Highly Efficient Ni–Ce–O Mixed Oxide Catalysts via Gel-coprecipitation of Oxalate Precursors for Catalytic Combustion of Methane

Nan Yi, Yong Cao,* Yong-Mei Liu, Wei-Lin Dai, He-Yong He, and Kang-Nian Fan*
Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials,
Fudan University, Shanghai 200433, P. R. China

(Received September 24, 2004; CL-041118)

The Ni–Ce–O mixed oxide catalysts prepared by oxalate gel-coprecipitation were found to be highly efficient for the catalytic combustion of methane. Particularly, the relationship between the microstrain of NiO lattice due to the formation of $Ce_xNi_{1-x}O_y$ solid solutions and the catalytic performance of Ni–Ce–O mixed oxides has been investigated as a function of the Ni/Ce ratio, showing that the lattice strain of the NiO crystals plays a significant role in the methane combustion reaction.

Catalytic combustion of methane has attracted increasing attention because of its capability to achieve a more efficient use of energy source with minimum pollutant emissions as compared to conventional flame combustion.[1–4] To date, the catalysts suggested for methane combustion are mainly based on supported noble metals, which however generally suffer from a rapid deactivation under reaction conditions due to sintering and loss of active species.[2–4]

In developing more suitable catalysts for the combustion of methane, transition metal mixed oxides have attracted considerable recent attention as new promising hydrocarbon combustion materials owing to their high thermal stability and relatively low cost compared to their conventional noble metal counterparts.[5–7] Despite an inferior activity to noble metals in general, a distinguished advantage of the metal mixed oxide catalysts is that numerous active solid-state phases can be obtained.[5,6] Among them, CeO_2-based mixed oxide systems appear to be particularly attractive for the combustion of methane owing to their unique redox properties and high oxygen storage capacities (OSC).[6,7] In the present study, for the first time, a novel type of Ni–Ce–O mixed oxide catalysts prepared by gel-coprecipitation of oxalate precursors were demonstrated to be highly efficient for methane combustion due to the formation of highly strained NiO crystals in the Ni–Ce–O mixed oxide materials.

The oxalate gel-coprecipitated Ni–Ce–O mixed oxide catalysts were prepared by following a modified procedure involving the gel-coprecipitation of oxalate precursors.[8] Briefly, two alcoholic solutions of mixed nitrates and 20% excess of oxalic acid were combined at room temperature under vigorous stirring. The resultant precipitate of oxalate was recovered by centrifuge and then dried at 110 °C overnight, followed by calcination in air at 550 °C for 3 h. The as-prepared samples were referred to NiCeO(OG)-*x*, where *x* denotes the molar ratio of Ni to Ce. For comparison, the reference samples denoted as NiCeO(OC)-*x* and NiCeO(KC)-*x* were prepared by aqueous oxalate coprecipitation and KOH coprecipitation methods, respectively. All catalysts were finally obtained by calcination in air at 550 °C for 3 h. The catalytic test was carried out in a fixed bed vertical quartz reactor packed with 0.1 g catalysts sample. The feed was constituted of a mixture of $CH_4/O_2/He$ with a molar ratio of 1/4/95 and a total gas flow of $24\,mL\cdot min^{-1}$ (GHSV ~ $48{,}000\,h^{-1}$). Permanent gases (N_2, O_2, CO, CO_2) were separated using a TDX–01 column connected to a TCD detector and other reaction products were analyzed by employing a Porapak Q column connected to a FID detector.

Figure 1 shows the methane conversion as a function of temperature in the range 200–700 °C over the Ni–Ce–O mixed oxide catalysts derived from different methods with a Ni/Ce molar ratio of 4. The light-off temperatures (T_{10}) and the half-conversion temperatures (T_{50}) of NiCeO(OG)-4 are observed to be much lower than those of the reference samples. It is remarkable that a half conversion temperature as low as 406 °C and a total conversion temperature below 500 °C can be achieved over the NiCeO(OG)-4 catalyst, which is comparable with that of Pt/CeO_2

Table 1. Catalytic performance and microstructural properties of various Ni–Ce–O mixed oxide catalysts[a]

