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**Research Article** 

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# Influence of Cr<sub>2</sub>O<sub>3</sub> on Catalytic Performance of M<sub>X</sub>O<sub>Y</sub>(M=Cu, Ni, Ce)/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> for Methane Combustion

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#### Abstract

High activity at low temperature and good stability at high temperature, the main characteristics of excellent catalysts, are incompatible for general methane combustion catalyst. This study investigated the effect of  $Cr_2O_3$  on catalytic performance of  $M_XO_Y(M=Cu, Ni, Ce)/Al_2O_3$ -ZrO<sub>2</sub> catalysts for methane combustion and evaluated the catalytic activity to obtain methane combustion catalysts with high activity at low temperature and good stability at high temperature. Finally, Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), and X-ray diffraction (XRD) were used. Results demonstrate that CuO/Cr<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst has the highest activity. However, compared with CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, the modification effect of  $Cr_2O_3$  is not evident. When M = Ni, the effect of  $Cr_2O_3$  is the most evident; its  $T_{10\%}$  is 357 °C and  $\Delta T_{50\%}$  is 41 °C. This finding indicates that NiO/Cr<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst has high catalytic activity and good thermal stability. After aging at 1000 °C, the specific surface area of NiO/Cr<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst has good catalytic activity and thermal stability; its  $T_{10\%}$  is approximately 400 °C and  $\Delta T_{50\%}$  is approximately 10 °C. This study provides a reference for finding methane combustion catalysts with high activity at low temperature and excellent thermal stability at high temperature.

Keywords: Methane, catalytic combustion, MXOY/Al2O3-ZrO2 catalyst, Cr2O3 additive

#### 1. Introduction

Shortage of conventional energy and the pollution of living environment have become two global concerns. Natural gas, a new energy, mainly exists in oil fields and natural gas fields, and a small amount is found in coal seams. Compared with other mineral fuels, natural gas, as the most widely used clean energy, has the advantages of clean combustion products and high calorific value [1]. Therefore, scholars pay extensive attention to natural gas chemistry, such as partial oxidation of methane to syngas, oxidative coupling of methane, and catalytic combustion of methane.

The reserves of natural gas and coal bed methane are abundant all over the world, and Russia, the United States, and China rank among the top three [2]. Methane in the atmosphere is mainly from industrial waste gas, natural gas engine exhaust, and ventilation air methane. Treatment of mixed gas containing low-concentration methane is difficult, thereby resulting in its extremely low recovery rate. A large number of low-concentration methane is directly discharged into the air, causing serious greenhouse effect. In addition, the ignition temperature of methane is as high as 530 °C in its normal combustion range (5%–15%), and the adiabatic combustion temperature is approximately 1900 °C.  $N_2$  and  $O_2$  in the air react at high temperature (>1500 °C), and

NO<sub>x</sub> is generated, causing serious environment pollution.

Scholars have carried out numerous studies of catalytic combustion of methane [3-5]. Noble metals, which have good low-temperature catalytic activity, are the most active catalysts among catalytic combustion materials. However, their high-temperature stability is poor. When the temperature is above 1000 °C, noble metals lose activity due to the increase in particle size, sintering, and evaporation. Moreover, noble metals are poisonous and expensive, thereby limiting their application in catalyzing high-temperature combustion of methane. Therefore, developing catalysts with low cost, high activity, and good stability is necessary.

This study explores the interaction between catalyst support and active components by using low-cost transition metal oxides as catalyst support and active materials to optimize the comprehensive performance of catalysts. The study results provide reference for developing methane catalytic combustion catalyst with high activity at low temperature and good stability at high temperature.

