CH_4 deep oxidation over active and thermally stable catalysts based on Sn–Cr composite oxide

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Catalysts based on Sn–Cr composite oxide (SnCr) and modified with sulfate or a small amount of Pd were prepared and studied for CH_4 deep oxidation. XRD suggests that a solid solution may be formed between Sn and Cr. As a result, the thermal stability of SnCr catalyst is significantly enhanced, and more active oxygen species are formed in it, thus leading to improved activity. The addition of sulfate into SnCr binary oxide (SnCr–$SO_4{}^{2-}$) promotes its activity markedly, perhaps due to further increased thermal stability, higher surface area and the formation of strong acid sites, which were previously found to be favorable for hydrocarbon activation. Pd supported on SnCr (Pd/SnCr) shows much higher activity than SnCr, which is close to SnCr–$SO_4{}^{2-}$. The main reason leading to the enhanced activity, however, is ascribed to the superior performance of Pd itself for CH_4 oxidation, and the synergism between Pd and tin oxide. Pd/SnCr–$SO_4{}^{2-}$ exhibits slightly higher activity than SnCr–$SO_4{}^{2-}$ and Pd/SnCr with the same Pd loading. Ultimately, it is noted that SnCr–$SO_4{}^{2-}$ displays not only superior CH_4 oxidation activity, but also excellent resistance to sulfur poisoning and long term stable performance, indicating that it is a promising catalyst with the potential to be applied in some real CH_4 oxidation processes.

Catalytic deep oxidation of CH_4 at low temperature is an effective approach to utilize it as an energy source or prevent it from polluting the atmosphere.[1–3] Currently, supported noble metals such as Pt and Pd or their combinations are well-known active catalysts for this reaction, among which Pd is the most active one.[4,5] However, due to the limited sources and high price of precious metals,[6] over recent years, researchers have endeavored to develop cheaper catalysts, such as composite base metal oxides or supported Pd catalysts with much lower Pd loadings but comparable catalytic performance.[4,7] For the second class of catalysts, a suitable support is of great importance for their activity and continues to be an interesting research topic.

In a preliminary communication, we reported that SnO_2 modified with Cr showed much higher CH_4 oxidation activity as well as thermal stability than pure SnO_2.[8] This has been attributed to the possible formation of a solid solution structure in the sample, which resulted in a much higher surface area of the catalyst and the formation of more active oxygen species. However, the activity of Sn–Cr composite oxide is still lower than that of supported Pd catalysts such as Pd/SnO_2 and Pd/SnO_2–$SO_4{}^{2-}$.[9,10] Therefore, the search for suitable methods to further promote the performance of Sn–Cr composite oxide is desirable and is our main objective in this work.

Previously, we found that the addition of sulfate into SnO_2 improved its CH_4 oxidation activity significantly.[9] The predominant cause of this effect has been attributed to the formation of strong acid sites in SnO_2–$SO_4{}^{2-}$,[9,11–15] which have been found to be favorable for the activation of hydrocarbons,[11–20] and its larger surface area. The same effects were also observed for some other metal oxides such as zirconia and titania, which resulted in enhanced activity for hydrocarbon-related reactions such as oxidation, isomerization, *etc.*[11–20] In addition, both pure and sulfated SnO_2 were found to be excellent supports for Pd, as demonstrated by the superior CH_4 oxidation activity of Pd/SnO_2 and Pd/SnO_2–$SO_4{}^{2-}$.[9,10] A concerted interaction between Pd and SnO_2 was proposed to account for the activity enhancement of these samples.[9,21–23]

Compared with pure SnO_2, the SnCr catalyst used in this work contains a large quantity of Sn and shows some similar properties.[8] The promoting effects of sulfate and Pd on SnO_2, indeed, could also occur with Sn–Cr composite oxide. Therefore, in an endeavor to develop more stable and active catalysts, the Sn–Cr composite oxide was doped with sulfate and both the sulfated and unsulfated Sn–Cr binary oxides were employed as supports for Pd. All of the catalysts prepared were evaluated for CH_4 deep oxidation under the same conditions. To elucidate the reasons leading to the different reaction performance of the catalysts, they were characterized by means of N_2-BET, XRD, H_2-TPR and CH_4-TPR techniques.

