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Article

SnO₂-based solid solutions for CH₄ deep oxidation: Quantifying the lattice capacity of SnO₂ using an X-ray diffraction extrapolation method

Qi Sun [†], Xianglan Xu [†], Honggen Peng, Xiuzhong Fang, Wenming Liu, Jiawei Ying, Fan Yu, Xiang Wang ^{*}

College of Chemistry, Nanchang University, Nanchang 330031, Jiangxi, China

ARTICLE INFO

Article history:

Received 28 February 2016

Accepted 22 April 2016

Published 5 August 2016

Keywords:

SnO₂-based solid solution

X-ray diffraction extrapolation method

Lattice capacity

Methane deep oxidation

Carbon monoxide oxidation

ABSTRACT

A series of SnO₂-based catalysts modified by Mn, Zr, Ti and Pb oxides with a Sn/M (M = Mn, Zr, Ti and Pb) molar ratio of 9/1 were prepared by a co-precipitation method and used for CH₄ and CO oxidation. The Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺ cations are incorporated into the lattice of tetragonal rutile SnO₂ to form a solid solution structure. As a consequence, the surface area and thermal stability of the catalysts are improved. Moreover, the oxygen species of the modified catalysts become easier to be reduced. Therefore, the oxidation activity over the catalysts was improved, except for the one modified by Pb oxide. Manganese oxide demonstrates the best promotional effects for SnO₂. Using an X-ray diffraction extrapolation method, the lattice capacity of SnO₂ for Mn₂O₃ was 0.135 g Mn₂O₃/g SnO₂, which indicates that to form stable solid solution, only 21% Sn⁴⁺ cations in the lattice can be maximally replaced by Mn³⁺. If the amount of Mn³⁺ cations is over the capacity, Mn₂O₃ will be formed, which is not favorable for the activity of the catalysts. The Sn rich samples with only Sn-Mn solid solution phase show higher activity than the ones with excess Mn₂O₃ species.

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1. Introduction

It is well known that CH₄ and CO are greenhouse gases and air pollutants. Catalytic oxidation has proven to be the most effective way to eliminate CH₄ and CO. To date, various types of catalysts have been tried, which can be divided into two categories, noble metal catalysts and non-noble metal catalysts [1–4]. Noble metal based catalysts, especially platinum group catalysts, have been extensively studied and found to be the most active catalysts for CH₄ and CO oxidation [1,2]. However, some major disadvantages, such as limited availability, high

cost and inferior thermal stability at elevated temperatures, have hindered their widespread exploitation in real exhaust treatment processes. Therefore, considerable attention has been devoted to the development of catalysts based on metal oxides without noble metals or with a significantly decreased amount of noble metals. Among all the metal oxides, manganese oxides and tin dioxides have attracted a lot of attention owing to their special properties, which have been reviewed in detail recently [5,6].

SnO₂ is an n-type semiconductor with a wide band gap ($E_g = 3.6$ eV), which has been widely used in gas sensors [7–9], lith-

^{*} Corresponding author. Tel: +86-15979149877; E-mail: xwang23@ncu.edu.cn

[†] These authors contributed equally to this work.

This work was supported by the National Natural Science Foundation of China (21263015, 21567016 and 21503106), the Education Department Foundation of Jiangxi Province (KJLD14005 and GJJ150016), and the Natural Science Foundation of Jiangxi Province (20142BAB213013 and 20151BBE50006), which are greatly acknowledged by the authors.

DOI: 10.1016/S1872-2067(15)61119-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 8, August 2016

ium-ion batteries [10,11], electrodes for photovoltaic devices [12–14] and catalytic materials [15–27]. Because of its facile surface and lattice oxygen and high thermal stability (melting point, 1630 °C), the catalytic properties of SnO₂ have received more and more attention. In the last 5 years, our group has systematically investigated the catalytic chemistry of SnO₂ for both pollution control [18–27] and green energy production reactions [28,29]. It is revealed that the catalytic properties of SnO₂ can be enhanced by substituting part of the Sn⁴⁺ in the crystal lattice with other cations such as Fe³⁺ [22], Cr³⁺ [23,24], Ta⁵⁺ [25], Ce⁴⁺ [26] and Nb⁵⁺ [27] to form solid solutions with a tetragonal rutile structure. As a consequence, catalysts with significantly improved oxygen mobility, activity and thermal stability can be obtained.

Solid solutions with different chemical compositions are important catalysts for various catalytic reactions and have attracted a lot of attention. A typical example is ceria-zirconia solid solution, which has been widely applied in automotive emission control as an oxygen storage material [30–32]. With the formation of a solid solution structure, both the oxygen storage capacity and thermal stability can be improved remarkably. For two cations to effectively form a solid solution, they must have similar size radii and electronegativities [33,34]. The tolerance factor, a calculation method based on the ionic radii of the metal cations and O²⁻ anion in the structure, has been proposed as a way of determining the possibility of forming a solid solution or the stability of the formed solid solution [35,36]. In our previous work on Sn-Nb solid solutions, we developed an easy X-ray diffraction (XRD) extrapolation method to accurately determine the lattice capacity, which is defined as the maximum amount of guest cations that can be doped into a host's lattice to form a stable solid solution [27].

