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Synthesis of mesoporous tungsten carbide by an impregnation–compaction route, and its NH_3 decomposition catalytic activity

Xiangzhi Cui,[a] Hua Li,[b] Limin Guo,[a] Dannong He,[c] Hangrong Chen[a] and Jianlin Shi*[a]

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A mesoporous tungsten carbide (WC) with high surface area (138 $m^2 g^{-1}$) has been synthesized at 700 °C using a modified template replicating route in which the pore entrances were sealed under external pressure after the W source impregnation. X-Ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray (EDX) spectroscopy and nitrogen sorption techniques were employed to characterize the replicated material. The prepared tungsten carbide with high surface area is well crystallized and has a partially ordered mesoporous structure. Temperature programmed reaction (TPR) and time-on-stream (TOS) results show that the prepared mesoporous tungsten carbide has high and stable catalytic activity for the decomposition reaction of NH_3, and the complete NH_3 decomposition temperature was obtained at 500 °C. This mesoporous WC appears to be a good catalyst for use for NH_3 decomposition.

1. Introduction

Carbide materials, especially tungsten carbide (WC), have received considerable attention in recent years because of their high catalytic activities resembling metallic Pt in heterogeneous catalysis, NH_3 synthesis, ethylene hydrogenation and cyclohexane dehydrogenation, methane reforming and CO hydrogenation.[1–5] Moreover, their relatively low cost and especially high resistance to chemical erosion and catalyst poisoning make them outstanding candidates for catalytic applications among other catalysts.[6] Unfortunately, WC materials prepared by conventional methods usually have low surface area (5–30 $m^2 g^{-1}$) due to the difficulties of synthesis.[7–9] The temperature-programmed reaction method is the major route to prepare tungsten carbides with high surface area,[7] and J. M. Giraudon *et al.*[8] explored the mechanism of reduction and carburization of this route and obtained tungsten carbides with a surface area as high as 30 $m^2 g^{-1}$, which is, however, still not high enough if compared to other materials. Li *et al.*[9] prepared hollow spherical WC particles with mesoporosity and conducted an electrocatalytic investigation, however, the surface area of the prepared WC was only 4.9 $m^2 g^{-1}$.

Ammonia decomposition is an important reaction, and there has been an increased interest in NH_3 decomposition as a potential CO_x-free source of on-site H_2 generation for PEMFC.[10] The reaction of NH_3 decomposition is also important in the cleaning-up of syngas derived from coal[11] and biomass gasification.[12] Recently, Sourabh *et al.*[13] reported the catalytic activity of tungsten carbide with a surface area of 1.5 $m^2 g^{-1}$ toward NH_3 decomposition, and the complete NH_3 decomposition temperature on WC is 550 °C, however, the prepared WC needs to be treated with a gas mixture (H_2/CO) prior to the NH_3 decomposition reaction. The NH_3 decomposition on a commercial Fe ammonia synthesis catalyst (Amomax-10) with a surface area of 0.17 $m^2 g^{-1}$ reached a conversion rate as low as 35% at 650 °C as reported by Sourabh *et al.*[13] As we know, the catalytic performances of the materials are strongly dependent on the surface area and particular structures. Nanoporous-structured tungsten carbides of high surface area and appropriate pore size are highly desired for the applications as catalysts.

