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Article

SnO₂ nano-sheet as an efficient catalyst for CO oxidation

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ABSTRACT

Polycrystalline SnO₂ fine powder consisting of nano-particles (SnO₂-NP), SnO₂ nano-sheets (SnO₂-NS), and SnO₂ containing both nano-rods and nano-particles (SnO₂-NR+NP) were prepared and used for CO oxidation. SnO₂-NS possesses a mesoporous structure and has a higher surface area, larger pore volume, and more active species than SnO₂-NP, and shows improved activity. In contrast, although SnO₂-NR+NP has only a slightly higher surface area and pore volume, and slightly more active surface oxygen species than SnO₂-NP, it has more exposed active (110) facets, which is the reason for its improved oxidation activity. Water vapor has only a reversible and weak influence on SnO₂-NS, therefore it is a potential catalyst for emission control processes.

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1. Introduction

SnO₂ is an n-type semiconductor with abundant surface deficient oxygen species [1,2] and lattice oxygen that is also reducible [1,3]. In addition, it is stable chemically with a melting point of 1630 °C [4]. Over the past decades, its properties as a gas sensing material have been widely studied [5–7]. Although it is also a potential catalytic material, especially for air pollution control reactions, studies on its catalytic properties are relatively few. During the past four years, our group has performed a series of systematic work on understanding its catalytic chemistry [3,8–16]. Regular SnO₂ fine powder prepared by the traditional precipitation method generally has a low surface area below 20 m²/g after calcination above 500 °C [9,11,12], which limits its CO and CH₄ oxidation reactivity. The introduction of other metal cations such as Fe [17,18], Cr [3,17,18], Mn [18], Ce [9], or Ta [8] into its lattice to form a solid solution can increase its surface area significantly and induce the formation of more active oxygen species, thus increasing its activity as

well as thermal stability. On the other hand, some metal cations in the +3 valence state can react with SnO₂ to form A₂B₂O₇ pyrochlore compounds, in which Sn occupies the B site [14,15]. These pyrochlore compounds generally possess very good thermal stability and oxygen vacancies, which makes them potential catalysts for environmental catalytic reactions. In addition, SnO₂ was also reported to be a good support for noble metals as catalysts for CO and CH₄ oxidation [11]. Fuller and co-workers [19] found that Pd/SnO₂ showed much higher activity than Pd/SiO₂ due to a synergetic effect between Pd and SnO₂. Furthermore, the addition of water vapor into the reaction feed can improve the CO oxidation reactivity on Pd/SnO₂, which has been confirmed by our experiments on Pd/SnO₂/Al₂O₃ catalysts [12]. When studying Pd/SnO₂ catalysts, Eguchi and co-workers [20] also found the presence of synergism between the noble metal and the support, which enhanced the activity of the catalysts significantly.

Besides these studies on regular SnO₂ fine powder, our most recent results demonstrated that a SnO₂ nano-rod also showed

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superior CO oxidation reactivity [10], although its surface area is extremely low ($1 \text{ m}^2/\text{g}$). The formation of uniform nano-rod microcrystals creates preferentially exposed (110) facets, which have been reported to be the active facets for SnO_2 [10,21]. Using density functional theory calculations, Yang and co-workers [21] also proved that the (110) planes are the active facets of SnO_2 . As a result, the electronic properties of the Sn cations were altered, and the SnO_2 nano-rod showed the reaction behavior of noble metal catalysts. H_2 temperature-programmed reduction (H_2 -TPR) testified that different from the regular SnO_2 fine powder, the lattice oxygen of this nano-rod is non-reducible due to the formation of a rigid crystal structure. Therefore, CO oxidation on it would follow the Langmuir-Hinshelwood or Eley-Rideal mechanism, which is typical of noble metal catalysts. For comparison, using a simple co-precipitation method, uniform mesoporous Cu- SnO_2 nano-sheets with a high surface area ($196 \text{ m}^2/\text{g}$) and more active surface oxygen species were successfully prepared, which also showed remarkable activity for CO oxidation [16].