As a continuation of our previous work, in this study, we prepared SnO₂ solid solutions doped with Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺ cations using a co-precipitation method and investigated the catalytic oxidation of CH₄ and CO. It was found that all the cations can be incorporated into the crystal lattice of the tetragonal SnO₂ to form stable solid solutions if the doping amount is not in excess. The Sn-Mn-O solid solution demonstrated the highest activity. To gain a deeper understanding of the properties of the Sn-Mn-O solid solution, the capacity of Mn³⁺ cations in the SnO₂ lattice was also identified by the XRD extrapolation method. The results show that the capacity effect exists in the Sn-Mn-O catalysts, which is similar to that previously found for Sn-Nb-O solid solutions.

2. Experimental

2.1. Catalyst preparation

A series of SnM (M = Mn, Zr, Ti and Pb) mixed oxide catalysts with a Sn/M molar ratio of 9/1 were prepared by a co-precipitation method. All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. Zr(NO₃)₄·5H₂O (AR) and Mn(NO₃)₂ (50 wt% aqueous solution) were purchased from Sinopharm Chemical Reagent Co., Ltd.

(Shanghai, China). Titanium butoxide (98.0%) was purchased from Aladdin Industrial Corporation (Shanghai, China). Pb(NO₃)₂ (AR), SnCl₄·5H₂O (AR), (25–28) wt% aqueous ammonia solution and (65–68) wt% nitric acid solution were purchased from Xilong Chemical Company (Guangdong, China). Distilled deionized water was used throughout the experiments. In detail, the desired amount of SnCl₄ (0.5 mol/L) and M(NO₃)_x (0.5 mol/L) solution were mixed and stirred thoroughly at room temperature for 1 h. An aqueous ammonia solution (0.5 mol/L) was dripped slowly into the above solution mixture until the pH = 9, which was followed by another continuous stirring for 1 h. The precipitate was vacuum-filtered and washed with distilled deionized water until the filtrate was Cl⁻ free with total dissolved solids of less than 20 ppm. The precipitate was dried at 110 °C overnight (about 12 h), and then calcined at 600 °C in an air atmosphere for 4 h with a ramp of 2 °C/min to obtain the final catalysts, which were named SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 according to the Sn/M molar ratios. To explore the lattice capacity and to optimize the catalyst formulation, a series of Sn-Mn mixed oxide catalysts with different Sn/Mn molar ratios were also prepared using the same procedure, which were named SnMn9.5-0.5, SnMn9-1, SnMn8-2, SnMn7-3, SnMn6-4, SnMn5-5 and SnMn4-6. For comparison, pure SnO₂ and Mn₂O₃ were also prepared using the same method.

2.2. Catalyst characterization

N₂ adsorption-desorption measurements of the catalysts were performed at -196 °C on an ASAP 2020 instrument. All of the samples were degassed under vacuum at 200 °C for at least 4 h before the measurement, and the Brunauer-Emmett-Teller (BET) specific surface areas were calculated based on the linear part of the BET plot ($p/p_0 = 0.05-0.25$). The pore size distributions of the samples were calculated using the Barrett-Joyner-Halenda (BJH) method. The average pore sizes of the samples were obtained from the peak positions of the distribution curves. The total pore volume of each catalyst was calculated at a relative pressure of $p/p_0 = 0.99$.

The powder XRD patterns were recorded on a Bruker AXS D8Focus diffractometer operating at 40 kV and 30 mA, with a Cu K_α irradiation ($\lambda = 1.5405 \text{ \AA}$). Scans were taken with a 2θ range from 10° to 90° and with a step of 2°/min. To keep the data comparable, all of the samples were tested continuously under the same conditions. The mean crystallite sizes of the samples were calculated using the Scherrer equation based on the strongest peak of SnO₂ with hkl Miller indices of (110). The calculated experimental error for 2θ measurement of the peaks was 0.01°, which ensured reliable identification of the peak shifts observed after solid solution formation.

Inductively coupled plasma optical emission spectrometry (ICP) was performed on a VARIAN ICP-715ES instrument to confirm the chemical compositions of the Sn-Mn mixed oxide catalysts. As shown in Table 3, the measured Sn/Mn molar ratios of all the catalysts are the same (within experimental error) as the ratios used for the preparation of the samples, proving that there was no evident change of the chemical

compositions during the preparation process.

