Catalysis Today 274 (2016) 123–128

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Synthesis of nanostructured tungsten carbonitride (WN_xC_y) by carbothermal ammonia reduction on activated carbon and its application in hydrazine decomposition

Jun Sun, Binglian Liang, Yanqiang Huang*, Xiaodong Wang*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

ARTICLE INFO

Article history:
Received 17 September 2015
Received in revised form 19 January 2016
Accepted 22 January 2016
Available online 11 February 2016

Keywords:
Hydrazine decomposition
Activated carbon
Tungsten carbonitride
Microcalorimetry
Microthruster

ABSTRACT

A carbothermal NH_3 reduction method was introduced for the synthesis of nanostructured tungsten carbonitride using support carbon and NH_3 as carbon source and nitrogen source, respectively. A series of samples synthesized by this route from WO_3/AC were characterized by X-ray diffraction, temperature-programmed surface reaction-mass spectroscopy, transmission electron microscopy, and microcalorimetry. The results demonstrated that a nanostructured tungsten carbonitride (WN_xC_y) was successfully synthesized on activated carbon at 800 °C and the resulting WN_xC_y was uniformly dispersed on the carbon support with particle size less than 2 nm. The WN_xC_y/AC prepared by the carbothermal NH_3 process has stronger capability for CO adsorption and exhibited better catalytic performance for hydrazine decomposition than the WC_x/AC-H catalyst prepared by the carbothermal H_2 reduction process. Further bench-scale tests indicated that it could be a promising substitute for the traditional Ir/Al_2O_3 catalyst in hydrazine decomposition technology.

1. Introduction

Using nitrides and carbides of cheaper metals as catalysts has gathered substantial academic and industrial interests since the first report by Boudart's group in the 1970s [1–3]. Transition metal carbides and nitrides were reported to exhibit catalytic behavior resembling that of noble metal catalysts in a lot of reactions, such as methane reforming [4], ammonia synthesis and decomposition [5], hydrodenitrogenation and hydrodesulfurization [6,7], hydrogenation [8], and hydrazine decomposition [9–11].

In order to optimize application of the carbides and nitrides in catalysis, many methods, such as gas-phase reactions of volatile metal compounds [12], reaction of gaseous reagents with solid state metal compounds [13], pyrolysis of metal complexes [14], solution reactions [15], temperature-programmed reaction [16,17], and carbothermal reduction [18,19], have been developed to introduce C atoms or N atoms into transition metal lattice to obtain carbides or nitrides. However, the study of inserting C atoms and N atoms simultaneously into metal lattice is rare and scarcely reported. Recent research [20–24] showed that a new type of tungsten carbonitride (WN_xC_y) film was obtained by atom layer deposition or chemical vapor deposition process and behaved as an effective diffusion barrier for Cu metallization in semiconductor field. As far as we know, there are no studies about the preparation and utilization of metal carbonitride in catalysis. Therefore, in this work, for the first time, we introduced a useful method of carbothermal NH_3 reduction for the synthesis of metal carbonitride and successfully synthesized a nanostructured WN_xC_y on activated carbon support via this process. To further evaluate the catalytic activity of the obtained tungsten carbonitride, hydrazine decomposition was used as a probe reaction and the catalytic behavior of the WN_xC_y was explored in both microreactor and microthruster. The technique of hydrazine decomposition has been widely applied to attitude control of spacecrafts and satellites [25–28]. The obtained WN_xC_y catalyst exhibited excellent catalytic performance in hydrazine decomposition reaction and was found to be promising substitute for the expensive commercial Ir/Al_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation

The WO_3/AC precursors were prepared with different W loadings by repeated impregnation of activated carbon (provided by

* Corresponding authors. Fax: +86 411 84685940.
E-mail addresses: yqhuang@dicp.ac.cn (Y. Huang), xdwang@dicp.ac.cn (X. Wang).

http://dx.doi.org/10.1016/j.cattod.2016.01.031
0920-5861/

NORIT Company, S_{BET} = 1280 m^2/g) with an aqueous solution of ammonium metatungstate. The samples were dried at 120 °C overnight and calcined at 500 °C for 4 h in N_2. Subsequently, the WO_3/AC precursors were reduced in NH_3 with the following heating ramp: from room temperature to 450 °C in 40 min, then to the synthesis temperature (e.g. 700 °C, 800 °C, 900 °C) at a rate of 1 °C min^{-1} and held for 1 h. The carbothermal H_2 reduction process had a similar process except that the reduced gas was changed to H_2. For comparison, the Ir/Al_2O_3 catalyst was also prepared by impregnating the support with an aqueous solution of H_2IrCl_6, and then drying at 120 °C for 12 h and calcining at 350 °C for 4 h, and finally reducing in H_2 for 2 h.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns of the samples were obtained with an X'pert (PANalytical) diffractometer operated at 40 kV and 100 mA, using Ni-filtered Cu-Kα radiation. Temperature-programmed surface reaction-mass spectroscopy (TPSR-MS) experiments were performed using a U-shaped quartz reactor with a mass spectrograph (BALZERS Omnistar 422) to analyze products. Transmission electron microscopy (TEM) analysis was performed on a JEM-2000EX (JEOL) microscope. Microcalorimetry of CO adsorption was performed at 40 °C using a Calvet-type microcalorimeter (Setaram BT 2.15) as described in detail elsewhere [29,30].

