CH_4 Deep Oxidation on SnO_2-Based Composite Oxides: Novel, Active, and Stable Catalysts

Xiang Wang* and You-chang Xie
Institute of Physical Chemistry, Peking University, Beijing 100871, P. R. China

(Received November 27, 2000; CL-001082)

SnO_2-based composite oxides containing Fe and Cr were prepared using the combination of redox reaction and co-precipitation, and studied for CH_4 deep oxidation. It was found that Fe and Cr were incorporated into SnO_2 (Cassiterite) to form some catalysts that are more active and far more resistant to thermal sintering than pure SnO_2. Solid solution structure is possibly formed in these catalysts.

Deep oxidation of CH_4 at low temperature is an effective and promising approach to utilize it as an energy source, or prevent it from polluting the atmosphere.[1] Traditional catalysts used for hydrocarbon combustion are supported noble metals such as Pt/Al_2O_3 and Pd/Al_2O_3.[2] These catalysts, however, are not active enough for low-temperature CH_4 oxidation.[1] Moreover, due to the limited availability and high price of noble metals, over recent years, considerable attention has been paid to base metal oxides. Previously, pure and modified SnO_2 were reported to be active oxidation catalysts.[3,4] However, total oxidation of CH_4 on SnO_2-based composite metal oxides has not yet been investigated, except those using SnO_2 as the support for Pd.[5] We thus reported here the preparation of Sn–Fe, Sn–Cr and Sn–Fe–Cr composite oxide catalysts that are more active for CH_4 oxidation and far more resistant to thermal sintering than pure SnO_2.

The precipitation method as in reference[6] was employed to prepare SnO_2 precursor (225 m^2/g). Sn–Fe, Sn–Cr and Sn–Fe–Cr were prepared via the stoichiometric reaction between $SnCl_2$ suspension (1 g/15 mL distilled H_2O) and K_2CrO_4 (0.50 M) or $Fe(NO_3)_3$ (0.33 M) aqueous solutions, followed by precipitation with 1 M KOH. The compositions of the samples are Sn/Fe = 33/67, Sn/Cr = 60/40, and Sn/Fe/Cr = 50/25/25 (atomic ratio), respectively. Prior to activity evaluation, the catalysts were calcined at 600 °C in static air for ~6 h. CH_4 oxidation activity was tested at 1 atm in a U-shaped fixed-bed microreactor (i.d. = 6 mm) packed with 0.2 mL 40–60 mesh catalyst. The volume composition of the feed gas is CH_4 1.5%, O_2 18% and balanced by high purity N_2, with a total flow rate of 70 mL/min. A K-type thermocouple was put in the catalyst bed to monitor the reaction temperature. The reactants and products were analyzed with an on-line 1102G GC equipped with a TCD. No CO was formed over the catalysts at any temperature.

$T_{10\%}$, $T_{50\%}$, and $T_{90\%}$, the temperatures corresponding to 10%, 50% and 90% CH_4 conversion, are compared in Table 1. The three temperatures of unmodified SnO_2 are 370, 445 and 500 °C. The incorporation of Fe or Cr into Sn, apparently, improves the activity of the obtained catalysts, as evidenced by their lower $T_{10\%}$, $T_{50\%}$ and $T_{90\%}$. Sn–Cr shows the best activity among all the samples, with its three temperatures being ~45 °C lower than those of SnO_2. The steady-state CH_4 oxidation rates on the catalysts are also included in Table 1. The rates based on per gram of Sn–Fe, Sn–Cr and Sn–Fe–Cr are obviously higher than that of SnO_2. The specific rates (normalized by surface area) of Sn–Fe and Sn–Fe–Cr are similar to that of SnO_2 due to their much larger surface areas, while that of Sn–Cr is still markedly higher. It is evident that Sn–Fe, Sn–Cr and Sn–Fe–Cr are more active for CH_4 oxidation than pure SnO_2.

Table 1. Physicochemical properties and catalytic activity of SnO_2-based catalysts

Catalysts	SnO_2	Sn–Fe	Sn–Cr	Sn–Fe–Cr
$T_{10\%}$/°C	370	350	320	340
$T_{50\%}$/°C	445	420	390	420
$T_{90\%}$/°C	500	480	460	470
Rate/×10^{-5} mmol $s^{-1}g^{-1}$ [a]	2.23	6.70	29.0	8.93
Rate/×10^{-7} mmol $s^{-1}m^{-2}$ [a]	7.69	8.26	40.9	6.03
BET Surface area/m^2g^{-1}	29	81	70	148
Crystallite Size/Å	159	45	53	37

[a] Measured at 340 °C (CH_4 conversion on the samples is below 10% except that on Sn–Cr is 13%).