#### 2. State of the art

At present, scholars have carried out numerous studies on metal oxide catalysts. Benjamín Torres–Olea et al. [6] used  $Al_2O_3 - ZrO_2$  mixture to catalyze the conversion of glucose to 5-hydroxymethylfurfural. Despite the excellent activity

and selectivity, the performance of the catalyst was unstable after repeated use. Zheng Xiaoming et al. [7] studied CO oxidation reaction catalyzed by  $Pt / ZrO_2 - \gamma - Al_2O_3$ . They found that doping  $ZrO_2$  was beneficial to desorption recovery of oxygen species on the catalyst, thereby promoting CO oxidation activity and a reaction between surface-active oxygen species and hydrogen. However, the catalyst was inactivated at high temperature. GUO et al. [8] studied the effect of doping La in  $Zr - Co / \gamma - Al_2O_3$ catalyst on Fischer-Tropsch synthesis and found that La could improve the antisintering ability of the catalyst to a certain extent. He Xiang-e et al. [9] modified Pd / Al<sub>2</sub>O<sub>3</sub> with  $ZrO_2$  and introduced an appropriate amount of  $ZrO_2$ to promote the interaction between support and active substances and improve the stability of the catalyst. Li Lina et al. [10] investigated the catalytic performance of  $Fe_2O_3 / Y_2O_3 - ZrO_2 - \gamma - Al_2O_3$ (abbreviated as  $YSZ - \gamma - Al_2O_3$ ) catalysts for methane combustion. X-ray photoelectron spectroscopy test results demonstrated that  $ZrO_2$  and  $Y_2O_3$  could not only increase and stabilize the surface concentration of  $Fe_2O_3$ , but also weaken the interaction between  $Fe_2O_3$  and  $\gamma - Al_2O_3$ . The catalyst has high activity at low temperature and good stability at high temperature. Sun Yiqing et al. [11] added ZrO2 to  $Ni / Al_2O_3$  catalyst, thereby enhancing the dispersion of Ni species in the catalyst and improving the catalyst activity in  $CO_{\rm x}$  methanation. Moreover, the catalyst has better stability at high temperature. Rodolfo et al. [12] doped lanthanide to modify  $Pd / CeO_2$  and found that  $Ce^{4+}$  was reduced by larger  $Ce^{3+}$ . In addition, the concentration of oxygen vacancy was increased, and the activity and stability of the catalyst were improved. Han D et al. [13] modified  $Al_2O_3$ with MgO- ZrO<sub>2</sub> to catalyze the preparation of synthesis gas CO and  $H_2$ . Thus, the cycle stability and activity of the catalyst were improved and carbon deposition decreased. A A F et al. [14] added  $WO_3$  and  $La_2O_3$  to  $ZrO_2$ -supported iron catalyst to study the methane decomposition characteristics. The additives significantly improved the catalytic activity and stability. Jeong M et al. [15] introduced  $Fe^{3+}$  into cubic fluorite  $CeO_2 - ZrO_2$  lattice, thereby effectively improving the oxygen release and storage capacity of the catalyst. Methane was completely oxidized at the temperature as low as 280 °C, but sintering phenomenon occurred at high temperature. Osman et al. [16] added promoters  $CeO_2$  and  $ZrO_2$  to  $Ni / Al_2O_3$  catalyst, which significantly enhanced the catalytic oxidation methane activity and improved methane conversion rate. However, the high-temperature performance of the catalyst was poor. Jeong et al. [17] introduced a small amount of NiO as promoter into cubic fluorite  $CeO_2 - ZrO_2$  structure and enhanced the oxygen release and storage capacity of  $PdO/CeO_2 - ZrO_2 - \gamma - Al_2O_3$  catalyst. In this approach, the complete oxidation of methane was realized. Lucía M. et al. [18] studied the catalytic performance of  $CeO_2 - ZrO_2 - Sc_2O_3$  mixed oxides for methane combustion. They found that  $Zr^{4+}$  could replace  $Ce^{4+}$  in