Many studies have demonstrated that when prepared with a special morphology, SnO_2 possesses particular characteristics that improve its gas sensing properties [5–7,22]. However, studies on SnO_2 with different morphologies as catalytic materials have been rare. To more deeply understand the catalytic chemistry of SnO_2 and achieve improved catalysts for CO oxidation, in this study, SnO_2 catalysts with different morphology and compositions were prepared by various methods. Mesoporous SnO_2 nano-sheet with a much higher surface area than regular SnO_2 fine powder can be prepared, which displayed significantly improved CO and CH_4 oxidation reactivity. Using multiple characterization techniques, the reasons for the improved reaction performance were elucidated.

2. Experimental

2.1. Catalyst preparation

2.1.1. SnO_2 nano-sheets

SnO_2 nano-sheet was prepared according to the method reported in reference [23]. $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.7 g) was added into 50 mL distilled deionized (DDI) water (solution A). Urea (0.12 g) was added into 50 mL DDI water (solution B) to prepare a stable solution. Then solution B was added slowly into solution A with continuous stirring. After intense ultrasonic treatment, the solution mixture was transferred into a Teflon-lined stainless steel autoclave for crystallization at 160°C for 48 h. After cooling to room temperature, the solid was obtained by filtration, washed repeatedly and thoroughly with DDI water and dried at 110°C overnight in air atmosphere. The final catalyst was named SnO_2 -NS because the SEM image in Fig. 1(a, b) demonstrated that it consisted of neat and uniform nano-sheets.

2.1.2. SnO_2 nano-rods

SnO_2 nano-rods were prepared according to the method reported in reference [24]. In a typical synthesis process, 0.9 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added into 100 mL ethanol/DDI water (1:1, v/v) mixture followed by the addition of 1.6 g KOH. After in-

tense ultrasonic treatment, the solution mixture was transferred into a Teflon-lined stainless steel autoclave for crystallization at 180°C for 24 h. After cooling to room temperature, the product was obtained by filtration, washed repeatedly and thoroughly with DDI water and dried at 110°C overnight in an air atmosphere. The SEM image in Fig. 1(c) proved that this sample consisted of both SnO_2 nano-rods and nanoparticles, therefore it was named SnO_2 -NR+NP.

2.1.3. Regular SnO_2 nano powder

For comparison with our previous results, the traditional precipitation method was used to prepare regular SnO_2 nanopowder according to our previous publication [10]. This was named SnO_2 -NP because the SEM image in Fig. 1(d) demonstrated that it consisted of spherical particles.

2.2. Catalyst characterization

The microstructure and morphology of the synthesized products were characterized by scanning electron microscopy (SEM). Small amounts of the dried powders were dispersed in ethanol, and a few drops were dripped onto the silicon slice support. The samples were then viewed in a Hitachi S-4800 field emission scanning electron microscope at 30 kV.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus diffractometer instrument operating at 40 kV and 30 mA with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.154178 \text{ nm}$). Scans were taken in a 2θ range of 10° – 90° and with a step of $0.02^\circ/\text{s}$. The mean crystallite size of the samples was calculated with the Scherrer equation based on the strongest peak of SnO_2 with an (hkl) of (101), for which the 2θ value is 33.8° .

N_2 adsorption was used to examine the porous and textural properties of the samples. The measurements were carried out at -196°C on a Micromeritics ASAP 2020 apparatus. All the samples were pretreated in vacuum at 200°C for 5 h before the measurement. The surface area and pore volume were obtained by the Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

H_2 -TPR experiments were carried out on a FINESORB 3010C instrument with a 10% H_2/Ar gas mixture flow. The temperature was increased from room temperature to 800°C at a rate of $10^\circ\text{C}/\text{min}$. A 25 mg sample was used for the test. A thermal conductivity detector (TCD) was employed to monitor the H_2 consumption. For H_2 consumption quantification, a calibration experiment was carried out using a high purity CuO (99.99%) sample.

X-ray photoelectron spectroscopy (XPS) tests were carried out on a Perkin-Elmer PHI1600 system using a single Mg K X-ray source operating at 300 W and 15 kV. The spectra were obtained at ambient temperature with an ultrahigh vacuum. The binding energies were calibrated using the C 1s peak of graphite at 284.6 eV as a reference.