Hydrogen temperature-programmed reduction (H_2 -TPR) experiments were performed on a FINESORB 3010 C instrument in a 30 mL/min 10% H_2 –90% Ar gas mixture flow. Generally, 50 mg of the catalyst was used for the test. Prior to the experiments, the catalysts were re-calcined in a high purity airflow at 300 °C for 30 min to remove any surface impurities. The temperature was then increased from room temperature to 850 °C at a rate of 10 °C/min. A thermal conductivity detector (TCD) was employed to monitor the H_2 consumption. CuO (99.99%) was used as the calibration standard for the quantification of the H_2 consumption.

Scanning electron microscopy (SEM) images were taken on a Hitachi S-4800 field emission scanning electron microscope.

X-ray photoelectron spectroscopy (XPS) was performed on a PerkinElmer PHI1600 system using a single Mg K_{α} X-ray source operating at 300 W and 15 kV. The spectra were obtained at ambient temperature in an ultrahigh vacuum. The binding energy was calibrated using the C 1s peak of graphite at 284.5 eV as a reference [37,38].

2.3. Activity evaluation

The oxidation of CH_4 and CO over the catalysts was evaluated using a U-shaped quartz tube (ID = 6 mm) reactor with a down flow. A K-type thermocouple was placed on top of the catalyst bed with the thermocouple head point touching the catalyst to monitor the reaction temperatures. To measure the light-off behavior of the catalysts, all the data were collected on 100 mg of catalyst by increasing the temperature. For CH_4 deep oxidation, the volume composition of the feed gas was 1% CH_4 –21% O_2 and balanced by high purity N_2 . For CO oxidation, the volume composition of the feed gas was 1% CO–21% O_2 and balanced by high purity N_2 . The flow rates of the feed gases were 30 mL/min, which resulted in GHSV = 18000 mL h^{-1} g^{-1} for both CH_4 and CO oxidation. The reactants and products were analyzed on-line on a GC9310 gas chromatograph equipped with a TDX-01 column and a TCD detector. Before analysis, the reaction at each temperature point over the catalyst was stabilized for 30 min to obtain steady state reaction

data. The flow rate of the H_2 carrier gas was 30 mL/min.

3. Results and discussion

3.1. Studies on SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts

3.1.1. Activity tests for CH_4 and CO oxidation

For comparison, the activity of the catalysts was evaluated by both CH_4 deep oxidation and CO oxidation, as shown in Fig. 1. The CH_4 conversion as a function of the reaction temperature over the catalyst is shown in Fig. 1(a). Pure SnO_2 displays a certain activity owing to its active surface deficient oxygen and lattice oxygen species [23–27], on which 92% CH_4 conversion was achieved at 600 °C. The activity increased after the incorporation of Mn, Zr and Ti oxides. The highest activity was obtained with the Sn–Mn binary oxide catalyst, on which complete CH_4 conversion was obtained at 540 °C. However, the introduction of Pb oxide clearly degrades the activity of the resulting catalyst, on which only ~50% CH_4 conversion was achieved at 600 °C.

To gain a deeper understanding of the effect of the modification by the different metal oxides, the steady-state CH_4 oxidation rates at 420 °C were measured under differential conditions. As shown in Table 1, whereas the CH_4 conversion rates on SnZr9-1 and SnTi9-1 are slightly higher than that on pure SnO_2 , the conversion rate on SnMn9-1 was nearly ten times higher. This strongly confirms that the incorporation of manganese oxide results in the formation of much more active sites on the SnMn9-1 catalyst. On the contrary, the CH_4 conversion rate on SnPb9-1 was only about 7% of that on pure SnO_2 , indicating the addition of lead oxide was detrimental to the surface active sites. The overall activation energy in Table 1 also demonstrates that the activation of the CH_4 molecule becomes easier on SnMn9-1, but much more difficult on SnPb9-1.

To further clarify the effect of the modification by the different metal oxides on SnO_2 , the catalysts were also evaluated by the catalytic oxidation of CO, as shown in Fig. 1(b). Similar modification effects were observed. The addition of Mn, Zr and Ti oxides promoted the CO oxidation activity, but the addition

Fig. 1. Catalytic performance of SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts. (a) CH_4 deep oxidation; (b) CO oxidation.

Table 1

Physicochemical properties of SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts.

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	CH ₄ conversion rate ^a (10 ⁻⁴ mmol g ⁻¹ s ⁻¹)	E _a ^b (kJ/mol)
SnO ₂	19	0.03	12.8	0.83	127.1
SnMn9-1	56	0.09	5.0	7.95	115.8
SnZr9-1	45	0.13	9.2	1.05	129.6
SnTi9-1	45	0.08	5.9	0.94	126.6
SnPb9-1	69	0.08	3.3	0.06	178.3

^a Measured at 420 °C.

^b Calculated from the Arrhenius plots and formula.

of Pb oxide degraded the activity. The highest CO oxidation activity was also achieved on the SnMn9-1 catalyst.