Mesoporous materials with ordered pore structures and high surface areas are technologically important for a variety of applications such as in heterogeneous catalysis, adsorption, chemical sensing, electrodes, transportation/storage of fluids and gases, and also in some biological areas.[14–18] More recently, Raman *et al.*[19] and Dong *et al.*[20] synthesized mesoporous WC phase by a surfactant-assisted route, however, a relatively high temperature calcination at 900 °C in argon and hydrogen flow was needed, which led to a rather low surface area of 76 $m^2 g^{-1}$ as compared to common mesoporous materials by similar surfactant routes. Recently, the replicating method using ordered mesoporous silica as hard template and micro-reactor is regarded as an effective way to synthesize novel ordered nanostructure or nanoarray mesoporous materials, such as carbon, metal, transition metal oxides, sulfides, and polymer.[21–25] However, as far as we know there is no report up to now about the synthesis of mesoporous WC by this method, most probably due to the easy volatilization of W sources like PW_{12} in the thermal process during replication. Herein, we present a modified replication method to synthesize mesoporous WC with high surface area of 138 $m^2 g^{-1}$, which is the highest up to now as we could found in the literature, and crystallized framework using the cubic Ia3d mesoporous silica as hard template and PW_{12} as the W source. In this route the introduced PW_{12} was sealed in the pore channels by compaction under an external pressure to prevent the volatilization of W source during the following reactions with carbon source at a certain temperature, and WC particles can form only in pore channels which act as a closed micro-reactor. Besides, the exaggerated growth of formed WC nanoparticles can

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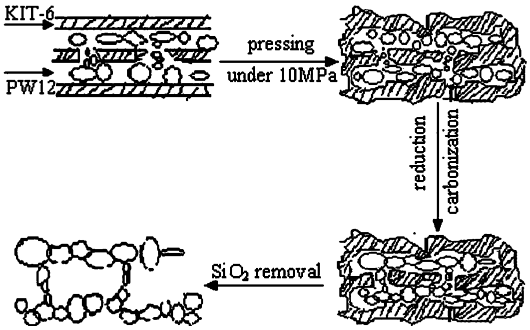
[a] *State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai, 200050, China. E-mail: jlshi@sunm.shcnc.ac.cn; Fax: +86-21-52413122; Tel: +86-21-52412714*
[b] *Suzhou University, 50 Donghuan Road, Suzhou, 215021, China*
[c] *National Engineering Research Center for Nanotechnology, 28 Jiangchuan Road, Shanghai, China*

also be prevented by the confinement effect of silica template and low reaction temperatures. This mesoporous material show high catalytic activity for the decomposition of NH_3 at relatively low temperature.

2. Experimental

A presentation of the modified template replicating route is shown in Scheme 1. The tungsten precursor, 12-phosphotungsten acid (PW_{12}), was introduced into the pore channels of silica template (KIT-6) by liquid impregnation method. After drying, the PW@KIT-6 composites were pressed into compact discs under 10 MPa so that the pore entrances of the mesoporous silica template were blocked and sealed, and the originally open pore structures were collapsed, forming a compact mixture of PW@KIT-6. Then the PW_{12} was reduced and carbonized after heat treatment under a certain atmosphere. Finally the removal of silica template yielded the mesoporous WC replica. The compaction process was employed to prevent the PW_{12} precursor from volatilization and exaggerated growth of WC during heat treatment.



Scheme 1 The procedure for the modified replicating (impregnation—compaction) route for the synthesis of mesoporous tungsten carbide by sealing the pore channels of template.

2.1 Material preparation

The cubic Ia3d mesoporous silica KIT-6 was prepared according to the method described in the literature.[26] Typically, 6 g of surfactant P_{123} and 6 g of *n*-butanol were dissolved in solution of 217 g distilled water and 11.4 g conc. HCl (37 wt%). To this homogeneous solution, 12.9 g of tetraethyl-orthosilicate (TEOS) was added under stirring at 37 °C and continuously stirred at 37 °C for additional 24 h. After that, the mixture was transferred to a Teflon-lined autoclave and heated at 100 °C for another 24 h. The solid product was filtered, washed with distilled water for several times and calcined at 550 °C for 5 h to remove the organic template.