CeO<sub>2</sub> cubic lattice, and uniform solid solution was formed. Therefore, doping appropriate amount of Ce is helpful to obtain Ce-Zr-O solid solution structure, and the reaction activity and thermal stability in catalytic reaction were further improved. Hu Ahui [19] discussed the surface acidbase property of Pd/X-OMA (X: La Ce Zr Mg) catalyst and its performance in methane catalytic combustion reaction. The results demonstrate that doping Ce and Zr can change the surface acid-base property of ordered mesoporous alumina. Weak surface acidity and strong surface basicity of the catalyst are conducive to catalytic combustion of methane. The catalyst can realize complete conversion of methane at 385 °C. Zheng Shu's research group [20] explored the catalytic performance of the catalyst with  $YSZ - \gamma - Al_2O_3$  as the support for methane combustion. In the study process,  $Y_2O_3$  and  $Cr_2O_3$  were found to be good promoters for  $CuO/ZrO_2 - Al_2O_3$  catalyst, and they have similar modification effects.

These studies focused on metal oxide catalysts, most of which considered  $Y_2O_3$  and  $CeO_2$  as promoters and added modified catalysts. However, the study of promoter  $Cr_2O_3$  is scarce. To obtain methane combustion catalyst with excellent comprehensive performance, ZrO2 with good chemical properties was used. p semiconductor is likely to generate oxygen holes. As a catalyst support, it has strong electron interaction with active components, thereby significantly influencing the oxidation, reduction, and adsorption properties of the catalyst [21]. However, its small specific surface area decreases sharply with the increase in the calcination temperature.  $\gamma - Al_2O_3$  is a widely used catalyst carrier because of its large specific surface area, high mechanical strength, and suitable pore structure. However, it is not resistant to high temperature.  $ZrO_2 - \gamma - Al_2O_3$  carrier with large specific surface area and good high-temperature stability can be obtained using the two catalysts. This study selected NiO, CuO, and CeO2 with high catalytic activity for methane as active components [22] and investigated the modification effect of  $Cr_2O_3$  for  $M_{\chi}O_{\chi}$  (metal oxide)/  $Al_2O_3 - ZrO_2$  series catalysts to determine a methane combustion catalyst with good comprehensive performance.

The remainder of this study is organized as follows. Section 3 describes the preparation method, activity test, and characterization method of catalysts. In Section 4, the influence of  $Cr_2O_3$  on catalytic performance of  $M_xO_y$  (metal oxide)/  $Al_2O_3 - ZrO_2$  catalysts for methane combustion was analyzed based on the characterization data and results in Section 3. Finally, Section 5 summarizes this study and draws conclusions.

## 3. Methodology

#### 3.1 Preparation of catalyst

 $Al_2O_3 - ZrO_2$  and  $Cr_2O_3 - ZrO_2 - Al_2O_3$  (abbreviated as CrSZ-  $Al_2O_3$ ) were prepared by sol-gel method. A certain proportion of  $ZrOCl_2 \cdot 8H_2O$  and  $Al(NO_3)_3 \cdot 9H_2O$  was dissolved in distilled water.  $Cr(NO_3)_3$  was added at the

molar ratio of 3.5%. After stirring, 1M of  $NH_4OH$  was added at a certain rate until the pH of salt solution was 10. The solution was stirred for 3 h and aged for 24 h. The gel was filtered and washed, and the aerogel samples were obtained by supercritical drying (260 °C, 8 MP) with ethanol as the medium. The active components were impregnated uniformly with the molar number of  $Cu(NO_3)_2$ ,  $Ni(NO_3)_2$ , and  $Ce(NO_3)_2$  crystal salts accounting for 10% of aerogel carrier. The samples were dried at 120 °C and calcined at 600 °C for 3 h to obtain  $M_xO_y(M = Cu, Ni, Ce) / Al_2O_3 - ZrO_2$ and  $M_xO_y(M = Cu, Ni, Ce) / CrSZ - Al_2O_3$  catalysts. The prepared  $NiO / Cr_2O_3 - ZrO_2 - Al_2O_3$  catalyst was calcined at 800 °C and 1000 °C for 5 h.