3.1.2. N₂ adsorption-desorption and XRD measurements

To investigate the influence of the different metal oxides on the textural properties of SnO₂, the catalysts were subjected to N₂ adsorption-desorption measurements, with the quantified results listed in Table 1. After calcination at 600 °C, the pure SnO₂ had a surface area of 19 m²/g. In contrast, all the catalysts show improved surface areas after the introduction of the secondary metal oxides. Notably, SnPb9-1 had the highest surface area (69 m²/g) among all the catalysts. Considering the fact that this catalyst showed the lowest activity for both CH₄ and CO oxidation, it is reasonable to conclude that the surface area is not a critical factor for the activity of the catalysts.

All the samples exhibited type IV isotherms with H2-type hysteresis loops in the relative pressure range of $p/p_0 = 0.4$ – 0.7 , which is typical for a mesoporous structure formed by interparticle assembly. As shown in Table 1, in comparison with pure SnO₂, the addition of the secondary metal oxides apparently increases the pore volume but decreases the pore size, indicating that the initial bigger mesopores of SnO₂ could have been replaced by a larger amount of smaller mesopores in the modified catalysts. In summary, the addition of the secondary metal oxides evidently alters the initial textural properties of SnO₂.

Fig. 2. XRD patterns of SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts.

The phase compositions of the catalysts were also analyzed by XRD, as shown in Fig. 2. All the modified catalysts show only the typical diffraction characteristic of a tetragonal rutile SnO₂ phase, implying that Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺ cations could have been incorporated into the lattice matrix of SnO₂ to form a solid solution structure. In tetragonal rutile SnO₂, a Sn⁴⁺ cation has a coordination number of 6 and a radius of 0.69 Å. In this study, XPS was used to confirm that the doping metals are in the forms of Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺, which will be discussed in detail later. If these cations also have a coordination number of 6, their radii are 0.65, 0.72, 0.61 and 0.78 Å, respectively, which are close to that of Sn⁴⁺. According to the basic principles [33,34], stable solid solutions are theoretically able to be formed between SnO₂ and these metal oxides.

To confirm this, the 2θ and d values of the three strongest peaks of the rutile SnO₂ phase, peaks (110), (101) and (211), were carefully identified for all the samples, as shown in Table 2. It was found that after the incorporation of different metal oxides the three diffraction peaks shifted slightly and the d values changed somewhat compared with pure SnO₂. These changes are typical of solid solution formation, further demonstrating that Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺ cations were doped into the crystal lattice of SnO₂ to replace part of the Sn⁴⁺ cations to form solid solution structures [39–41]. It has previously been reported that lattice distortion and charge imbalance could take place during the formation of a solid solution structure, thus inducing the formation of more mobile oxygen species and impeding the crystallization of the material at elevated temperatures [23,30,41]. As a consequence, more active catalysts with higher thermal stability can generally be achieved [23,42].

3.1.3. H₂-TPR and XPS measurements

H₂-TPR was used to investigate the redox properties of the modified catalysts, with the profiles shown in Fig. 3. Pure SnO₂ displays a major peak at 669 °C, which is assigned to the reduction of Sn⁴⁺ to metallic Sn⁰ [23,26]. After the introduction of the secondary metal cations into the SnO₂ lattice to form a solid solution structure, this major reduction peak shifts for all the catalysts. Interestingly, SnMn9-1, the most active catalyst, also shows an additional low temperature peak at 230 °C, which is assigned to the reduction of surface deficient oxygen species [26,27]. A large amount of deficient oxygen species is generally present on the surface of SnO₂, which can be depleted completely after calcination at temperatures above 400 °C [17]. Apparently, the incorporation of Mn³⁺ cations into the SnO₂ lattice can stabilize these surface deficient oxygen species even at high temperatures, which is of advantage for the activity of

Table 2

Quantified XRD results of SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts.

Sample	Mean crystallite size (nm)	(110)		(101)		(211)	
		2θ (°)	d (Å)	2θ (°)	d (Å)	2θ (°)	d (Å)
SnO ₂	9.8	26.54	3.36	33.86	2.65	51.90	1.76
SnMn9-1	5.1	26.60	3.35	33.98	2.64	51.92	1.76
SnZr9-1	6.1	26.53	3.36	33.80	2.65	51.72	1.77
SnTi9-1	5.9	26.68	3.34	33.98	2.64	52.18	1.75
SnPb9-1	4.8	26.51	3.36	33.79	2.65	51.74	1.77

Fig. 3. H₂-TPR profiles of SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts.

the catalyst. It is somewhat surprising that the addition of Pb⁴⁺ cations into the lattice of SnO₂ significantly decreases the reduction temperature and divides the reduction into two parts. However, this catalyst still exhibited the lowest activity among all the catalysts, possibly owing to the nature of Pb as a catalyst poisoner.