2.3. Microreactor tests

The catalytic activity of hydrazine decomposition was firstly evaluated in a fixed-bed continuous-flow microreactor at atmospheric pressure. The temperature of the reaction was controlled by a water bath below 100 °C and by an oven above 100 °C, respectively. About 50 mg of catalyst was diluted with silica and loaded in a U-shaped quartz microreactor. The feed gas containing 3 vol% N_2H_4 in Ar was introduced to the reactor at a flow rate of 85 mL min^{-1}. The feedstock and the products were analyzed using an on-line chromatograph (Agilent 6890A) equipped with a thermal conductivity detector and an automatic injection valve. Argon was the carrier gas. The decomposition of hydrazine proceeds have two typical reaction can be described as Eq. (1) and Eq. (2).

$$N_2H_4(g) \rightarrow N_2(g) + 2H_2(g) \Delta H(25\,^{\circ}C) = -95.2\ kJ/mol \quad (1)$$

$$3N_2H_4(g) \rightarrow 4NH_3(g) + N_2(g) \Delta H(25\,^{\circ}C) = -469.3\ kJ/mol \quad (2)$$

3.1. Bench-scale tests

The bench-scale tests for hydrazine decomposition were performed with our specially designed reactor system [10,11,31]. The schematic diagram of the bench-scale tests system can be shown in Fig. S1. Briefly, the catalysts used for bench-scale tests are of columned shape, about 1.5 mm in length and 1 mm in diameter. For each test, about 0.67 g of catalyst was loaded in a 1 Newton microthruster (30 mm in length and 7 mm in diameter) and the amounts were 0.90 g when alumina was used as supports in order to get the same volume.

The injection of hydrazine was realized by pressurized N_2 at 0.8 MPa and the hydrazine feeding rate was kept at 0.49 g s^{-1}. The feeding of hydrazine was controlled by on-off of an electromagnetic valve. Before ignition, the catalyst bed was preheated to ignition temperature (T_i) at 160 °C. The continuous test lasted 30 s, and then the catalysts bed was cooled to 160 °C before the next 30 s start-shutdown cycle began. The parameters, including catalyst bed temperature (T_c), chamber pressure (P_c), and ignition delay (t_0, t_{90}), were recorded and calculated automatically by computer. P_c and T_c are the parameters indicating the extent of the hydrazine decomposition. t_0 and t_{90} are the time taken for the pressure of the chamber to reach 10% and 90% of its stable-state pressure, respectively, indicating the initial activity of the catalyst. The specific activity is defined as the chamber pressure produced per time and per mass of hydrazine feeding (MPa g^{-1} s^{-1}).

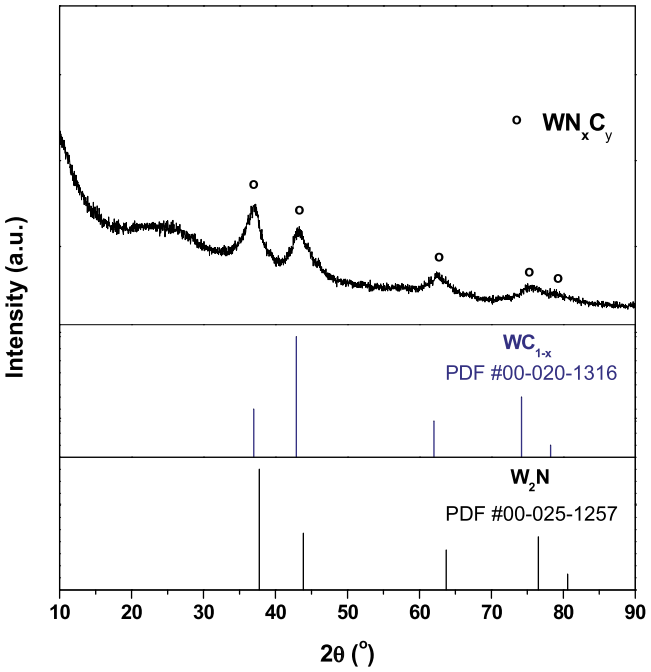

Fig. 1. XRD pattern of sample prepared by carbothermal NH_3 reduction at 800 °C from WO_3/AC.

4. Results and discussion

4.1. Synthesis of WN_xC_y/AC via carbothermal NH_3 reduction

XRD pattern of the sample prepared by carbothermal NH_3 reduction at 800 °C from WO_3/AC with tungsten loadings of 16.7 wt.% is presented in Fig. 1 and gives characteristic peaks of the sample at 37.1°, 43.1°, 62.5°, and 75.4°, which deviates from those of W_2N (PDF #00-025-1257) to the left about 1.0° and from those of WC_{1-x} (PDF #00-020-1316) to the right about 0.1–1.5°, respectively. This result also coincides with that of WN_xC_y reported in literature [21] and indicates that the product synthesized by the carbothermal NH_3 reduction process is neither tungsten nitride nor tungsten carbide, but tungsten carbonitride (WN_xC_y).

Fig. 2 shows the XRD patterns of WO_3/AC samples prepared by carbothermal NH_3 reduction at different synthesis temperatures. It is surprising to find that only typical peaks of WN_xC_y with no peaks of WO_3 can be observed at the temperature of 500 °C. The result indicates that WO_3 is highly dispersed on the activated carbon, which is similar to the result reported in literature [19]. The observed peaks of WN_xC_y synthesized at 500 °C suggest that nitridation and carbonization reactions started at 500 °C during the carbothermal NH_3 reduction process. The peak intensity of the samples becomes stronger with the increase of the temperature from 500 °C to 800 °C. In the case of the sample pretreated at 850 °C, additional peaks due to W_2C were detected. When the temperature was further elevated to 900 °C, diffraction peaks due to WC were observed as well at 31.5° and 48.4° and a mixed phase of WN_xC_y, W_2C, and WC were obtained.

The profile of TPSR-MS during carbothermal NH_3 reduction of WO_3/AC is shown in Fig. 3. The signals at M = 2, 17, 18, 44