Experimental

Catalyst preparation

The SnO_2 precursor with a high specific surface area (225 m^2 g^{-1}) was prepared *via* the precipitation method as in ref. 24 and subsequently calcined at 600 °C to get pure SnO_2 catalyst. Sn–Cr binary catalyst (denoted SnCr) with a Sn : Cr molar ratio of 3 : 2 was synthesized by the stoichiometric reaction between a $SnCl_2 \cdot 2H_2O$ suspension (1 g per 15 mL distilled H_2O) and K_2CrO_4 (0.50 M). The reaction can be described simply by the following equation:

$$3\,Sn^{2+} + 2\,Cr^{6+} \rightarrow 3\,Sn^{4+} + 2\,Cr^{3+} \qquad (1)$$

Typically, a calculated amount of K_2CrO_4 solution was dripped slowly into the $SnCl_2 \cdot 2H_2O$ suspension, which was under

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constant stirring. After reaction, 1 N KOH solution was added dropwise into the mixture to precipitate out the metal cations completely (pH *ca.* 9.7). Afterwards, the precipitates were vacuum-filtered and washed with distilled water repeatedly, until all of the K^+ and Cl^- were removed and simultaneously the water passing through the precipitates was neutral. The clean precipitates were then dried at 110 °C overnight and used as precursors to prepare other catalysts.

SnCr–SO_4^{2-} was obtained by impregnating the SnCr precursor with a 0.5 M H_2SO_4 solution (15 mL solution per gram SnO_2) for *ca.* 7 h at room temperature, followed by filtration and drying at 110 °C overnight. Pd/SnCr (0.5 wt%) and Pd/SnCr–SO_4^{2-} (0.5 and 0.2 wt%) were obtained by impregnating the SnCr and SnCr–SO_4^{2-} dried at 110 °C with a 0.002 g mL^{-1} H_2PdCl_4 aqueous solution. Prior to the activity evaluation, all the samples were calcined at 600 °C in an air atmosphere for *ca.* 6 h.

Catalyst characterization

The BET specific surface areas of the catalysts were measured by nitrogen adsorption–desorption at −196 °C with an ST-30 instrument.

XRD patterns were recorded on a Rigaku D/MAX-rA X-ray diffractometer with Cu-Kα radiation of 40 kV × 100 mA and an Ni filter. For phase composition analysis, the scan step was 0.1° with a preset counting time of 4 s. For mean crystallite size measurements, the scan step was 0.01° with a preset counting time of 4 s. The crystallite sizes of all the samples were evaluated from the broadening of the strongest peak of SnO_2, peak (110), and based on the Scherer equation after the necessary correction.

H_2 and CH_4 temperature programmed reduction experiments (H_2-TPR and CH_4-TPR) were generally performed with 50 mg catalyst in a 30 mL min^{-1} H_2–N_2 (5.1%) or CH_4–N_2 (5.5%) gas mixture flow, respectively, the temperature being increased with a ramp of 10 °C min^{-1}. A thermal conductivity detector (TCD) was used to monitor H_2 or CH_4 consumption. Prior to entering into the catalyst bed, the gas flows were purified with a MnO oxygen trap and a 5 Å molecular sieve H_2O trap. One or two other 5 Å molecular sieve traps were placed at the outlet of the reactor to remove the products formed such as H_2O, H_2S, CO_2, *etc.* When the traps were saturated, the baseline became noisy. With this method, we ensured that the profiles obtained were mainly based on H_2 or CH_4 consumption, and not perturbed by the products formed. More detailed procedures have been described elsewhere.[25]

Activity evaluation

Catalytic tests were carried out in a U-shaped fixed-bed microreactor (i.d. = 6 mm) with a continuous downflow. Typically, 0.2 mL 40–60 mesh catalysts were used for activity evaluation. The volume composition of the feed gas was 1.5% CH_4 and 18% O_2, balanced by high purity N_2. The total feed flow rate was 70 mL min^{-1}, corresponding to a gas hourly space velocity (GHSV) of 21,000 h^{-1}. More detailed procedures have been described elsewhere.[25,26]

Results

The effects of sulfate and Pd on Sn–Cr composite oxide

Activity evaluation. $T_{10\%}$, $T_{50\%}$ and $T_{98\%}$, the temperatures corresponding to 10, 50 and 98% CH_4 conversion on the catalysts, are listed in Table 1. In this work, $T_{98\%}$ is regarded as the CH_4 complete conversion temperature. It is noted here that over all of the catalysts, CO_2 is the only C-containing product.