As a supplement to the H₂-TPR results, XPS was employed to identify the valence states and surface compositions of the samples modified by different metal cations, with the results shown in Fig. 4. Fig. 4(a) presents the Sn 3*d* signals of all the samples. The doublet peaks at ~494 and ~486 eV are ascribed

to Sn 3*d*_{3/2} and 3*d*_{5/2} for Sn⁴⁺, respectively, which is in agreement with the XRD and H₂-TPR results, indicating that in all the catalysts, the Sn was fully oxidized and present as Sn⁴⁺ [43,44]. Fig. 4(b) presents the Mn 2*p* signals of the SnMn9-1 catalyst. The binding energies of Mn 2*p*_{1/2} and Mn 2*p*_{3/2} are ~653 and ~642 eV, respectively, which are nearly identical to those reported for Mn₂O₃ [45,46], proving that Mn³⁺ cations are dissolved in the lattice matrix. Fig. 4(c) presents the Zr 3*d* signals of the SnZr9-1 catalyst. A set of doublet peaks at 184.1 and 181.7 eV for Zr 3*d*_{3/2} and Zr 3*d*_{5/2} respectively, are observed, in agreement with the binding energies reported for ZrO₂ [47]. Fig. 4(d) presents the Ti 2*p* signals of SnTi9-1 catalyst. A set of doublet peaks at 458.7 and 464.4 eV for Ti 2*p*_{3/2} and Ti 2*p*_{1/2}, respectively, are observed, indicating that Ti exists in the Ti⁴⁺ oxidation state in a tetragonal structure [48]. Fig. 4(e) presents the Pb 4*f* spectra of the SnPb9-1 catalyst. A set of doublet peaks at 137.5 and 142.2 eV for Pb 4*f*_{7/2} and Pb 4*f*_{5/2}, respectively, are consistent with the reported binding energies of PbO₂ [43,49,50].

In summary, the XPS results confirm that in the solid solutions formed by the different metal oxides with rutile SnO₂, the secondary metals are present as Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺ in the lattice matrix of SnO₂.

3.2. Studies on Sn-Mn catalysts with different Sn/Mn molar ratios

As discussed above, SnO₂ modified by manganese oxide demonstrates the highest activity among all the catalysts. In-

Fig. 4. XPS profiles of SnMn9-1, SnZr9-1, SnTi9-1 and SnPb9-1 catalysts.

Table 3

Physicochemical properties of Sn-Mn catalysts with different Sn/Mn molar ratios.

Sample	Sn/Mn molar ratio by ICP	Surface area (m ² /g)	Mean crystallite size (nm)	Pore volume (cm ³ /g)	Pore size (nm)	CH ₄ conversion rate ^a (10 ⁻⁴ mmol g ⁻¹ s ⁻¹)	E _a ^b (kJ/mol)
SnO ₂	—	19	9.8	0.03	12.8	0.83	127.1
SnMn9.5-0.5	—	30	6.9	0.08	7.5	5.13	112.6
SnMn9-1	8.7/1.3	56	5.1	0.09	5.0	7.95	115.8
SnMn8-2	7.8/2.2	56	5.3	0.10	5.3	6.45	115.1
SnMn7-3	6.9/3.1	50	5.5	0.16	7.6	5.36	111.2
SnMn6-4	5.9/4.1	42	5.9	0.14	9.1	3.30	109.3
SnMn5-5	4.9/5.1	42	6.1	0.26	16.4	3.57	110.5
SnMn4-6	—	31	7.3	0.27	22.4	3.79	109.5
Mn ₂ O ₃	—	10	34.8	0.04	17.5	3.17	111.6

^a Measured at 420 °C.^b Calculated from the Arrhenius plots and formula.

corporation of Mn³⁺ cations in the lattice matrix of SnO₂ to form a stable solid solution can effectively stabilize the surface deficient oxygen species, improve the activity of the lattice oxygen and enhance the thermal stability of the resulting catalyst, which are believed to be the predominant reasons for the significantly improved reaction performance of the SnMn9-1 catalyst. To gain a deeper fundamental understanding of the properties of solid solutions and as an endeavor to optimize the catalyst formulation, Sn-Mn mixed oxides with different Sn/Mn molar ratios were prepared and subjected to CH₄ deep oxidation.

3.2.1. N₂ adsorption-desorption measurements

The textural properties of the catalysts were first analyzed by the N₂ adsorption-desorption method, with the results shown in Table 3. With the combination of SnO₂ and Mn₂O₃, all the catalysts show larger surface areas and pore volumes, but smaller pore sizes and crystallite sizes than those of the two pure samples. The highest surface area of ~56 m²/g was obtained with SnMn9-1 and SnMn8-2 catalysts. The addition of too much manganese oxide clearly has a negative effect on the surface areas.