## 3.2 Determination of activity of catalyst

The catalytic combustion reaction was carried out on a quartz tube fixed bed microreactor with  $\Phi 12$  mm. An amount of 0.80 g catalyst (40–60 mesh) was used. The gas volume ratio was VCH<sub>4</sub>:VAir=1:25, and the flow rate was 30 ml·min<sup>-1</sup>. The reaction program temperature rise is as follows:

 $20^{\circ}\text{C} \xrightarrow{4^{\circ}\text{C/min}} 280^{\circ}\text{C} \xrightarrow{2^{\circ}\text{C/min}} 650^{\circ}\text{C} \xrightarrow{4^{\circ}\text{C/min}} 850^{\circ}\text{C}$ 

The reaction tail gas was analyzed by GC-930 gas chromatograph manufactured by Shanghai Haixin Company. Flame ionization detector was used. The chromatographic column was carbon molecular sieve and connected to the methanator with Ni catalyst. The stability of the catalyst was tested by secondary evaluation.

#### 3.3 Characterization of catalyst

#### (1) X-ray diffraction (XRD)

The phase composition of the catalyst was measured by Japanese Physical Science D/max-2200PC X-ray diffractometer, with Cu rake, tube voltage of 30 KV, x - ray tube current of 20 mA, scanning rate of 8°·min<sup>-1</sup>, scanning range of 10°-80° and step size of 0.08°.

## (2) Specific surface area test (BET)

Micromeritics ASAP 2010 adsorption instrument and  $N_2$  isothermal adsorption method were used to measure the specific surface area of the samples. The specific surface area was calculated by two-parameter BET equation. Prior to measurement, the samples were conducted with 473 °K vacuum treatment for 30 min.

## (3) SEM test of catalyst

The morphology, average particle size, and dispersion of the catalysts were tested by S-3000 N scanning electron microscope of Hitachi Company.

### (4) Aging test

The catalyst was calcined at 1000 °C for 5 h in muffle furnace.

## 4. Result Analysis and Discussion

#### 4.1 Test of activity and specific surface area of catalyst

Fig. 1 shows the variation curve of the methane conversion rate of  $M_x O_y (M = Cu, Ni, Ce) / CrSZ - Al_2O_3$ , and

 $M_X O_Y (M = Cu, Ni, Ce) / Al_2 O_3 - ZrO_2$  catalysts calcined at 600 °C with reaction temperature. The corresponding activity evaluation data and specific surface data are listed in Table 1. As shown in Fig. 1, the performance of the catalyst modified by  $Cr_2O_3$ , especially the activity, has been significantly improved. When the active component is NiO, the modification effect of  $Cr_2O_3$  is the most evident. In Fig. 1 (a), the stability of the catalyst modified by  $Cr_2O_3$ (expressed by the temperature difference  ${}_{\Delta}T_{50\%}$  between the second evaluation and the first evaluation [23]) is similar to that of the unmodified catalyst. However, the initial activity is evidently improved, and  $T_{10\%}$  is decreased by 57 °C, which is consistent with the large specific surface area of  $NiO/CrSZ - Al_2O_3$ . In Fig. 1 (b), when the active component is  $CeO_2$ , the performance of the catalyst modified by  $Cr_2O_3$  is improved.  $\Delta T_{50\%}$  decreases, and  $T_{10\%}$ is reduced by 37 °C. According to the data in Fig. 1(c) and Table. 1, when the active component is CuO, the activity and the thermal stability of the modified catalyst are improved. Despite the large specific surface area of  $CuO/ZrO_2 - Al_2O_3$  catalyst, it decreases substantially after the second evaluation. This finding may be consistent with its poor high-temperature thermal stability.