0.4 g KIT-6 powder was added into 5 mL of ethanol solution containing 1.2 g PW_{12} at room temperature. After stirring for 3 h at room temperature, the mixture was further stirred continuously at 50 °C to evaporate the ethanol, the resultant dry powders were pressed into compact discs under 10 MPa to seal PW_{12} precursor within the template. The compacts were heated from room temperature to 650 °C at 10 °C min^{-1} and held at 650 °C for 3 h under a mixed gas flow of Ar and H_2 (1:0.05), then heated again from 650 °C to 700 °C at 3 °C min^{-1} and then held at 700 °C for 5 h under ternary mixed gas flow of Ar, H_2 and CO (1:0.05:1), finally the compacts were cooled to room temperature under mixed gas flow of Ar and H_2 (1:0.05). The silica template was afterwards removed with 2 M HF solution over night. The template-free product was washed with distilled water thoroughly, collected by centrifugation, dried in vacuum at 40 °C. This product was named as WC-P. For comparison, the sample prepared according to the above procedure but without compaction was named as WC-NP.

2.2 Material characterization

X-Ray diffraction (XRD) patterns of prepared samples were recorded on a Rigaku D/Max-2550V X-ray diffractometer with a Cu-Kα radiation target (40 kV, 40 mA). The scanning rates were 0.6° per min and 6° per min for the low-angle and high-angle XRD measurements, respectively. The N_2 sorption measurement was performed using Micromeritics Tristar 3000 at 77 K, and specific surface area and the pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Transmittance electron microscopy (TEM) images were obtained on a JEOL 200CX electron microscope operating at 160 kV. Energy-dispersive X-ray (EDX) spectrum was collected from an attached Oxford Link ISIS energy-dispersive spectrometer fixed on a JEM-2010 electron microscope operated at 200 kV. Field emission scanning electron microscopy (FE-SEM) was conducted on JSM-6700F field emission scanning electron microscopy.

The catalytic reactions for NH_3 decomposition were carried out under ambient pressure in a temperature-programmed, fixed-bed quartz-glass reactor using a thermal conductivity detector (TPD) of a gas chromatograph (HP 6890 series GC system). In a typical reaction, 50 mg WC replica was loaded in a quartz tube reactor, and then thermally treated from room temperature to 450 °C at 6 °C min^{-1} and from 450 °C to 650 °C at 1 °C min^{-1}. NH_3 gas was introduced and used as reaction gas under the carrying by He (NH_3:He = 1:54, volume ratio), and the total gas flow amounted to 55 sccm.

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the XRD patterns of the prepared samples. The wide-angle XRD (Fig. 1a) patterns reveal that both samples with and without compaction are mainly composed of WC phase whose three main peaks were seen clearly according to the JCPDS (25–1047), indicating the well-crystallized framework of the prepared products. Both samples WC-P and WC-NP show broadened XRD diffraction peaks, suggesting that the prepared WC samples should be nanosized. However, the diffraction peaks of WC-P are even more broadened than those of WC-NP, most probably due to the confinement effect of the sealed micro-reactor in WC-P by compaction, which effectively prevented the volatilization of tungsten source and the growing of WC particles. It is noted that the sample WC-P shows a distinguishable small-angle reflection peak (211) according to the small-angle XRD patterns in Fig. 1b, which is corresponding to the main diffraction peak of the cubic Ia3d symmetry of mesoporous silica KIT-6 template with a

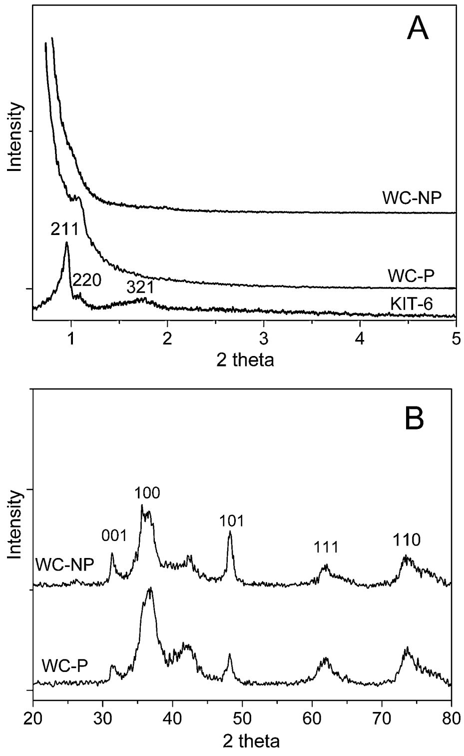


Fig. 1 XRD patterns for the samples, A: small-angle XRD patterns and B: wide-angle XRD patterns.