The three temperatures on unmodified SnO_2 are 370, 440 and 520 °C, respectively. However, the temperatures with SnCr catalyst are typically *ca.* 50 °C lower, indicating that the incorporation of Cr into Sn can achieve a much more active catalyst. Interestingly, the addition of sulfate into SnCr decreased its $T_{10\%}$, $T_{50\%}$ and $T_{98\%}$ to 10, 30 and 70 °C, respectively. Apparently, sulfate has a positive effect on the activity of SnCr, especially at high CH_4 conversion. Both SnCr and sulfated SnCr were thus employed as supports for Pd. Pd/SnCr (0.5 wt%) and Pd/SnCr–SO_4^{2-} (0.2 wt%) exhibit a similar activity to SnCr–SO_4^{2-}, as evidenced by their essentially identical temperatures, whereas, Pd/SnCr–SO_4^{2-} (0.5%) shows a somewhat higher activity, with complete CH_4 oxidation taking place at 390 °C. Obviously, both unsulfated and sulfated SnCr are promising supports for Pd.

N_2-BET and XRD analysis. The specific surface areas of SnO_2, SnCr and SnCr–SO_4^{2-} are also listed in Table 1. Pure SnO_2 has the lowest surface area among all of the samples, indicating that it has low thermal stability and crystallized well during the calcination. Interestingly, the surface area of SnCr is more than twice that of pure SnO_2, revealing that the combination of Sn and Cr promotes the thermal stability of the sample. The surface area of SnCr–SO_4^{2-} is 25 m^2 g^{-1} higher than that of SnCr. Obviously, the addition of sulfate further improves the heat resistance of SnCr. It is mentioned here that the surface areas of the samples containing Pd should be close to that of their corresponding supports due to the very low Pd loading, which is also testified to by XRD patterns similar to those of their supports, and will be discussed in the following paragraphs.

To identify the bulk phase compositions of the catalysts, they were analyzed using the XRD technique; the patterns of SnO_2, SnCr and SnCr–SO_4^{2-} are compared in Fig. 1. In order to ascertain the crystallinity of the samples quantitatively, the mean crystallite sizes were measured and are included in Table 1. Pure SnO_2 shows sharp and intense diffraction peaks assigned to rutile SnO_2 (cassiterite),[24,27,28] indicating that the high surface area SnO_2 precursor sintered and crystallized well during the calcination. Its large crystallite size of 159 Å reveals its high crystallinity, which is in good agreement with its low surface area. In contrast, SnCr exhibits three broadened peaks

Table 1 Effects of SO_4^{2-} and Pd on the crystallite sizes and reaction performance of SnCr[a]

Catalyst	BET surface area/m^2 g^{-1}	Mean crystallite size/Å	$T_{10\%}$/°C	$T_{50\%}$/°C	$T_{98\%}$/°C
SnO_2	29	159	370	440	520
SnCr	70	53	320	390	480
SnCr–SO_4^{2-}	95	34	310	360	410
Pd/SnCr (0.5%)	—	50	300	360	410
Pd/SnCr–SO_4^{2-} (0.5%)	—	35	290	340	390
Pd/SnCr–SO_4^{2-} (0.2%)	—	—	310	360	420

[a] All the catalyst were calcined at 600 °C in air for *ca.* 6 h.

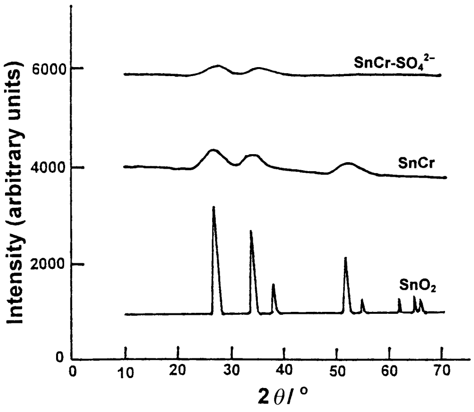

Fig. 1 XRD patterns of SnO_2, SnCr and sulfated SnCr–SO_4^{2-} catalysts calcined at 600 °C in an air atmosphere for *ca.* 6 h.