Catalysts	S_{BET} $/m^2\cdot g^{-1}$	Mean crystallite size/nm[a]		Lattice parameter /Å[b]	Microstrain[c]		T_{10}[d]/°C	T_{50}[e]/°C
		NiO	CeO_2		$\varepsilon_{NiO}/\%$	$\varepsilon_{CeO_2}/\%$		
NiCeO(OG)-1	64.1	3.9	6.1	5.419	1.04	5.35	290	427
NiCeO(OG)-2	65.5	4.6	5.3	5.414	1.22	4.28	282	421
NiCeO(OG)-4	67.9	5.3	4.7	5.408	1.83	2.55	267	406
NiCeO(OG)-6	67.9	6.1	4.1	5.408	1.56	3.25	274	412
NiCeO(OG)-8	58.9	5.8	2.6	5.405	1.37	6.45	280	419
NiCeO(OC)-4	12.4	10.5	6.6	5.419	0.92	3.51	336	474
NiCeO(KC)-4	16.1	20.8	11.5	5.421	0.83	1.76	402	514
CeO_2	45.0	/	15.3	5.430	/	0.23	519	594
NiO	6.8	43.3	/	/	0.12	/	451	508

[a] The mean crystallite size of NiO and ceria crystals calculated from the Scherrer equation. [b] The lattice parameters calculated by the square method according to the Cohen procedure.[10] [c] The microstrain of the NiO or CeO_2 crystals obtained from the broadening of X-ray diffraction lines.[11] [d] Reaction temperature at which CH_4 conversion is 10%. [e] Reaction temperature at which CH_4 conversion is 50%.

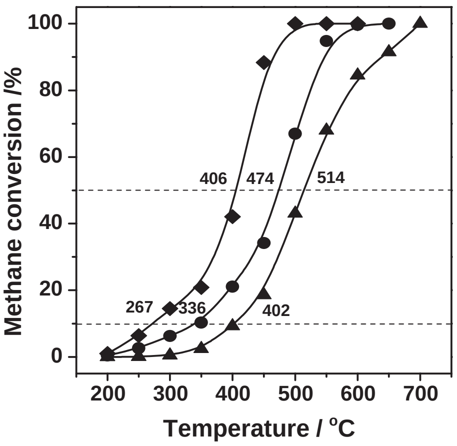

Figure 1. CH_4 conversion *vs.* combustion temperature over (a) NiCeO(OG)-4 (◆); (b) NiCeO(OC)-4 (●), and (c) NiCeO(KC)-4 (▲).

under the same reaction conditions.[9] The superior performance of the NiCeO(OG)-x catalysts prepared by gel-coprecipitation of oxalate precursors can be further seen from Table 1. One can see that the catalytic activity of all the mixed oxide catalysts is much higher than those of both pure ceria and pure nickel oxide.

Table 1 also summarizes the textural results as well as the microstructural parameters of the Ni–Ce–O mixed oxide catalysts prepared by various methods. It is seen that the BET specific surface area of the oxalate gel-coprecipitated samples is significantly higher than those of the reference samples prepared by conventional methods. Nevertheless, it has been found that there is only a weak relationship between the surface area or particle sizes and the performance of the NiCeO(OG)-x samples, indicating that the external texture is not the key factor governing the catalytic performance of the present samples prepared by oxalate gel-coprecipitation. On the other hand, it is seen that the catalytic performance does not show direct correlation with the lattice parameters, suggesting that the formation of solid solution of $Ce_xNi_{1-x}O_y$ is also not the decisive parameters in determining the catalytic performance of the present NiCeO(OG)-x samples.[7] However, by a careful correlation the microstructural data included in the Table 1, it could be found that there is a strong relationship between the lattice strain of the NiO crystals (ε_{NiO}) and the catalytic performance of the NiCeO(OG)-x catalysts with various Ni/Ce ratios.