The data of the specific surface of the samples in Table. 1 show that the specific surface area is consistent with the activity.  $NiO/CrSZ - Al_2O_3$  has large specific surface area. After the second reaction at 850 °C, the specific surface area is 97.83  $m^2 \cdot g^{-1}$ , which is consistent with its high activity and high stability. The specific surface area of the catalyst with CeO2 as active component is similar before and after modification probably because the influence of  $Cr_2O_3$  on the dispersion of  $CeO_2$  on the support is less evident than that on NiO. The decreasing trend of the specific surface area of the catalyst after second evaluation is consistent with the change in its thermal stability. When the active component is CuO. although the specific surface area of  $CuO/CrSZ - Al_2O_3$  modified by  $Cr_2O_3$  is not as large as that of unmodified  $CuO / ZrO_2 - Al_2O_3$ , it has better activity and stability. This condition is caused by the doping of  $Cr_2O_3$  suboxide in  $ZrO_2$  that forms the stable fluorite structure of  $ZrO_2$ , which can conduct oxygen ions at high temperature [24], thereby increasing the reaction speed to a large extent.

#### 4.2 Phase characterization of catalyst (XRD)

Fig. 2 (left) shows the XRD spectra of fresh  $M_x$  (= Ni, Ce, Cu) $O_y$  / CrSZ –  $Al_2O_3$  and  $M_x$  (= Ni, Ce, Cu) $O_y$  / Zr $O_2$  –  $Al_2O_3$  catalysts. None of the six catalysts has fraction peak of *m*- Zr $O_2$ , indicating that Zr $O_2$  is likely to exist in high-temperature phase t, and c- Zr $O_2$  crystalline forms below 600 °C. Curves 1 and 3 show that no characteristic peaks of (t+c)–Zr $O_2$ , and Zr $O_2$  zirconium exist in the amorphous state. The amorphous state is a short-range ordered and long-range disordered structure; it shows a steamed-bread shape on the XRD peak spectrum, which corresponds to the diffraction

peak with the maximum peak intensity of  $(t+c) - ZrO_2$ . The short-range ordered structure of the amorphous state is similar to the crystal structure of  $(t+c) - ZrO_2$ . Consequently, the conversion from amorphous  $ZrO_2$  to  $(t+c) - ZrO_2$  only needs to overcome less lattice distortion energy. The amorphous state of ZrO2 gel is likely to transform to  $(t+c) - ZrO_2$ , rather than precipitate the normally low-temperature stable m- ZrO<sub>2</sub> crystalline phase. This finding can be verified by the characteristic peak of (t+c) – ZrO<sub>2</sub> in Fig. 2 (right). The peaks of curves 1, 2, 3, and 4 are similar except for the difference in the height of the ZrO<sub>2</sub> peaks. However, 1 and 3 have much better activity than 2 and 4, respectively, because  $Cr_2O_3$  causes the active components to disperse on the amorphous ZrO<sub>2</sub> support, and the catalyst with large specific surface area is obtained. The characteristic diffraction peak of 2 is stronger than that of 1, and the crystal form of the solid solution phase tends to be complete. Thus, its specific surface area becomes smaller

than 1. NiO is more likely to disperse on the surface of  $ZrO_2 - Al_2O_3$  because of  $Cr_2O_3$ . The peak shapes of curves 3 and 4 are similar, and 4 has stronger characteristic diffraction peak than 3. The grains of the solid solution phase increase, which is consistent with its smaller specific surface area. The characteristic peak of the dark brown  $CuAl_2O_4$  spinel with low activity is formed at  $2\theta=37.35^\circ$ . This finding is one of the reasons for the small specific surface area of  $CuO/CrSZ - Al_2O_3$ . The peak shapes of curves 5 and 6 are also similar. The characteristic diffraction peaks of  $CeO_2$  appear at  $2\theta=29.16^\circ$ ,  $33.32^\circ$ ,  $48.54^\circ$ , and 57.16°, but the characteristic peaks of  $ZrO_2$  and  $Al_2O_3$  disappear. The radii of  $Al^{3+}$  (53.5pm) and  $Zr^{4+}$  (84 pm) are smaller than that of  $Ce^{4+}$  (97pm). They enter the lattice of  $CeO_2$ , replace  $Ce^{4+}$ , and form alternative solid solutions [26].