with low intensity, which can also be assigned to the rutile SnO_2 (cassiterite) phase. Compared with pure SnO_2, its crystallite size is much smaller, indicating its much lower crystallinity, which is consistent with its higher surface area. In addition, the 2θ of the three peaks of SnCr shift to higher values than those of pure SnO_2 (results not shown). Moreover, even if SnCr was calcined at 1100 °C, rutile SnO_2 (cassiterite) was still the only phase observed, although the peak intensities became higher.[26] Therefore, a solid solution structure is possibly formed between Sn and Cr.[29] As a lattice impurity for SnO_2, Cr effectively prevents the SnO_2 particles from contacting each other and growing during the calcination, thus alowing SnCr to maintain a higher surface area.

SnCr–SO_4^{2-} shows only two diffraction peaks with even lower intensities than the corresponding peaks of SnCr, implying that the addition of sulfate further impedes the crystallization of SnCr.[9,14,20] This is also demonstrated by the smaller crystallite size of SnCr–SO_4^{2-}. It is noted here that Pd/SnCr and Pd/SnCr–SO_4^{2-} show identical XRD patterns to their corresponding supports. Apparently, the addition of a small quantity of Pd onto SnCr and SnCr–SO_4^{2-} has no effect on their crystallinity and perhaps their surface areas, as testified to by their unchanged crystallite sizes.

H_2- and CH_4-TPR tests. In an attempt to elucidate the reasons leading to the enhanced activity of SnCr upon the addition of sulfate and Pd, the samples were studied by TPR techniques.

The H_2-TPR profiles of the samples are illustrated in Fig. 2(A). Pure SnO_2 has only one peak centered at 760 °C, which has been assigned to the reduction of Sn^{4+} to metallic Sn, perhaps with Sn^{2+} as the intermediate.[27,28,30] In contrast, two peaks sitting at 280 and 625 °C are observed for SnCr. Under the conditions adopted in this work, bulk Cr_2O_3 is not reducible by H_2 below 800 °C, as also reported by Zaki *et al.*[31] The 625 °C peak, therefore, could also be due to the reduction of lattice oxygen attached to Sn. Its lower reduction temperature could be a consequence of its lower crystallinity compared to that of pure SnO_2, as numerous studies have proven that the lattice oxygen of a metal oxide can be reduced more easily when it is poorly crystallized.

Previously, Fabritchnyl *et al.*[32] found that on the surface of Cr-promoted SnO_2, oxygen defects are present, which can be removed *via* adsorption of oxygen from the gas phase, thus leading to the formation of more mobile and active oxygen species in the samples. The 280 °C peak of SnCr, therefore, could also correspond to the reduction of dissociatively adsorbed oxygen species in SnCr, since both Sn and Cr oxides[31] are not reducible at such a low temperature.