3.2.2. Quantifying the lattice capacity of SnO₂ for manganese oxide by the XRD extrapolation method

To gain a better understanding of the effect of modification by Mn₂O₃ on SnO₂, the phase compositions of the Sn-Mn samples with different Sn/Mn molar ratios were analyzed by XRD. As shown in Fig. 5(a), pure SnO₂ demonstrates three diffraction peaks at 26.54° (110), 33.86° (101) and 51.90° (211), which are typical for the tetragonal rutile SnO₂ phase. In contrast, pure Mn₂O₃ demonstrates three diffraction peaks at 23.26° (211), 33.02° (222) and 55.28° (440), which are typical of the Mn₂O₃ phase. For the Sn-Mn binary catalysts, no Mn₂O₃ phase was detected for Sn/Mn molar ratios above 8/2. However, as the amount of Mn increases in SnMn7-3 (decreasing Sn/Mn molar ratio), the Mn₂O₃ phase starts to appear and gradually becomes stronger.

As reported previously for Sn-Nb mixed oxides, the SnO₂ lattice has a certain capacity for Nb⁵⁺ cations, in which only 25% Sn⁴⁺ cations can be replaced by Nb⁵⁺ to form a stable solid solution. The excess Nb was present as free Nb₂O₅ on the surface of the catalysts [27]. Therefore, the lattice capacity of SnO₂ for

Mn³⁺ was also quantified in this study by the XRD extrapolation method described in this earlier publication.

In detail, the intensity of the strongest peak (222) of Mn₂O₃ phase (*I*) for each sample was measured and normalized by that of the strongest peak (110) of the SnO₂ phase (*I*₀), which was used as an internal standard to compensate for any possi-

Fig. 5. XRD analysis of Sn-Mn catalysts with different Sn/Mn molar ratios. (a) XRD patterns; (b) Lattice capacity of rutile SnO₂ for Mn₂O₃.

ble experimental deviation to obtain reliable I/I_0 ratios. The I/I_0 ratios were then plotted against the Mn_2O_3 contents of the samples to obtain a correlated line, as shown in Fig. 5(b). It is noted here that the chemical compositions of the samples were also confirmed by ICP (Table 3). The strict linear line crosses the x -axis at 0.135 g $\text{Mn}_2\text{O}_3/\text{g}$ SnO_2 , which is equal to a Sn/Mn molar ratio of 79/21. In other words, to form a stable solid solution, only 21% Sn^{4+} cations in the crystal lattice of rutile SnO_2 can be replaced by Mn^{3+} cations. Based on this threshold value, it is not difficult to understand that for those samples with Sn/Mn molar ratios higher than 79/21, such as SnMn8-2, SnMn9-1 and SnMn9.5-0.5, only a tetragonal rutile SnO_2 phase can be observed. In these samples, Mn^{3+} cations are completely dissolved into the SnO_2 lattice to form solid solutions, thus escaping the detection of XRD. For those samples with Sn/Mn molar ratios lower than 79/21, after the formation of the solid solution the excess Mn forms a Mn_2O_3 phase, which increases with the increase of Mn content, as evidenced by the gradually increased peak intensities of the Mn_2O_3 phase.

3.2.3. SEM analysis on the morphology of the catalysts

To gain a deeper insight into the morphologies and microstructures of the Sn-Mn catalysts, some typical samples were analyzed by SEM, as shown in Fig. 6. All the samples consist of irregular spherical particles with different grain sizes. Pure SnO_2 has an average particle size of 18 nm, indicating the initial 9.8 nm crystallites agglomerated into bigger particles. Similarly, for SnMn7-3 and SnMn6-4, the two samples with excess manganese oxide, the initial crystallites of ~5 nm also aggregated considerably into much bigger particles with average sizes of approximately 47 and 55 nm, respectively. In contrast, for SnMn9-1 and SnMn8-2, the two samples that completely form a solid solution structure, the aggregation of their initial crystallites was effectively impeded, as evidenced by superfine particles in their SEM images.

Fig. 7. H_2 -TPR profiles of Sn-Mn catalysts with different Sn/Mn molar ratios.

3.2.4. H_2 -TPR analysis

The redox properties of the catalysts with different Sn/Mn ratios were also probed by H_2 -TPR experiments, as shown in Fig. 7. Pure Mn_2O_3 exhibited two reduction peaks at 351 and 455 °C, which are attributed to the reduction of Mn_2O_3 to Mn_3O_4 and Mn_3O_4 to MnO , respectively [51]. For the Sn rich samples with Sn/Mn molar ratios higher than 79/21, besides the major reduction peak ascribed the reduction of Sn^{4+} to Sn^0 at high temperature, a small reduction peak at ~230 °C was observed, which was ascribed to the reduction of surface deficient oxygen species [17]. No evident reduction of Mn_2O_3 was observed. For clarity, the enlarged H_2 -TPR profiles of these catalysts for the reduction of the surface deficient oxygen species are plotted separately and shown as an inset in Fig. 7.

However, starting with the SnMn7-3 catalyst, the peaks due to the reduction of the Mn_2O_3 phase begin to appear and be-

Fig. 6. SEM images of Sn-Mn mixed oxide catalysts with different Sn/Mn molar ratios. (a) SnO_2 ; (b) SnMn9-1; (c) SnMn8-2; (d) SnMn7-3; (e) SnMn6-4.