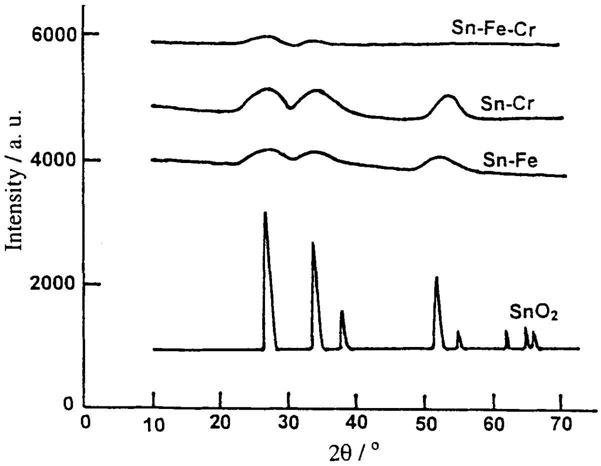

Figure 1. XRD patterns of the catalysts.

The catalysts have been characterized by XRD (Figure 1). Unmodified SnO_2 shows intensive diffraction peaks of SnO_2 (Cassiterite), indicating the high surface area SnO_2 precursor sintered and crystallized during the calcination. In contrast, Sn–Fe, Sn–Cr and Sn–Fe–Cr display only two or three broadened peaks with low intensity, revealing that the samples are nearly amorphous. Careful analysis substantiates that these peaks belong also to SnO_2 (Cassiterite). Therefore, to see their crystallinity quantitatively, the mean crystallite sizes of the samples are measured from the broadening of the strongest peak of SnO_2, peak (110), and based on Scherer equation (Table 1). Not surprisingly, SnO_2 has much larger particle size than that of the composite oxides, in line with the BET surface area results (Table 1). This demonstrates that the incorporation of Fe and Cr into SnO_2 markedly improves the obtained samples' resistance to thermal sintering.

Indeed, the high surface areas and amorphous compositions of the composite oxide catalysts could be one of the main reasons leading to their enhanced activity.

Interestingly, though the contents of Fe and Cr in the modified samples are high, no any peaks relating to them are observed. The same phenomenon was observed by Zhao et al.[6] when studying the dispersion behaviors of several metal oxides on SnO_2. They ascribed the reason to the formation of monolayerly dispersed oxides on the surface of SnO_2. However, in our case, the contents of Fe and Cr are much higher than the general monolayer dispersion capacity.[6,7] We thus incline to believe that the evasion of XRD detection of Fe and Cr oxides is not mainly due to the formation of monolayers on the surface of SnO_2. It is of more possibility that Fe or Cr cations were doped into the lattice of SnO_2 to form solid solution structure. Sn–Fe and Sn–Cr were thus calcined at 900 and 1100 °C and subjected to XRD analysis; SnO_2 (Cassiterite) is still the only observed phase (result not shown). The lack of segregated Fe and Cr related phases provides additional proof to testify the formation of solid solution structure in the composite oxides.

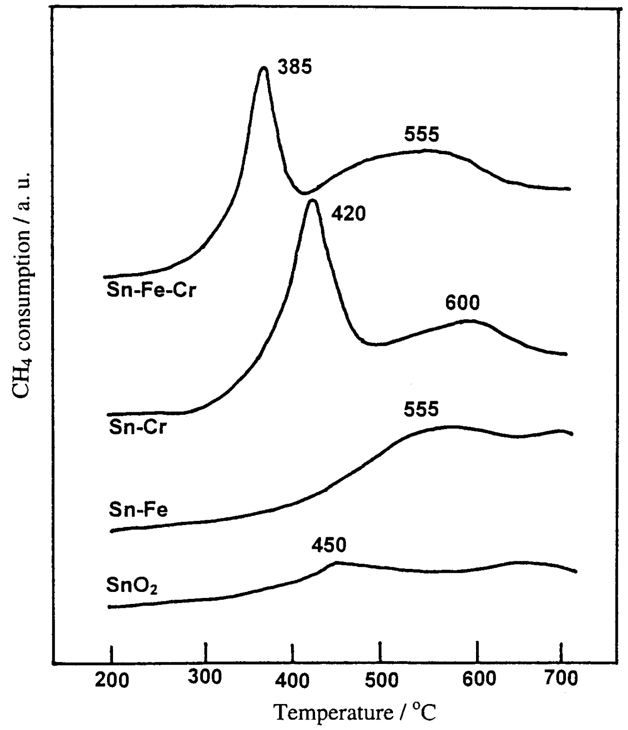

Figure 2. CH_4-TPR profiles of the catalysts.