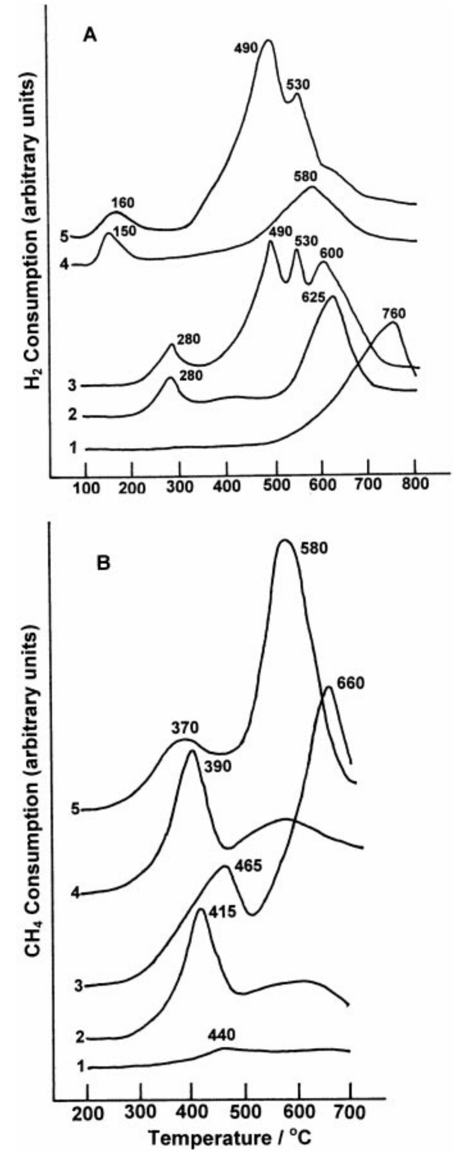

Fig. 2 H_2-TPR (A) and CH_4-TPR (B) profiles of the catalysts calcined at 600 °C in an air atmosphere for *ca.* 6 h. Curves are labelled as: 1, SnO_2; 2, SnCr; 3, SnCr–SO_4^{2-}; 4, Pd/SnCr (0.5%); 5, Pd/SnCr–SO_4^{2-} (0.5%).

As to SnCr–SO_4^{2-}, besides the 280 °C peak and a peak around 600 °C, two additional peaks positioned at 490 and 530 °C are observed. They could be due to the reduction of sulfate in the sample.[14,33]

The addition of Pd into SnCr and SnCr–SO_4^{2-} typically lowered the reduction temperatures of the peaks, especially in the lower temperature region. Obviously, the reduction of various oxygen species in the samples was enhanced, perhaps due to H_2 spillover effects on Pd.

Therefore, in an endeavor to exclude the H_2 spillover effect and obtain more direct information on the nature of the oxygen species in the samples, they were also studied by the CH_4-TPR method [Fig. 2(B)]. Pure SnO_2 displays a negligible peak at 440 °C, which could be assigned to the reduction of a small amount of adsorbed oxygen species on its surface. In the H_2-TPR profile, because of the large Y axis scale, the corresponding reduction was obviously not observed. The lattice oxygen of SnO_2, obviously, is not reducible by CH_4 below 800 °C. In comparison, SnCr has a sharp peak centered at 415 °C and a broadened peak above 480 °C, revealing the formation of more active oxygen species, perhaps dissociatively adsorbed oxygen in this sample.[8] This is in line with the H_2-TPR results. Compared with SnCr, the reduction of SnCr–SO_4^{2-} becomes more evident, with a new and large peak appearing at 660 °C, indicating that the sulfate is also reducible by CH_4. The addition of Pd into SnCr and SnCr–SO_4^{2-} again enhanced the reduction of the oxygen species, as revealed by the lower temperatures of the corresponding peaks. This could be due to the high activity of Pd in the activation of C–H–.[34] Indeed, CH_4-TPR results clearly substantiate that SnCr doped by sulfate and Pd shows a higher ability to activate the potent C–H bonds of CH_4, which could be related to the enhanced activity of the achieved catalysts.

Stability measurements of SnCr–SO_4^{2-}

Due to the limited sources and high price of precious metals, there is a strong motivation to develop catalysts based on base metal oxides.[4,7] In this work, SnCr–SO_4^{2-}, though containing no Pd, shows similar activity to the supported Pd catalysts, revealing that it is a promising catalyst to meet these requirements. Therefore, it has been studied in more detail.

First, SnCr–SO_4^{2-} was subjected to a sulfur deactivation test, with the results shown in Fig. 3(A). In detail, the catalyst was first run at 410 °C, its $T_{98\%}$, for *ca.* 2 h until the CH_4 conversion was stabilized at 98%, then pure SO_2 was injected (1 mL per injection) into the feed flow at intervals of 20 min while keeping the temperature constant. Clearly, 15 injections totaling 15 mL SO_2 over 5 h had no negative effects on the catalyst, indicating excellent resistance to sulfur poisoning.

Next, the stability of SnCr–SO_4^{2-} was measured at 600 °C for *ca.* 720 h (30 days) under the adopted reaction conditions [Fig. 3(B)]. Again, no deactivation of the catalyst was observed. This further demonstrates that SnCr–SO_4^{2-} is a durable and promising catalyst for CH_4 oxidation, which has the potential to be applied in some real aftertreatment processes.