position shift towards a higher angle. This suggests that the replica possesses a certain grade of pore structure ordering. While no distinguishable small angle diffraction peak of sample WC-NP can be identified, indicating that the replicated sample prepared from the compacted precursor mixture has retained, at least partially, the mesopore structure of the template, and also implying that W precursor was reduced and carbonized within the pore structure of the template during the heat treatment. Without compaction, the open pore structure would lead to the volatilization of the W source at high reaction temperature, and the reduced and carbonized WC could migrate to the outside of the pore channels. In addition, the formed WC particles out of pore structure may aggregate and/or grow larger freely without the confinement of pore structure, thus the ordered pore structure of the template cannot be inherited into the replica, corresponding to the absence of any small angle diffraction peaks of the sample WC-NP.

The TEM images of sample WC-NP prepared without compaction in Fig. 2 show the consistent results with the XRD analysis. Some WC particles were aggregated together from the selected areas in Fig. 2a due to the presence of WC component not confined in the pore channels of the silica template during the process of high temperature carbonization. The large aggregated WC particles can be found to be composed of randomly and tightly packed small crystallites without visible nanoporous structures (Fig. 2b). From these images we can know that W source may have volatilized, or formed WC particles which migrated out of the pore structures of the silica template during the heat treatment (reduction and formation of WC) due to the open pore structure of WC-NP.

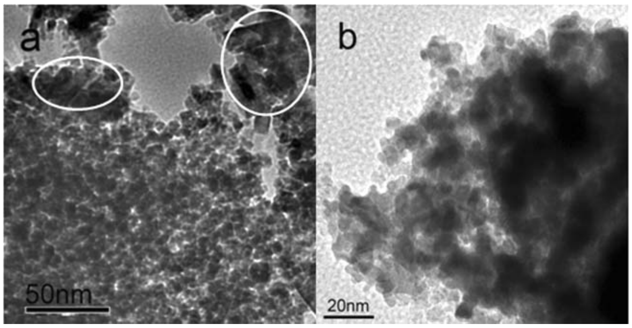


Fig. 2 TEM images of sample (WC-NP) without compaction.

From the typical TEM images of sample WC-P in Fig. 3, it can be clearly seen that the prepared WC retained ordered mesoporous structure, though not as perfect as the template, in contrast to the random structure of sample WC-NP. Such a mesoporous structure should be attributed to the sealed micro-environment as a micro-reactor for the formation of mesostructured WC of sample WC-P derived from the compacted precursor mixture of PW@KIT-6. TEM image in Fig. 3a is along the [100] direction, and those in Fig. 3b and Fig. 3c are along the [110] direction, indicating that the WC replica has basically inherited the cubic mesoporous structure of the parent mesoporous silica after the removal of silica template, though some disordered areas exist as shown in Fig. 3b. This is consistent with the small-angle XRD result that only one diffraction peak can be seen in sample WC-P. Fig. 3d shows the high-resolution TEM image of a single WC nanorod from the prepared mesoporous WC product, it can be seen that the WC nanorod is composed of nanoparticles with a diameter of about 6–7 nm, which is in accordance with the pore size of the silica template (6.54 nm). The crystal stripes of mesoporous WC can also be seen clearly, and the *d*-spacing value of 0.28 nm belongs to the (001) reflection of WC phase ($d = 0.2840$ nm, JCPDS 25–1047).