Fig. 8. Catalytic performance of Sn-Mn catalysts with different Sn/Mn molar ratios. (a) CH₄ conversion; (b) Arrhenius plots.

come more and more evident with increasing Mn content. Indeed, the H₂-TPR results in Fig. 7 provide extra evidence that a stable solid solution structure can be formed if the Sn/Mn molar ratios are higher than 79/21. Surface deficient oxygen species can be stabilized at elevated temperatures on the catalysts that contain a complete Sn-Mn solid solution phase without excess Mn₂O₃, which is believed to be beneficial for the oxidation activity over the catalysts.

3.2.5. Activity and stability evaluation for CH₄ oxidation

The activity of the catalysts was evaluated by CH₄ deep oxidation, with the results presented in Fig. 8. Fig. 8(a) shows the CH₄ conversion versus temperature profiles of the catalysts, which reflect the overall performance over the catalysts. Pure Mn₂O₃ shows certain activity to CH₄ oxidation because it contains an abundance of active lattice oxygen species. Under the same conditions, pure SnO₂ clearly displays lower activity than pure Mn₂O₃. Interestingly, the Sn rich samples with a complete solid solution structure, such as SnMn9.5-0.5, SnMn9-1 and SnMn8-2, exhibit higher activity than the pure Mn₂O₃, especially in the low temperature region. In contrast, the samples that contain a Mn₂O₃ phase show similar activity to pure Mn₂O₃ at low temperatures, but clearly lower activity at high temperatures. However, all the Sn-Mn binary catalysts are more active than the pure SnO₂ catalyst.

The Arrhenius plots of the catalysts, which were achieved under differential conditions and reflect the inherent activity of the catalysts, are shown in Fig. 8(b). Apparently, the catalysts with more Sn-Mn solid solution phase form more active sites for CH₄ deep oxidation. The CH₄ conversion rates on the catalysts at 420 °C, together with the overall activation energy, are compared in Table 3. The highest CH₄ conversion rate was achieved on SnMn9-1. Further increasing the Mn content, which accompanies the formation of more Mn₂O₃, gradually degrades the conversion rates. It is evident that the presence of excess Mn₂O₃ is not favorable for the activity of the catalysts. The Sn rich samples that contain only a solid solution phase are more active. It is noted that SnMn9-1, which has a Sn/Mn molar ratio of 9/1, is the most active among all the catalysts.

To investigate the application potential of the catalysts, SnMn9-1 was subject to a long-term stability test at 530 °C in the absence or in the presence of water vapor. As shown in Fig. 9, there was ~13% decrease for the conversion of CH₄ after the addition of 5% water vapor. However, there was no evident decline in CH₄ conversion during 100 h of continuous testing, either with or without water vapor, proving that this catalyst was not only active, but also resistant to deactivation by water vapor.

4. Conclusions

SnO₂-based catalysts modified by Mn, Zr, Ti and Pb oxides with a Sn/M molar ratio of 9/1 were prepared by a co-precipitation method and used for CH₄ and CO oxidation. XRD demonstrates that these secondary metal cations are incorporated into the crystal lattice of tetragonal rutile SnO₂ to form a solid solution structure. The valance state of the metals was determined to be Mn³⁺, Zr⁴⁺, Ti⁴⁺ and Pb⁴⁺, as evidenced by XPS. As a consequence, the surface areas, thermal stability and pore volumes of the catalysts are improved. In addition, the oxygen species of the modified catalysts become easier to be reduced. Therefore, the oxidation activity over the catalysts was improved, except for the one modified by Pb oxide. The incorporation of manganese oxide in the SnO₂ lattice demonstrated the best performance enhancement. To gain a deeper

Fig. 9. Stability tests on SnMn9-1 for CH₄ deep oxidation in the absence or presence of 5% water vapor.

understanding and to optimize the catalyst formulation, a series of Sn-Mn mixed oxide catalysts with different Sn/Mn molar ratios were also prepared and subjected to CH₄ deep oxidation. Using the XRD extrapolation method, it was revealed that the lattice capacity of SnO₂ for Mn₂O₃ was 0.135 g Mn₂O₃/g SnO₂, which is equal to a Sn/Mn molar ratio of 79/21. If the Sn/Mn molar ratio is below this, the excess Mn would be present as Mn₂O₃, which is not favorable for the activity of the catalyst. The Sn rich samples with only a Sn-Mn solid solution phase generally show higher activity than the ones with excess Mn₂O₃ species.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 1293–1302 doi: 10.1016/S1872-2067(15)61119-6

SnO₂-based solid solutions for CH₄ deep oxidation: Quantifying the lattice capacity of SnO₂ using an X-ray diffraction extrapolation method

Qi Sun, Xianglan Xu, Honggen Peng, Xiuzhong Fang, Wenming Liu, Jiawei Ying, Fan Yu, Xiang Wang*
Nanchang University

With an XRD extrapolation method, 21% Sn⁴⁺ in the SnO₂ lattice can be maximally replaced by Mn³⁺ to form a stable solid solution. Catalysts consisting of Sn-Mn solid solution without extra Mn₂O₃ display higher CH₄ oxidation activity.