2.3. Activity evaluation

The catalysts were evaluated for CO and CH_4 oxidation in a continuous flow reactor with a gas composition of 1% CO (or

1% CH₄), 21% O₂ and balanced by high purity N₂. Typically, 100 mg catalyst particles (0.2–0.3 mm) were used for each measurement with a flow rate of 30 mL/min, which corresponded to a weight hourly space velocity (WHSV) of 18000 mL h⁻¹ g⁻¹. The reactants and products were analyzed online on a GC9310 gas chromatograph equipped with a TDX-01 column and a TCD.

3. Results and discussion

3.1. SEM images of the catalysts

SEM was used to investigate the morphology of the SnO₂ samples prepared with the different methods. The images are shown in Fig. 1. Fig. 1(a) and (b) demonstrated that the SnO₂-NS sample consisted of uniform sheets with many loose pores and a thickness of 10 nm, indicating that SnO₂ nano-sheets were successfully prepared. However, Fig. 1(c) shows an image containing both nano-rods and irregular spherical particles. Apparently, with the method used in this study, 100% pure nano-rods were not successfully synthesized. The sample comprised both nano-rods and nanoparticles. In contrast, SnO₂-NP, the sample prepared with a traditional precipitation method for comparison purpose, consisted of relatively uniform spherical particles with an average diameter of 21 nm (Fig. 1(d)), except that some particles have accumulated into larger grains. In summary, with the different methods, SnO₂ with different morphologies were obtained.

3.2. Activity evaluation

The activity of the SnO₂ catalysts prepared by different methods was first evaluated using CO oxidation as the probe reaction. The results are shown in Fig. 2(a). SnO₂-NP, the reference sample, showed the lowest activity among the three catalysts, with complete CO oxidation achieved at 360 °C. SnO₂-NS, the nano-sheet sample, showed the highest activity on which complete CO oxidation occurred at 240 °C. The parallel shift of the CO conversion curve to a 100 °C lower temperature region in comparison with SnO₂-NP also testified its much im-

Fig. 1. SEM images of SnO₂ catalysts with various morphologies. (a, b) SnO₂-NS; (c) SnO₂-NR+NP; (d) SnO₂-NP.

Fig. 2. Catalytic performance of SnO₂ catalysts with various morphologies for CO (a) and CH₄ (b) oxidation.

proved oxidation activity. SnO₂-NR+NP showed also higher CO oxidation activity than the regular SnO₂-NP sample, but which was lower than that of SnO₂-NS. Thus, SnO₂ with special morphologies showed significantly improved CO oxidation activity over the regular SnO₂ nanoparticles.

To gain a deeper understanding of the modification due to the morphology change, the reaction rate at 140 °C and the activation energy of the catalysts were calculated. The measurements were performed under differential condition with CO conversion below 20% to exclude mass and heat transfer effects. As listed in Table 1, SnO₂-NS showed the highest reaction rate and lowest activation energy, and SnO₂-NP showed the lowest reaction rate and highest activation energy. In comparison, both the reaction rate and activation energy over SnO₂-NR+NP were between those of the above two samples.

The CH₄ oxidation reactivity of the samples was also probed and compared in Fig. 2(b). The reaction rate at 440 °C and activation energy are listed also in Table 1. Since CH₄ contains only

Table 1

Reaction performance over SnO₂ catalysts with various morphologies.

Sample	CO oxidation ^a		CH ₄ oxidation ^b	
	Rate (10 ⁻⁷ mmol g ⁻¹ s ⁻¹)	E _a (kJ/mol)	Rate (10 ⁻⁷ mmol g ⁻¹ s ⁻¹)	E _a (kJ/mol)
SnO ₂ -NS	2.2	51.1	3.0	133.3
SnO ₂ -NR+NP	0.87	53.0	1.9	137.9
SnO ₂ -NP	0.0095	81.2	1.3	154.1

^a Calculated at 140 °C. ^b Calculated at 440 °C.

Fig. 3. XRD patterns of SnO₂ catalysts with various morphologies.

four strong C–H bonds, it requires a much higher activation energy for reaction compared with CO oxidation [9]. Therefore, the reactivity difference was not as evident as in the CO oxidation case. However, both the reaction rate and activation energy basically followed the same sequence as CO oxidation. In summary, CO and CH₄ oxidation results testified that with the formation of SnO₂ nano-sheets and nano-rods, more active sites were introduced onto the surface of the samples, hence improving the activity.