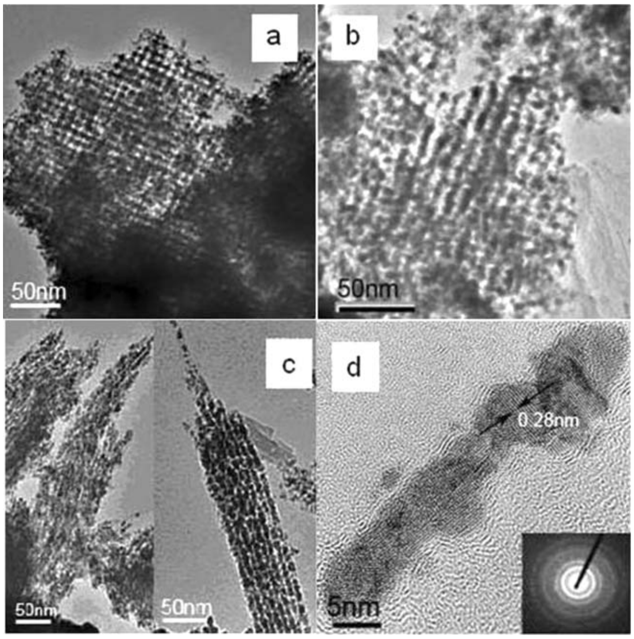


Fig. 3 TEM images of sample WC-P in the view of [100] (a) and [110] (b, c) directions, respectively; High-resolution TEM image of the sample (d); The inset in (d) is the selected area electron diffraction (SAED) pattern of WC-P.

The prepared mesoporous WC product is well crystallized and has a polycrystalline character from the selected area electron diffraction (SAED) pattern (inset in Fig. 3d).

The representative FE-SEM images of the prepared sample WC-P can be found in Fig. 4a and Fig. 4b. The overall morphology of prepared mesoporous WC material is irregular from the low-resolution FE-SEM image (Fig. 4a), however, many rod-like particles can be seen in the high-resolution image (Fig. 4b) which are about 100 nm in diameter and several hundred nanometers in length. In addition, no Si signals can be detected from the EDX spectrum (Fig. 4c) meaning that the silica template has been removed completely for WC-P. A special advantage of the present approach for the synthesis of mesoporous WC is that the mesoporous WC structure can be formed at a relatively low temperature of 700 °C, which prevents the WC nanoparticles from over-growing and ensures the preservation of the mesoporous structure.

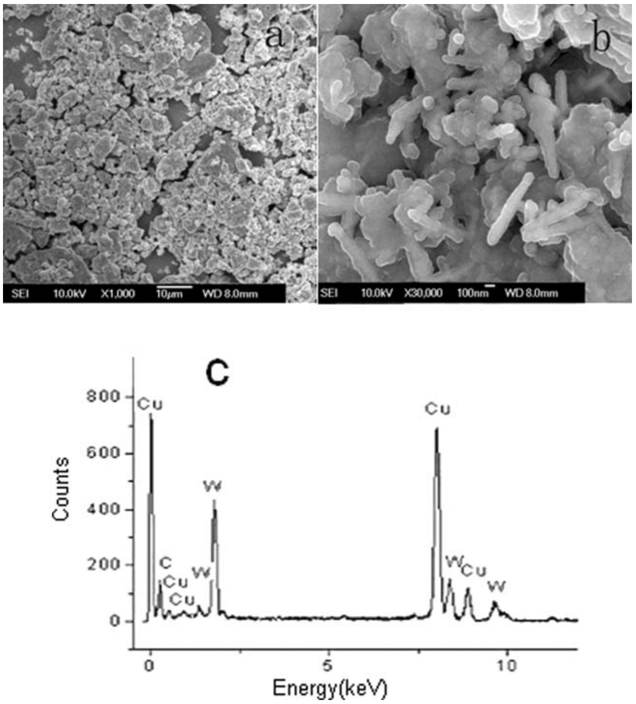


Fig. 4 FE-SEM images of the sample WC-P (a, b) and its EDX spectrum (c).