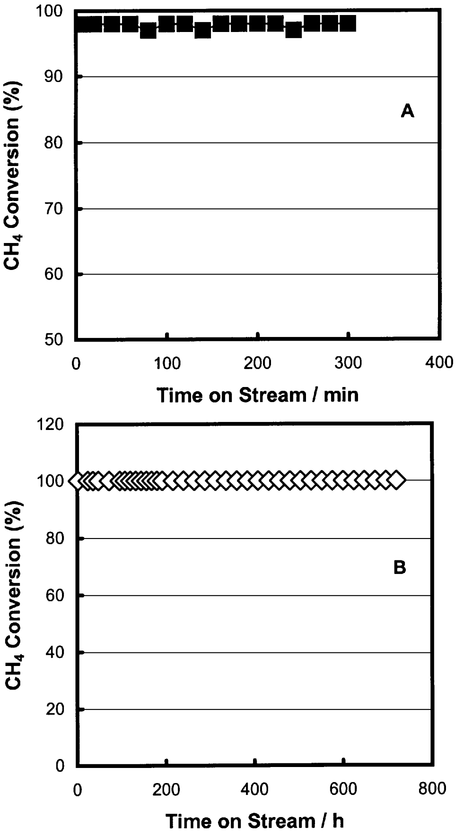

Fig. 3 Stability measurements of SnCr–SO_4^{2-} calcined at 600 °C in an air atmosphere for *ca.* 6 h. (A) Effect of SO_2 on its CH_4 oxidation activity at 410 °C. (B) Long term durability test at 600 °C.

Table 2 The effects of calcination temperature on SnCr–SO_4^{2-}

T_{calcin}/°C	Mean crystallite size/Å	$T_{10\%}$/°C	$T_{50\%}$/°C	$T_{98\%}$/°C
600	34	310	360	410
700	52	320	380	450
800	81	350	410	530
900	140	360	430	560

The effects of calcination temperature on SnCr–SO_4^{2-}

It is well known that CH_4 deep oxidation is a strongly exothermic process. Therefore, the thermal stability of a catalyst is of great importance for the maintenance of good long term performance. SnCr–SO_4^{2-} was thus calcined at different temperatures and evaluated for CH_4 deep oxidation. As shown in Table 2, upon increasing the calcination temperature from 600 to 900 °C, its $T_{10\%}$, $T_{50\%}$ and $T_{98\%}$ increase from 310, 360 and 410 °C to 360, 430 and 560 °C, respectively. At the same time, the crystallite size of SnCr–SO_4^{2-} increases from 34 to 140 Å. Apparently, SnCr–SO_4^{2-} calcined at higher temperature is better crystallized and less active. However, even if SnCr–SO_4^{2-} was calcined at 900 °C, CH_4 was still able to light off on it at 360 °C and oxidized completely at 560 °C, indicating that it was not severely sintered. In other words, the thermal stability of SnCr–SO_4^{2-} is good.

Again, TPR techniques were used to study the changes that occurred in SnCr–SO_4^{2-} when calcined at different temperatures. H_2-TPR profiles of the samples are shown in Fig. 4(A). The profile of SnCr–SO_4^{2-}calcined at 700 °C shows similar features to that of pure SnCr [see Fig. 2(A)]. Compared with SnCr–SO_4^{2-}calcined at 600 °C, the 490 and 530 °C peaks that correspond to the reduction of sulfate disappear, indicating that most of the sulfate is lost from SnCr–SO_4^{2-} during calcination at 700 °C.[13,19] Upon further increasing the calcination temperature to 900 °C, the temperature of the 600 °C peak shifts to 700 °C. Simultaneously, the area of the 280 °C peak becomes smaller, though its temperature does not change. This substantiates that SnCr–SO_4^{2-} is better crystallized at higher temperature. As a consequence, the reduction of lattice oxygen becomes more difficult and the amount of defects becomes less as well.

CH_4-TPR profiles of SnCr–SO_4^{2-} calcined at different temperature are illustrated in Fig. 4(B). Similarly to the H_2-TPR results, we can obviously see the loss of sulfate from the sample when it was calcined above 600 °C. Moreover, the amount of dissociatively adsorbed oxygen species becomes less, as evidenced by the smaller integrated peak area of the sample calcined at higher temperatures. These, indeed, could be the main reasons leading to the deterioration in the activity of SnCr–SO_4^{2-} when it is calcined at high temperatures.