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SnO₂ 基固溶体用于甲烷深度氧化: X射线衍射外推法测定 SnO₂ 晶格容量

孙 琪[†], 徐香兰[†], 彭洪根, 方修忠, 刘文明, 应家伟, 余 帆, 王 翔^{*}

南昌大学化学学院, 江西南昌330031

摘要: CH₄ 和 CO 是两种主要的温室效应气体和空气污染物, 催化氧化是最有效的消除 CH₄ 和 CO 的方法. 研发不含贵金属的金属氧化物催化剂或者减少催化剂中贵金属用量为该领域研究热点. SnO₂ 是一种重要的宽禁带 n 型半导体材料, 广泛应用于气敏器件、锂离子电池以及光电设备. SnO₂ 表面富含活泼的缺位氧且具有良好的热稳定性, 因此其在催化方面的性能近年来逐渐受到人们关注. 在过去的 5 年中, 本团队深入研究了 SnO₂ 材料在空气污染治理和绿色能源生产等领域的应用及其催化性质. 发现通过其它阳离子如 Fe³⁺, Cr³⁺, Ta⁵⁺, Ce⁴⁺ 和 Nb⁵⁺ 等的掺杂, 替换晶格中部分 Sn⁴⁺, 形成金红石型 SnO₂ 固溶体结构, 显著提高了催化剂物种的流动性、活性和催化剂本身的热稳定性.

固溶体材料是一类重要的催化剂, 受到广泛关注. 一个典型的例子是铈锆固溶体, 其作为储氧材料已广泛应用于汽车尾气净化器. 形成固溶体结构后, 氧化铈的储氧能力和热稳定性得到显著提高. 为有效形成固溶体, 两个阳离子需要具有相似的离子半径和电负性. 以往, 人们基于结构中金属阳离子和氧阴离子的离子半径提出了容忍因子的判别方法, 以此来判断固溶体是否能有效形成及所生成固溶体的稳定性. 我们在前期工作中, 以 Sn-Nb 固溶体为例, 提出了简单的 X 射线衍射 (XRD) 外推法来计算固溶体晶格容量, 即形成稳定固溶体时客体阳离子取代主体晶格阳离子的最大值.

作为延续工作, 本文采用共沉淀法制备了一系列 Sn/M (M = Mn, Zr, Ti, Pb) 摩尔比为 9/1 的 SnO₂ 基催化剂, 并用于 CH₄ 和 CO 催化氧化. 结果表明, Mn³⁺, Zr⁴⁺, Ti⁴⁺ 和 Pb⁴⁺ 均可以掺杂进四方金红石型 SnO₂ 晶格中, 形成稳定的固溶体结构. 其中 Sn-Mn-O 固溶体表现出最高活性. 为了深入研究 Mn₂O₃ 在 SnO₂ 中的晶格容量及最优催化剂配比, 采用共沉淀法制备了一系列不同 Sn/Mn 摩尔比的样品, 采用 XRD, N₂-BET, H₂-TPR, SEM 和 XPS 等手段对其物理化学性能进行了表征, 并考察了对 CH₄ 的催化氧化性能. 通过 XRD 外推法测定了 Mn³⁺ 离子在 SnO₂ 中的晶格容量为 0.135 g Mn₂O₃/g SnO₂, 相当于 Sn/Mn 摩尔比为 79/21. 这表明形成稳定的固溶体后, SnO₂ 晶格中最多只有 21% Sn⁴⁺ 可以被 Mn³⁺ 替代; 当 Mn³⁺ 含量超过晶格容量时, 过量的 Mn³⁺ 在催化剂表面形成 Mn₂O₃, 对催化剂活性不利. 类似于 Sn-Nb-O 固溶体, 在 Sn-Mn-O 催化剂体系中亦观察到明显的晶格容量效应. 纯相的 Sn-Mn-O 固溶体比含过量 Mn₂O₃ 晶相的 Sn-Mn-O 催化剂具有更高活性.

关键词: 二氧化锡基固溶体; X射线衍射外推法; 晶格容量; 甲烷深度氧化; 一氧化碳催化氧化

收稿日期: 2016-02-28. 接受日期: 2016-04-22. 出版日期: 2016-08-05.

*通讯联系人. 电话: 15979149877; 电子信箱: xwang23@ncu.edu.cn

[†]这些作者对本文工作贡献相同.

基金来源: 国家自然科学基金 (21263015, 21567016 和 21503106); 江西省教育厅基金 (KJLD14005 和 GJJ150016); 江西省自然科学基金 (20142BAB213013 和 20151BBE50006).

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).