

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 , CeO₂-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 ($\epsilon(\text{NiO})$) 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 °C overnight , and calcined at 550 °C 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% CH₄-4% O₂-95% He with flow rate of 24 ml/min (GHSV = 48 000 h⁻¹). N₂ , O₂ , CO and CO₂ 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 CH₄ conversion *versus* temperature over the catalysts. The light-off temperature at 10% CH₄ conversion (*t*₁₀) and the half-conversion temperature at 50% CH₄ conversion (*t*₅₀) of Ni-Ce-O(4) are much lower than Ni-Ce-O(*C*) , NiO and CeO₂ , indicating that its catalytic activity for the catalytic combustion of methane was high.

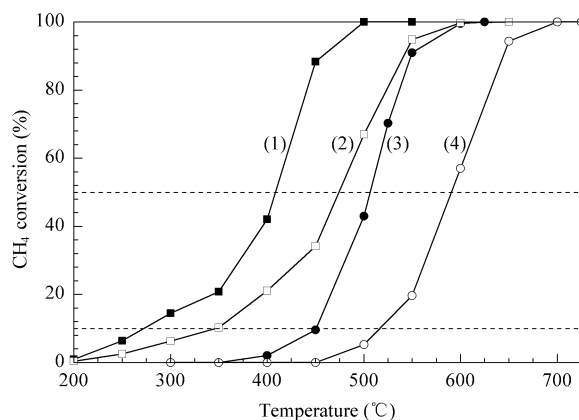


Fig 1 CH₄ conversion as a function of temperature over different catalysts

(1) Ni-Ce-O(4) , (2) Ni-Ce-O(C) , (3) NiO , (4) CeO₂

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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 CeO₂ and NiO, to reach the same

CH₄ 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 /°C	t ₅₀ /°C	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 CeO₂ 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 CeO₂ 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_xO₂ 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 t₅₀ for methane combustion over Ni-Ce-O mixed oxide with different Ni/Ce molar ratios. There was a good correlation between ε(NiO) and t₅₀, 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 (t₅₀) as low as 406 °C and a total conversion temperature at 100% CH₄ conversion (t₁₀₀) below 500 °C 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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草酸盐凝胶共沉淀法制备 Ni-Ce-O 甲烷催化燃烧催化剂

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摘要: 采用草酸盐凝胶共沉淀法制备了系列 Ni-Ce-O 复合氧化物催化剂, 考察了制备方法及催化剂组成对其催化甲烷燃烧性能的影响。结果表明, 草酸盐凝胶共沉淀法制备的 Ni-Ce-O 催化剂上甲烷的催化燃烧活性明显高于常规方法制备的 Ni-Ce-O 催化剂; Ni-Ce-O 催化剂的组成显著影响其催化性能。当镍/铈比值为 4 时, 在 406 °C 时即可使 50% 甲烷转化。Ni-Ce-O 复合氧化物中 NiO 的晶格微应变是影响其催化甲烷燃烧性能的重要因素。

关键词: 镍, 铈, 复合氧化物, 甲烷, 催化燃烧, 草酸盐凝胶共沉淀, 晶格微应变

(Ed YHM)

第四届全国环境催化与环境材料学术会议征文通知 (第一轮)

环境保护在我国社会与经济可持续发展战略中占有重要的地位, 并已越来越受到各级政府和社会公众的重视。环境材料与催化过程在环境污染控制、资源利用与新能源转化、以及开辟绿色工业工艺过程方面起着不可替代的作用。我国相继于 1999、2001 和 2003 年分别在杭州、银川和上海召开了第一、第二和第三届全国环境催化学术研讨会, 取得了很好的效果。为了进一步加强环境催化与环境材料方面的学术交流, 经中国化学会和中国化学会催化专业委员会批准, 第四届全国环境催化与环境材料学术会议初步定于 2005 年 10 月在北京召开, 会议由中国科学院生态环境研究中心筹办, 中石化齐鲁石化研究院和石油大学(北京)协办。会议将邀请国家相关管理部门、环保企业、材料生产企业以及科学研究与技术开发单位参加。本届会议是环境催化与环境材料工作者的一次盛会, 将全面展示和总结两年来我国环境催化与环境材料领域取得的新成果、新进展, 为同行提供相互交流、沟通和深入讨论的机会, 促进相互了解与合作, 推动我国环境催化与环境材料学科和相关产业的发展。欢迎相关单位与企业在会议上做专题报告和广告。

现在开始向有关的高等院校、科研院所、公司、厂矿和企业的科研、技术与管理人员征集学术论文与专题报告, 欢迎大家积极投稿并光临本次盛会。征文(学术论文与专题报告) 范围如下:

1. 环境污染控制过程中的催化问题(催化剂制备、催化反应以及催化控制机理), 包括气态污染物(包括固定源与机动车排放) CO、NO_x、SO_x、POSs、VOCs 和氯(氟) 烃等的催化消除, 工业和生活污水及废液中污染物的催化转化与净化, 固态产品或废弃物中污染物的催化处理;

2. 绿色工业与工艺过程开发中的催化问题, 包括清

洁生产、环境友好以及绿色化学中的催化材料和催化过程等;

3. 新能源的开发以及资源转化与利用中的催化问题, 包括石油、煤和天然气转化与利用过程中硫、氮和重金属等污染物的催化消除相关技术, 催化燃烧及催化辅助燃烧, 燃料电池, 光催化转化, 催化制氢, 二氧化碳和甲烷的综合利用与催化转化等;

4. 环境材料与环境体系中的催化过程, 包括非金属矿物粘土和煤矸石等自然环境过程中涉及的催化过程等;

5. 环境材料的表征、反应性能、环境安全性以及再生与回收利用;

6. 非常规技术在环境催化 and 环境保护中的作用, 如低温等离子体技术和臭氧技术在环境控制过程的应用。

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第二轮正式通知将依照所收到的代表回执于 2005 年 9 月 10 日前寄出。

第四届全国环境催化学术会议筹备组