Table 1 The pore parameters of the samples calculated from the N_2 sorption isotherms

Sample	BET surface area/m^2 g^{-1}	Pore size/nm	Pore volume/cm^3 g^{-1}
WC-NP	138	4.8	0.28
WC-P	56.2	10.8	0.23
KIT-6	820	6.51	1.26

KIT-6: d_{211} = 9.52 nm, thickness of pore wall = 4.5 nm.

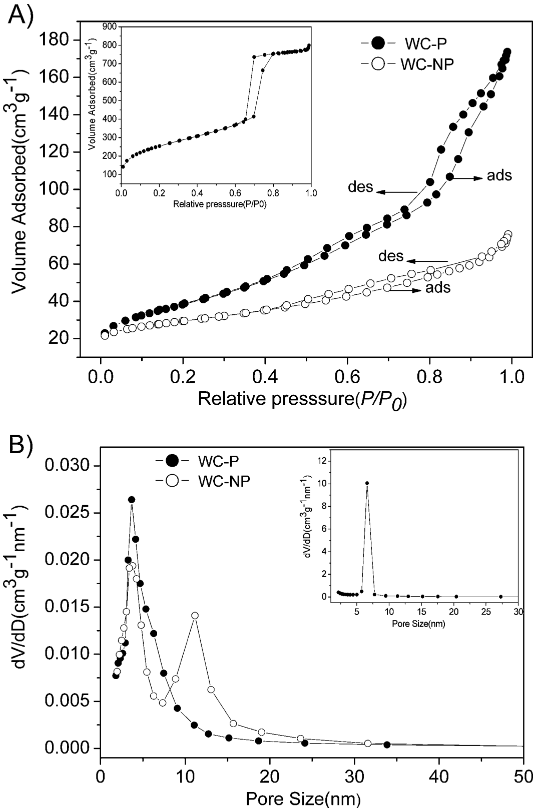


Fig. 5 A: Nitrogen sorption isotherms of the prepared WC samples and the mesoporous silica (KIT-6) (inset); B: the corresponding pore size distribution curves.

Fig. 5 gives the N_2 sorption isotherms of the prepared samples and the corresponding pore size distribution curves. For sample WC-P, the N_2 sorption isotherm shows typical type IV character of mesoporous solids,[27] which is similar to that of mesoporous silica (KIT-6) template in the inset of Fig. 5A. The adsorption volume of WC-P is much higher than that of sample WC-NP according to the sorption isotherms in Fig. 5A. The BET specific surface areas and the calculated pore parameters of the two samples are listed in Table 1. WC-P has a surface area up to 138 m^2 g^{-1}, much higher than that of WC-NP (56.2 m^2 g^{-1}), also considerably higher than the reported value of mesoporous WC (76 m^2 g^{-1}) by a surfactant-directing route.[19,20] In addition, the corresponding pore size distribution of WC-P shows one sharp peak as compared to the bimodal pore size distribution of the latter (Fig. 5B), and the average pore size of WC-P is 4.8 nm much smaller than that of WC-NP of 10.8 nm. The pore size of sample WC-P matches well with the wall thickness of silica template (4.5 nm) as shown in Table 1, and the diameter of the WC nanorods (6–7 nm, Fig. 3d) is also well corresponding with the pore size of the mesoporous silica template (6.5 nm, inset of Fig. 5B). This indicates that the WC-P prepared by the modified replicating route well inherits the mesoporous structure of silica template.