3.3. Texture/structure properties of the catalysts

To identify the phase composition and crystallinity of the SnO₂ samples prepared by the different methods, XRD analysis was performed. The results are shown in Fig. 3. All the samples showed the diffraction features of the tetragonal rutile SnO₂ phase, testifying that although they have different morphologies, they consisted of the pure rutile SnO₂ phase. However, the different peak intensity of the diffraction peaks indicated that the three samples have different crystallinity. The crystallite sizes of the samples were calculated and listed in Table 2. SnO₂-NP, the regular fine powder sample, has the largest crystallite size, while SnO₂-NS, the nano-sheet sample, has the smallest. In addition, the crystallite size of SnO₂-NR+NP was

Table 2

Texture/structure properties of the SnO₂ catalysts with various morphologies measured by XRD and N₂ adsorption.

Sample	Crystallite size (nm)	$I_{(110)}/I_{(101)}$	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
SnO ₂ -NS	2.4	75	54	0.47	16.8
SnO ₂ -NR+NP	11.4	100	28	0.17	12.5
SnO ₂ -NP	29.7	65	19	0.16	10.4

also much smaller than that of SnO₂-NP but larger than that of SnO₂-NS. This indicated that with the formation of special morphologies, the crystallization of the SnO₂ can be impeded.

It was formerly reported that the (110) plane is the active crystal facet for SnO₂ [10,21]. A SnO₂ sample with preferentially exposed (110) facets generally has improved oxidation reactivity. Therefore, to elucidate if the samples have preferentially exposed the (110) plane, the $I_{(110)}/I_{(101)}$ ratios of the samples were calculated and also listed in Table 2. The intensity of the (101) peak, the strongest peak, was used as an internal standard. While SnO₂-NS and SnO₂-NP have a similar value for this ratio, SnO₂-NR+NP has an evidently improved one, which testified that this sample has more exposed (110) facets. This was possibly due to the presence of SnO₂ nano-rods in its composition. Thus, the preferentially exposed (110) facets would be one of the reasons for its improved CO and CH₄ oxidation reactivity.

The textural and structural properties of the catalysts were also measured by N₂ adsorption. The results are shown in Fig. 4 and Table 2. SnO₂-NS possessed a surface area of 54 m²/g, which was nearly 2 times that of SnO₂-NR+NP and 3 times that of SnO₂-NP. The change in surface area was in line with the sequence of the crystallinity of the samples measured by XRD.

As shown in Fig. 4, all the samples have a type IV adsorption isotherm with a H3 hysteresis loop. However, compared with SnO₂-NR+NP and SnO₂-NP, SnO₂-NS has a much larger pore volume and pore size (Table 2), indicating that this sample possessed a large amount of mesopores. The presence of a large quantity of mesopores in the solid would facilitate the diffusion of reactants and products, which would improve the activity of the SnO₂-NS catalyst.

Fig. 4. N₂ adsorption isotherms and pore size distributions (inset) of the SnO₂ catalysts with various morphologies.

Fig. 5. H_2 -TPR profiles of SnO_2 catalysts with various morphologies.

3.4. H_2 -TPR study on the redox properties

The redox properties of the SnO_2 samples with different morphologies were tested by H_2 -TPR. The results are shown in Fig. 5. The quantification of the H_2 consumption amount and O/Sn atomic ratio for the samples are also listed in Table 3. SnO_2 -NP showed a reduction peak at 715 °C, which was assigned to the reduction of SnO_2 to metallic Sn [3,25]. In comparison, the same reduction peaks of SnO_2 -NR+NP and SnO_2 -NS were shifted to 710 and 687 °C, respectively, indicating that the lattice oxygen species of the latter two were more reducible and active, especially SnO_2 -NS. The O/Sn atomic ratios of the samples were around 2.0/1, which is the stoichiometric ratio for the reduction of Sn^{4+} to Sn^0 . This further confirmed that Sn was fully oxidized in the three samples, in agreement with the XRD phase identification results. The formation of much more active oxygen species in SnO_2 -NS would be another reason for the higher CO and CH_4 oxidation reactivity.