Lattice strain has recently been shown to have a significant effect on the surface chemistry and reactivity of transition-metal surfaces.[12–14] As shown in Figure 2, an excellent correlation between the microstrains in the NiO lattice and the catalytic performance of the novel NiCeO(OG)-x catalysts have also been identified in the present work, demonstrating the key role of lattice strain in determining the catalytic performance of a mixed oxide catalytic system. In a recent investigation of the influence of lattice strain on the oxygen storage capacities (OSC) of the $Ce_{1-x}Zr_xO_2$ solid solutions prepared by hydrothermal urea precipitation,[15] Si et al. demonstrated the presence of a linear relationship between the oxygen storage capacity (OSC) values and the lattice strains reflecting the density of oxygen defect sites in the $Ce_{1-x}Zr_xO_2$ samples. It is therefore reasonable that that the present NiCeO(OG)-x samples with relatively high lattice strain level may possess a higher density of oxygen defect sites easily accessible to reactants, thus leading to enhanced low temperature performance for catalytic methane combustion.

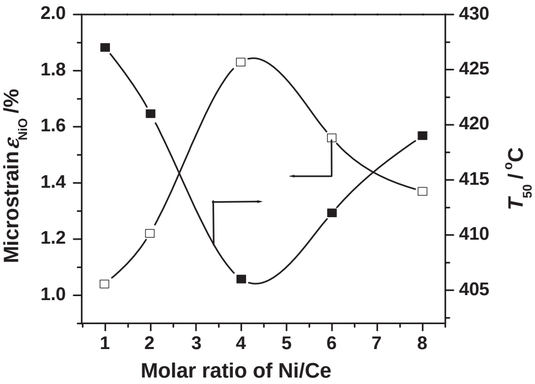

Figure 2. Correlation of microstrains (ε_{NiO}) in the lattice of the NiO nanocrystals and the temperature dependence for 50% conversion of CH_4 as a function of Ni/Ce molar ratios.

In summary, the Ni–Ce–O mixed oxide catalysts synthesized by oxalate gel-coprecipitation has been found to exhibit superior performance for the catalytic combustion of methane due to the formation of highly strained NiO crystals in the Ni–Ce–O mixed oxide materials. The present findings may provide new opportunities for the rational design of new advanced mixed oxide catalyst systems for more efficient hydrocarbon combustion.

This work was supported by the National Natural Science Foundation of China (Grant No. 20473021, 20203003), the National Major Basic Research Program of China (Grant No. 2003CB615807), and the Committee of Shanghai Science and Technology (Grant No. 02QA14006).

References

1 M. D. Fokema and J. Y. Ying, *Catal. Rev.—Sci. Eng.*, **43**, 1 (2001).
2 R. F. Hicks, H. H. Qi, M. L. Young, and R. G. Lee, *J. Catal.*, **122**, 280 (1990).
3 R. Burch and P. K. Loader, *Appl. Catal., B*, **5**, 149 (1994).
4 K. Muto, N. Katada, and M. Niwa, *Appl. Catal., A*, **134**, 203 (1996).
5 M. A. Pena and J. L. G. Fierro, *Chem. Rev.*, **101**, 1981 (2001).
6 K. Sekizawa, K. Eguchi, H. Widjaja, M. Machida, and H. Arai, *Catal. Today*, **28**, 245 (1996).
7 W. J. Shan, M. F. Luo, P. L. Ying, W. J. Shen, and C. Li, *Appl. Catal., A*, **246**, 1 (2003).
8 Q. Sun, Y. L. Zhang, H. Y. Chen, J. F. Deng, D. Wu, and S. Y. Chen, *J. Catal.*, **167**, 92 (1997).
9 F. Iamar, A. Trovareli, C. DeLeitenbury, and G. Dolcetti, *Chem. Commun.*, **1995**, 965.
10 H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," Wiley, New York (1954).
11 L. Lutterotti and P. Scardi, *J. Appl. Crystallogr.*, **23**, 246 (1990).
12 M. Gsell, P. Jakob, and D. Menzel, *Science*, **280**, 717 (1998).
13 S. Ohno, K. Yagyuu, K. Nakatsuji, and F. Komori, *Surf. Sci.*, **554**, 183 (2004).
14 B. L. Kniep, T. Ressler, A. Rabis, F. Grigsdies, M. Baenitz, F. Steglich, and R. Schlögl, *Angew. Chem., Int. Ed.*, **43**, 112 (2004).
15 R. Si, Y. W. Zhang, S. J. Li, B. X. Lin, and C. H. Yan, *J. Phys. Chem. B*, **108**, 12481 (2004).

Published on the web (Advance View) January 5, 2005; DOI 10.1246/cl.2005.108