Preparation of Ni-Ce-O Mixed Oxide by Oxalate Gel-Coprecipitation Method for Catalytic Combustion of Methane

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Catalytic combustion of methane has attracted much attention due to its highly efficient use of energy and low pollutant emission compared with conventional flame combustion [1]. Supported noble metal catalysts show high activity for methane combustion but they deactivated rapidly under the reaction conditions due to the sintering of active species [2]. Transition metal mixed oxides can also be used as catalysts for methane combustion [3~6] which can provide numerous active solid-state phases despite their lower activity than noble metal catalysts in general [3,4]. Among them　CeO_2-based mixed oxides appear to be particularly attractive for catalytic combustion of methane due to their unique redox properties and high oxygen storage capability [5,6]. In present study　a highly efficient Ni-Ce-O mixed oxide for methane combustion was prepared by oxalate gel-coprecipitation method and the correlation between the catalytic activity and the NiO crystal microstrain value　ε NiO　of the Ni-Ce-O mixed oxide was identified.

The Ni-Ce-O mixed oxide was prepared by a modified gel-coprecipitation method from an oxalate precursor [7]. Briefly　alcohol solutions of cerous nitrate and nickel nitrate were mixed and added into an alcohol solution with 20% excess of oxalic acid at room temperature under vigorous stirring. The resultant oxalate precipitate was recovered by centrifuge dried at 110 ℃ overnight　and calcined at 550 ℃ for 3 h. The as-prepared sample is named as Ni-Ce-O　x　where x represents the molar ratio of Ni to Ce. For comparison　a conventional sample denoted as Ni-Ce-O C　with Ni Ce molar ratio of 4 was prepared by the aqueous oxalate co-precipitation method. Catalytic tests were carried out in a fixed-bed quartz reactor packed with 0.1 g catalyst. The feed gas was 1%CH_4-4%O_2-95%He with flow rate of 24 ml min GHSV = 48 000 h^{-1}. N_2　O_2　CO and CO_2 were analyzed by a GC 122 gas chromatograph　Shanghai Analytical Instrument Factory　with a TDX-01 column and a TCD detector　other products were analyzed by an FID detector with a Porapak Q column.

Fig 1 shows the CH_4 conversion *versus* temperature over the catalysts. The light-off temperature at 10% CH_4 conversion　t_{10}　and the half-conversion temperature at 50% CH_4 conversion　t_{50}　of Ni-Ce-O 4　are much lower than Ni-Ce-O C　NiO and CeO_2　indicating that its catalytic activity for the catalytic combustion of methane was high.
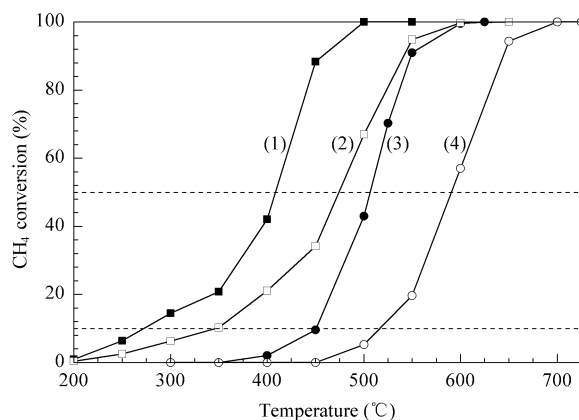
Fig 1　CH_4 conversion as a function of temperature over different catalysts

1　Ni-Ce-O 4　　2　Ni-Ce-O C　　3　NiO　　4　CeO_2

The characteristics of different catalyst samples are shown in Table 1. It can be seen that the catalytic activity of all the mixed oxide catalysts was much higher than that of CeO_2 and NiO to reach the same CH$_4$ conversion between 10% and 50% the temperature required for pure oxides was much higher than that of Ni-Ce-O mixed oxides prepared by the oxalate gel-coprecipitation method.

Table 1　Characteristics of different catalyst samples

Catalyst	A_{BET}　m^2　g	t_{10}　℃	t_{50}　℃	Lattice parameter　nm	Microstrain value	
					ε　NiO　%	ε　CeO$_2$　%
Ni-Ce-O　1	64.1	290	427	0.5419	1.04	5.35
Ni-Ce-O　2	65.5	282	421	0.5414	1.22	4.28
Ni-Ce-O　4	67.9	267	406	0.5408	1.83	2.55
Ni-Ce-O　6	67.9	274	412	0.5408	1.56	3.25
Ni-Ce-O　8	58.9	280	419	0.5405	1.37	6.45
Ni-Ce-O　C	12.4	336	474	0.5419	1.12	3.51
CeO$_2$	45.0	519	594	0.5430	—	0.23
NiO	6.8	451	508	—	0.12	—

The lattice parameter of CeO_2 was calculated by the square method according to the Cohen procedure and the microstrain value of the crystal lattice was calculated by X-ray diffraction Rietveld analysis [8].

The specific surface area of Ni-Ce-O 4 was much larger than that of Ni-Ce-O C . Thus the enhanced catalytic activity for methane combustion was likely due to its large surface area. The lattice parameter of the Ni-Ce-O x decreased with the increase of nickel loading indicating the formation of Ce_xNi_{1-x}-O_y solid solution in the bulk of the catalyst [5]. The combination of Ce and Ni oxides had a great influence on the lattice strain in both NiO and CeO_2 crystals and the lattice strain in the Ni-Ce-O x crystal was affected by the Ni Ce molar ratio. The maximum ε NiO of 1.83% was achieved for the NiO crystal lattice of Ni-Ce-O 4 suggesting the presence of high lattice defect density or high lattice distortion degree in the active phase of the sample.

Lattice strain has recently been shown to have a significant effect on the catalytic activity of transition-metal [9,10] and its effect on the oxygen storage capacity of $Ce_{1-x}Zr_xO_2$ solid solution has also been identified [11] . Therefore it is necessary to investigate the relationship between the catalytic activity of Ni-Ce-O x and the microstrain value which reflects the density of oxygen defect sites active for methane combustion. Table 1 also shows the correlation of ε NiO and t_{50} for methane combustion over Ni-Ce-O mixed oxide with different Ni Ce molar ratios. There was a good correlation between ε NiO$_2$ and t_{50} indicating the significant effect of the microstrain on the catalytic activity of Ni-Ce-O mixed oxide. It can be proposed that the increase of microstrain in NiO crystal leads to a higher catalytic activity for methane combustion.

In conclusion the Ni-Ce-O mixed oxide prepared by the oxalate gel-coprecipitation method is a highly efficient catalyst for methane combustion. A half conversion temperature t_{50} as low as 406 ℃ and a total conversion temperature at 100% CH$_4$ conversion t_{100} below 500 ℃ were achieved over Ni-Ce-O 4 . The microstrain value of the Ni-Ce-O x showed a good correlation with their catalytic performance for methane combustion which provides a new way to design the catalyst that is effective for methane combustion.

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Ni-Ce-O

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Ni-Ce-O
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Ni-Ce-O   .   4   406 ℃   50%   . Ni-Ce-O
NiO   .

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