3.5. XPS analysis of the surface properties of the catalysts

To further understand the surface properties of the SnO_2 catalysts with different morphologies, XPS measurements were

Table 3

H_2 -TPR quantification results of the SnO_2 catalysts with various morphologies.

Sample	Temperature (°C)	H_2 consumption (mmol/g)	O/Sn atomic ratio
SnO_2 -NS	687	12.2	2.0/1
SnO_2 -NR+NP	710	11.9	1.9/1
SnO_2 -NP	715	12.6	2.0/1

Table 4

XPS results of the SnO_2 catalysts with various morphologies.

Sample	Sn 3d binding energy (eV)		ΔE (eV)	O 1s binding energy (eV)		O_{ads}/O_{lat}
	$3d_{3/2}$	$3d_{5/2}$		O_{ads}	O_{lat}	
SnO_2 -NS	494.4	486.0	8.4	531.6	529.7	0.87
SnO_2 -NR+NP	495.0	486.6	8.4	531.8	530.3	0.63
SnO_2 -NP	495.7	487.1	8.6	531.6	530.2	0.30

performed. The results are shown in Fig. 6 and Table 4. The binding energies were calibrated by the C 1s internal standard. The binding energy of Sn 3d was typical for Sn^{4+} cations, indicating that the Sn species in all the samples were fully oxidized, in line with the XRD and H_2 -TPR results. The ΔE between Sn $3d_{3/2}$ and Sn $3d_{5/2}$ was calculated and listed in Table 4. This generally reflects the chemical environment change of the Sn species [9,26]. SnO_2 -NP has a value of 8.6 eV. In comparison, the values of SnO_2 -NR+NP and SnO_2 -NS were shifted to 8.4 eV, indicating that in these two samples, the Sn species has a similar chemical environment, but which is different from that of the regular fine powder. This was possibly due to the formation of the nano-sheet and nano-rod structure in these samples.

It was previously reported that the surface of SnO_2 has a large amount of deficient oxygen species [1,2]. The asymmetric O 1s peaks of the three samples in this study also confirmed the presence of multiple oxygen species. Therefore, the O 1s peaks of the three samples were deconvoluted and shown in Fig. 6(b). As reported previously, a deconvoluted O 1s peak with a higher binding energy was assigned to loosely bounded surface oxygen species (O_{ads}). The peak with the lower binding energy was

Fig. 6. XPS analysis of the SnO_2 catalysts with various morphologies. (a) Sn 3d spectra; (b) O 1s spectra.

Fig. 7. Water resistance of the SnO₂-NS.

assigned to the surface lattice oxygen species (O_{lat}) [9]. Based on this, the O_{ads}/O_{lat} ratios of the three samples were calculated and also listed in Table 4. On the surface of the SnO₂-NR+NP and SnO₂-NS samples, more loosely bounded oxygen species were present in comparison with SnO₂-NP. For CO oxidation, the presence of this active surface oxygen species is obviously beneficial for the activity of the catalyst.

3.6. Stability of SnO₂-NS in the presence of water vapor

For CO oxidation in practical emission control processes, generally, 1%–10% water vapor is present. The stability of a catalyst in the presence of an amount of water vapor determines its application potential. Therefore, SnO₂-NS, the most active catalyst in this study, was subjected to a stability test at 240 °C in the presence of 5% water vapor. As shown in Fig. 7, with the introduction of water vapor, the CO conversion dropped from 80% in the dry feed to 60% within 2 h, but which then remained constant without further decrease during the following 25 h test with water vapor. Most importantly, after removing the water vapor, the CO conversion was completely restored, testifying that the water deactivation was not permanent. This proved that SnO₂-NS was both active and also structurally stable, which makes it a potential catalyst for low temperature CO oxidation in emission control processes.