3.2. Catalytic activity for NH_3 decomposition

The temperature programmed reaction (TPR) profiles for NH_3 decomposition over prepared mesoporous WC products are shown in Fig. 6. The as-synthesized tungsten carbide replica was directly used as catalyst without any treatment. A control experiment showed that NH_3 does not thermally decompose significantly in the temperature range up to 700 °C without using the catalyst. NH_3 decomposition on sample mesopoorous WC-P

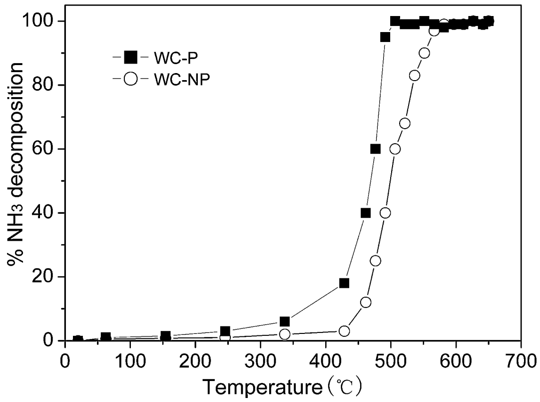


Fig. 6 TPR profiles for NH_3 decomposition on prepared WC-P and WC-NP products.

started at 340 °C and increased sharply at and above 450 °C. The complete conversion was achieved at 500 °C and maintained up to 650 °C. For comparison, the catalytic activity of sample WC-NP was also studied. Compared to WC-P, NH_3 decomposition reaction on WC-NP took place at higher temperature of 430 °C, and the complete decomposition temperature of NH_3 is at about 580 °C. This shows that mesoporous WC-P with a higher surface area and partially ordered pore structure has higher catalytic activity for the NH_3 decomposition reaction and considerably lower reaction temperature as compared to the reference.

In order to investigate the stability and induction activity of the mesoporous tungsten carbide (sample WC-P) during reaction, the variations in % NH_3 decomposition as a function of time-on-stream (TOS) at selected temperatures were measured and the results are shown in Fig. 7. The inlet concentration of NH_3 was 1 sccm, with the balance being He. The reaction was characterized by an induction period at different temperatures. At 450 °C, the activation of the catalyst took about 100 min and then reached the steady-state reaction period. Increasing the reaction temperature, the induction period reduced accordingly. As for 470 °C and 490 °C, periods for the catalyst activation were about 70 min and 55 min, respectively. At 510 °C, complete decomposition of NH_3 was obtained in about 5 min TOS for the space velocity utilized. No deactivation of the catalyst was observed for 6 h TOS at each of these temperatures, which reveals good catalytic stability for NH_3 decomposition on mesoporous WC prepared by an impregnation–compaction route.

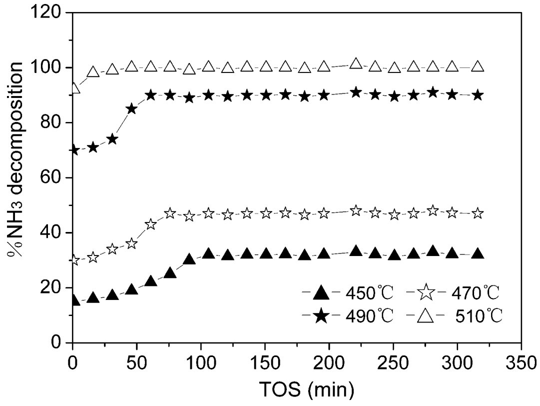


Fig. 7 TOS behavior of the mesoporous WC-P catalyst at various temperatures [concentration of NH_3 in inlet stream: 1 sccm].

4. Conclusion

Mesoporous tungsten carbides with a high surface area of 138 m^2 g^{-1} have been synthesized at a relatively low temperature by a modified template replicating route in which the W precursor was sealed within the pore structure of the silica template by compaction under an external pressure. The mesoporous WC replica prepared by this route is well crystallized and has partially ordered mesoporous structure. The mesoporous WC shows high and stable catalytic activity for the decomposition reaction of NH_3, and the complete NH_3 decomposition was achieved on this mesoporous material at about 500 °C, considerably lower than that of the non-mesostructured reference. Based on its similar catalytic characteristic to Pt, this high surface area mesoporous WC should be potentially applicable in various catalysis fields.

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