Discussion

The promotion effects of Cr

Previously, it has been shown that pure SnO_2 is an active catalyst for several redox reactions such as CO oxidation[35] and NO reduction with CO or hydrocarbons.[28,36] The addition of Cr into SnO_2 was found to enhance its catalytic activity significantly;[32,37–40] this is predominantly attributed to the presence of high valence state Cr on the surface of SnO_2[38,39] or the formation of very reactive oxygen species on the surface,

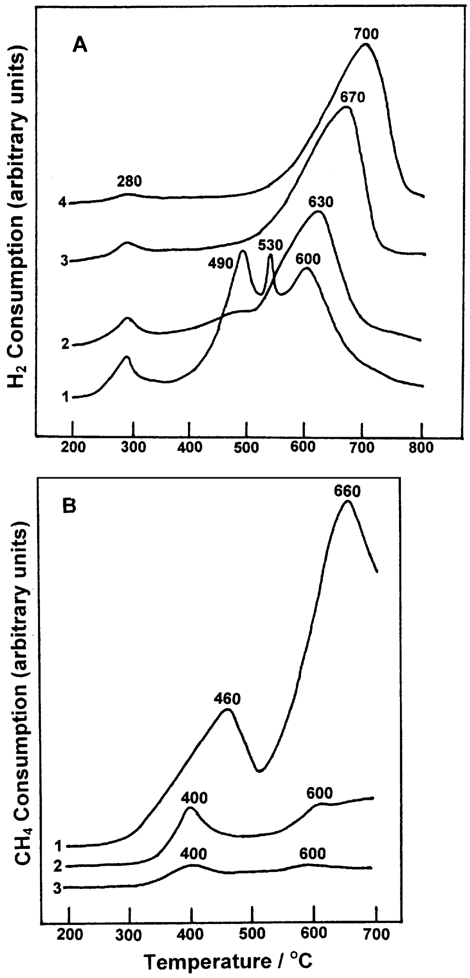

Fig. 4 H_2-TPR (A) and CH_4-TPR (B) profiles of SnCr–SO_4^{2-} calcined at different temperatures in an air atmosphere. Curves are labelled as: 1, 600; 2, 700; 3, 800; 4, 900 °C.

perhaps dissociatively adsorbed oxygen.[32,39] In the present work, TPR studies showed also the formation of more reducible and reactive adsorbed oxygen species in SnCr; in addition, the lattice oxygen of SnCr is more active due to its low crystallinity. Earlier work has already demonstrated that both adsorbed and lattice oxygen function in hydrocarbon total oxidation.[4,7,41] Therefore, the formation of more active oxygen species in SnCr could be one of the reasons for its much higher activity compared to that of pure SnO_2.

Furthermore, CH_4 deep oxidation was reported to be a typically diffusion controlled reaction, especially at high CH_4 conversion in the high temperature region. Therefore, a high surface area for a catalyst is of great importance for a high CH_4 oxidation activity.[42] The surface area of SnCr is more than twice that of pure SnO_2, as also evidenced by its smaller crystallite size (Table 1). The larger surface area of SnCr is hence regarded as another important reason for its significantly enhanced activity.

The promotion effects of SO_4^{2-}

As shown in Table 1, the addition of sulfate into SnCr further improved its CH_4 oxidation activity, especially at high conversions. For pure SnO_2, we found previously that the addition of sulfate can impede its crystallization during calcination at high temperature, thus resulting in a catalyst having lower crystallinity, larger surface area and higher CH_4 oxidation activity.[9] The same modification effects were found for some other metal oxides as well.[11,14–20] In this work it was found that, SnCr–SO_4^{2-} also has lower crystallinity and higher surface area than SnCr (Table 1). This could be one of the main reasons leading to its higher activity compared to that of un-sulfated SnCr.

Another important factor that should not be neglected here is the possible formation of strong acid sites in sulfated SnCr. Earlier work demonstrated that sulfated SnO_2 is a strong acid, which shows good ability to activate hydrocarbons, thus leading to its high activity for hydrocarbon-related reactions.[11–15] Furthermore, Ishikawa *et al.*[17] found that for catalytic combustion of propane over Pt supported on a series of metal oxides, the activity strongly depends on the acidity of the supports. In other words, the stronger the acidity of a support, the higher the activity of the catalyst. Pt supported on some SO_4^{2-} doped metal oxides, known as strong solid acids, are superior catalysts for propane combustion. A similar trend was found by Hua and Gao[18,19] when studying catalytic combustion of several organic compounds such as *n*-pentane, *n*-hexane, toluene *etc.*, over Pd/ZrO_2–SO_4^{2-} or Pt/ZrO_2–SO_4^{2-}. They concluded that the main reason leading to the superior activity of the catalysts was the formation of strong acid sites, which are believed to be favorable for the activation of C–H bonds in organic compounds.[11–20]