4. Conclusions

Pure SnO₂ samples with different morphologies and compositions were prepared and used for CO and CH₄ oxidation. SnO₂-NS consisted of uniform and neat nano-sheets with a thickness of 10 nm. N₂ adsorption results demonstrated that in comparison with SnO₂-NP, the SnO₂-NS possessed a much higher surface area and larger pore volume, and contained a large amount of mesopores, which would improve the contact of the reactants with the surface active sites and facilitate the mass transfer of reactants and products. H₂-TPR and XPS results showed that more active oxygen species were formed on the surface of this nano-sheet sample. As a result, SnO₂-NS displayed much improved CO and CH₄ oxidation reactivity in comparison with SnO₂-NP. As for SnO₂-NR+NP, SEM proved that it consisted of both nano-rods and nano-particles. Compared with SnO₂-NP, it has a slightly higher surface area, slightly larger pore volume, and slightly more active surface oxygen species, but possessed more active (110) facets, which were reported to be the active facet for SnO₂, therefore, it showed higher activity than SnO₂-NP but lower than that of SnO₂-NS. Water vapor has only reversible and mild deactivation on SnO₂-NS, which makes it a potential catalyst for exhaust emission control.

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Graphical Abstract

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SnO₂ nano-sheet as an efficient catalyst for CO oxidation

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Mesoporous SnO₂ nanosheet with a higher surface area, larger pore volume, and more active surface oxygen species showed improved catalytic activity for CO oxidation.

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高效SnO₂纳米片催化剂用于CO氧化

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摘要: SnO₂是一种具有丰富表面缺陷氧的n型半导体,其晶格氧亦可还原.另外其熔点高达1630℃,具有较高的热稳定性能.在过去的几十年中,SnO₂主要用作气敏材料.而其作为催化材料的性能,特别是用于大气污染治理则鲜见报道.在过去的几年中,本课题组系统研究了SnO₂的催化化学,发现利用传统共沉淀法制备的SnO₂纳米粉末,在焙烧温度高于500℃时,其比表面积通常低于20 m²/g,因而限制了其氧化活性.在SnO₂晶格中掺杂Fe、Cr、Mn、Ce和Ta等形成固溶体可有效提高其比表面积并产生更多的活性氧物种,因而其对CO和CH₄的氧化活性及稳定性大幅度提高.本课题组近期研究表明,采用熔盐法制备的高纯SnO₂纳米棒单晶比SnO₂纳米颗粒和纳米微球等具有更优异的CO氧化活性,260℃即可完全氧化CO.且在240–260℃狭窄温度区间发生转化率突跃,表现出类似贵金属的催化行为.值得指出的是,SnO₂纳米棒的比表面积(1 m²/g)远低于其他几种形貌的材料,且无活泼氧存在.但研究表明SnO₂纳米棒具有优先暴露的(110)活泼晶面,是导致其活性优良的主要原因.另外,我们采用简单共沉淀法成功制备了高比表面介孔Cu-Sn复合氧化物纳米片(196 m²/g),其在140℃即可将CO完全氧化,且具有优良的抗水失活性能.因此,SnO₂的形貌是影响其催化活性的主要因素之一,但迄今未见较系统深入的研究.

在上述工作基础上,本文通过水热法,不添加任何有机模板剂,成功制备了厚度约10 nm的介孔SnO₂纳米片和纳米棒及纳米颗粒混合物样品;采用常规共沉淀法制备了SnO₂纳米颗粒.并将以上三种不同形貌的SnO₂纳米材料用于CO氧化.利用SEM、XRD、N₂吸附-脱附、H₂-TPR和XPS探讨了不同形貌SnO₂催化剂的体相结构和表面性质及其对催化性能的影响.与SnO₂纳米颗粒相比,介孔SnO₂纳米片具有高的比表面积、孔体积及更活泼的氧中心,因此后者CO氧化活性远高于前者.在空速18000 mL/(g·h)时,SnO₂纳米片在260℃即可完全氧化CO.而SnO₂纳米颗粒的CO完全氧化温度高于360℃.SnO₂纳米棒和纳米颗粒的混合样品虽然其比表面积和孔体积及表面活性氧的活性仅略高于SnO₂纳米颗粒,但XRD定量结果表明,其具有更多的暴露(110)活泼晶面,因而活性也高于SnO₂纳米颗粒.SnO₂纳米片催化剂的寿命及抗水性能测试结果表明,该催化剂具有良好的稳定性,且水蒸气仅对其活性产生可恢复的影响.进一步优化其性能,SnO₂纳米片有可能用于实际汽车尾气状况下的CO催化清除.

关键词: 氧化锡催化剂; 纳米片; 纳米棒; 暴露活性晶面; 一氧化碳氧化

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