CH_4-TPR was used to study the nature of the samples in the absence of gas phase oxygen (Figure 2). SnO_2 has only one small reduction peak positioned at 450 °C, suggesting nearly the absence of reducible oxygen species in it. However, for the composite oxides, CH_4 reduction becomes evident. Especially in the profiles of Sn–Cr and Sn–Fe–Cr, a sharp reduction peak is observed around 400 °C besides the broadened high temperature peak. This clearly suggests the introduction of Fe and Cr into SnO_2 leads to the formation of more mobile and active oxygen species in the obtained samples.

Figure 3 illustrates the XPS spectra of O_{1s} peak of the samples. SnO_2 shows a sharp and symmetric peak with O/Sn atomic ratio 1.98, indicating the oxygen species on its surface is uniform lattice oxygen of SnO_2. However, the peak of the modified samples is broadened, with the binding energy shifting, more or less, to lower values. It is evident that on the surface of these samples, besides the lattice oxygen of SnO_2, other types of more reactive oxygen species, perhaps dissociatively adsorbed oxygen[8] are present. Both XPS and CH_4-TPR results demonstrate the presence of more active oxygen species in the composite oxides. This could be another indispensable reason leading to their improved activity.

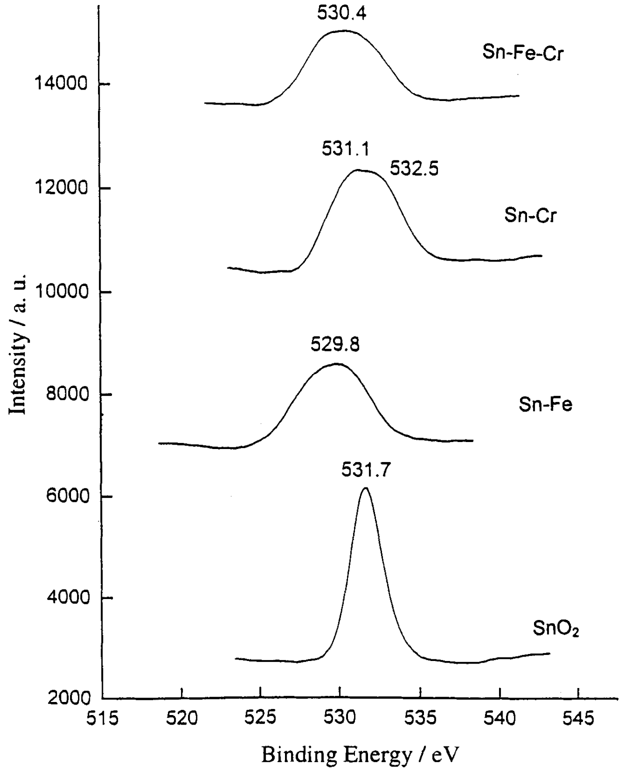

Figure 3. XPS spectra of O_{1s} peak of the catalysts.

In summary, using the combination of redox reaction and co-precipitation, Fe and Cr were introduced into SnO_2 to form catalysts that are more resistant to thermal sintering and display higher activity for CH_4 oxidation than pure SnO_2. Solid solution structure could be present in these composite oxide catalysts.

We gratefully acknowledge the financial support from the National Science Foundation of China.

References and Notes

1 W. S. Epling and G. B. Hoflund, *J. Catal.*, **182,** 5 (1999).
2 M. M. Zwinkel, S. G. Jaras, and P. C. Menon, *Catal. Rev. Sci. Eng.*, **35,** 319 (1993).
3 M. J. Fuller and M. E. Warwick, *J. Catal.*, **29,** 441 (1973).
4 M. J. Fuller and M. E. Warwick, *J. Catal.*, **34,** 45 (1974).
5 H. Widjaja, K. Sekizawa, and K. Eguchi, *Chem. Lett.*, **1998,** 481.
6 Y. Gao, H. B. Zhao, and B. Y. Zhao, *J. Mater. Sci.*, **35,** 917 (2000).
7 Y. C. Xie and Y. Q. Tang, *Adv. Catal.*, **37,** 1 (1990).
8 Z. Zhong, Q. Yan, X. Fu, and J. Gong, *Chem. Commun.*, **1996**, 1745.