W = 18000 mL/g h,800 ◦C, atmospheric pressure)

3.6 Surface reactions of CO_2 and CH_4 over Ni-WC_x and Ni-WC_x nanospheres

Figure 5 displays the results of CH_4-TPSR over the Ni-WCx and Ni-WCx nanospheres catalysts obtained in a gas stream of 10% CH_4/Ar. The consumption peaks of CH_4 at lower temperatures accompanied with the formation of H_2O, CO and CO_2 is a result of CH_4 interaction with the oxygen species that are formed during passivation [14]. The consumption of CH_4 at higher temperatures accompanied by obvious H_2 formation is ascribed to CH_4 dissociation on the catalysts. In the case of Ni-WC_x, CH_4 dissociation reaches maximum at 800 ◦C while over Ni-WC_x nanospheres, CH_4 dissociation reaches maximum at 769 ◦C. It is clear that CH_4 dissociation over Ni-WC_x nanospheres are easier to more significant than that over Ni-WC_x.

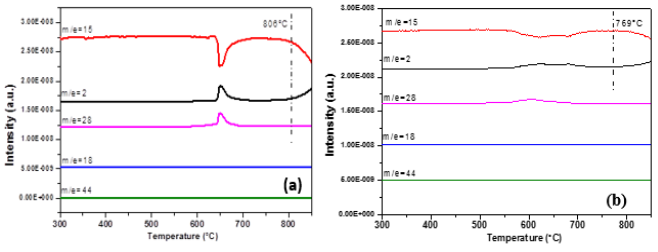

Figure 5: CH_4-TPSR profles of (a) Ni-WC_x and (b) Ni-WC_x nanospheres catalysts

Figure 6 displays the results of CO_2-TPO studies. In the case of Ni-WC_x, two peaks are observed, one at 650◦C and the other at 840◦C. In our previous studies, the former CO_2 consumption peak should be due to the oxidation of surface carbon while the latter to the bulk oxidation of WC_x. By contrast, the temperature for bulk oxidation of Ni - WC_x nanospheres is higher than that of Ni-WC_x .It shows that Ni - WC_x nanospheres catalyst have better oxidation resistance. It has to do with the results of CH_4-TPSR characterization the stability test .

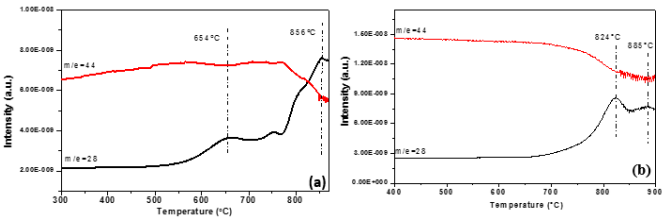

Figure 6: CO_2-TPO profles of (a) Ni-WC_x and (b) Ni-WC_x nanospheres catalysts

4. CONCLUSION

It is clear that WO_3 nanospheres has a higher specific surface area and can disperse metal Ni well. At the same time, it also can provide more reactive sites. After temperature programming carbonization, there is a strong interaction between metal Ni and tungsten carbide. The dissociation of CH_4 is catalyzed by Ni, while the activation of CO_2 takes place on the WC_x nanospheres, which renders Ni-WC_x nanospheres catalysts excellent activity and stability for DRM at atmospheric pressure.

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