For CH_4 oxidation, since its molecules consist of only four potent C–H bonds, the activation and rupture of the first one is crucial for the overall reaction, and generally is the rate-determining step.[1,43] The SnCr used in this work contains 60 mol% Sn oxide; therefore, there is a strong possibility that strong acid sites based on sulfate and tin oxide are also formed.[11–15] Indeed, this could be another reason accounting for the promoting effects of sulfate on the activity of SnCr. Furthermore, the decreased activity of SnCr–SO_4^{2-} calcined at higher temperature, which was accompanied by the loss of sulfate provides additional evidence for the importance of strong acid sites for the CH_4 oxidation activity of the sulfated samples.

The promotion effects of Pd

It is well known that supported Pd is the most active catalyst for CH_4 total oxidation among all of the studied catalysts.[4,5,44,45] Therefore, as we expected, the addition of a small amount of Pd into SnCr and SnCr–SO_4^{2-} enhanced their activity, especially for SnCr.

Since the 1970s, Pd/SnO_2 has been studied for some redox reactions such as low temperature CO oxidation and NO reduction with CO.[21–23,46–48] Strong concerted interaction or synergism was found between Pd and SnO_2, which was regarded as the main reason behind the superior performance of Pd/SnO_2 for the reactions. In detail, for CO oxidation, Bond *et al.*[21] found that both CO and O_2 could be activated on Pd sites and spillover to SnO_2. In contrast, Sheintuch *et al.*[47] provided evidence to show that only CO spillover from Pd to SnO_2 took place. On the contrary, when studying Pt/SnO_2 for CO oxidation, Grass and Lintz[48] proposed that O_2 was possibly activated on SnO_2 and then spilled over to Pt. One common thing found by these authors is the spillover of the reactants due to synergism between precious metals and SnO_2, which is believed to be responsible for the superior activity of the catalyst. More recently, Pd/SnO_2 was also found to be a more active catalyst for CH_4 deep oxidation than conventional Pd/Al_2O_3.[9,10,49] Eguchi *et al.*[49] attributed this mainly to the strong concerted interaction between Pd and SnO_2, which can suppress the decomposition of PdO, the possible active species, even at high temperature.

As mentioned above, the SnCr catalyst employed in this study is a tin-rich sample with 60 mol% Sn. Therefore, it is reasonable to believe that the concerted action between precious metals and SnO_2 could also be present between Pd and SnCr. As a consequence, the spillover of the reactants or the stabilization of PdO could also happen on Pd/SnCr, thus leading to its markedly enhanced CH_4 oxidation activity. As to Pd/ SnCr–SO_4^{2-}, because of the additional promotion effects of sulfate, it shows slightly higher activity than Pd/SnCr with the same Pd loading.

Conclusions

Catalysts based on Sn–Cr composite oxides (SnCr) and modified by sulfate or a small amount of Pd were studied for CH_4 deep oxidation. It was found that a solid solution structure could be formed between Sn and Cr. As a result, SnCr binary catalyst has lower crystallinity, higher surface area and contains more active oxygen species than pure SnO_2, which lead to its enhanced CH_4 oxidation activity. The addition of sulfate into SnCr binary oxide (SnCr–SO_4^{2-}) increased the activity of the sample significantly, especially at high temperature. This is due to the formation of strong acid sites, which were previously found to be favorable for hydrocarbon activation, and its lower crystallinity and higher surface area. Similarly, the introduction of 0.5 wt% Pd into SnCr (Pd/SnCr) also promoted its activity markedly; this is attributed to the superior performance of Pd itself for CH_4 oxidation and the synergetic interaction between Pd and tin oxide. Pd supported on SnCr–SO_4^{2-} (Pd/SnCr–SO_4^{2-}) exhibited similar activity to SnCr–SO_4^{2-} and Pd/SnCr. Finally, it is noted that SnCr–SO_4^{2-} showed not only remarkable CH_4 oxidation activity, but also excellent resistance to sulfur poisoning and long term durability, revealing that it is a promising catalyst with the potential to be applied in some practical CH_4 oxidation processes.

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