**Fig. 1.** Conversion of  $CH_4$  over  $M_x$  (= Ni, Ce, Cu) $O_y$  / CrSZ -  $Al_2O_3$  and  $M_x$  (= Ni, Ce, Cu) $O_y$  / Zr $O_2$  -  $Al_2O_3$  samples (new) indicates first evaluation; (old) indicates second evaluation

Table	1.	Catalytic	activities	and	Specific	surface	areas	of	$M_x (= Ni, Ce, Cu)O_y / CrSZ - Al_2O_3$	and
$M_x$ (= Ni, Ce, Cu) $O_y$ / Zr $O_2$ - Al <sub>2</sub> $O_3$ catalysts										

Sample	$S_{BET} / m^{2} g^{-1}$	$V_p / cm^{3.}g^{-1}$	$d_p/nm$	<i>T</i> <sub>10%</sub> /°C	$T_{50\%}/^{\circ}\mathrm{C}$	<i>T</i> <sub>90%</sub> /°C	△ <i>T</i> <sub>50%</sub>
$NiO / ZrO_2 - Al_2O_3$ (new)	133.54	0.42	12.53	414	474	522	40
$NiO / ZrO_2 - Al_2O_3$ (old)	65.97	0.34	18.44	435	514	586	
$NiO / CrSZ - Al_2O_3$ (new)	211.12	0.48	6.34	357	410	451	41
$NiO / CrSZ - Al_2O_3$ (old)	97.83	0.41	14.32	401	451	496	
$CeO_2 / ZrO_2 - Al_2O_3$ (new)	148.42	0.19	5.20	402	464	506	43
$CeO_2 / ZrO_2 - Al_2O_3$ (old)	41.54	0.12	12.78	433	507	558	
$CeO_2 / CrSZ - Al_2O_3$ (new)	169.17	0.39	4.70	365	423	471	31
$CeO_2 / CrSZ - Al_2O_3$ (old)	65.37	0.21	8.95	384	454	508	
$CuO / ZrO_2 - Al_2O_3$ (new)	234.99	0.45	7.63	332	382	417	33
$CuO / ZrO_2 - Al_2O_3$ (old)	51.97	0.34	24.42	361	415	459	
$CuO/CrSZ - Al_2O_3$ (new)	167.97	0.38	8.24	317	380	421	16
$CuO / CrSZ - Al_2O_3$ (old)	54.54	0.31	25.19	339	396	439	

Fig. 2 (right) shows the XRD patterns of  $M_x$  (= Ni, Ce, Cu) $O_y$  / CrSZ -  $Al_2O_3$  and  $M_x$  (= Ni, Ce, Cu) $O_y$  / Zr $O_2$  -  $Al_2O_3$  after second evaluation. The active component is NiO, and the diffraction peaks of curves a and b are enhanced. After high-

temperature reaction, a part of the high-temperature stable phase  $(t+c)-ZrO_2$  was transformed into monoclinic m- $ZrO_2$ , and the phenomenon was not found in curve a of the catalyst modified by  $Cr_2O_3$ . The characteristic diffraction peak of  $ZrO_2$  of curve a changes from amorphous  $ZrO_2$  prior to reaction to  $(t+c)-ZrO_2$  high-temperature phase instead of precipitating m-  $ZrO_2$  crystal phase, which is usually stable at low temperature [25]. Evidently,  $Cr_2O_3$ plays a stabilizing role for  $ZrO_2$ . m-  $ZrO_2$  is found on curves c and d when the active component is CuO. Particularly, a large amount of m-  $ZrO_2$  appears on curve d without  $Cr_2O_3$  modification. This finding is consistent with the worst high-temperature thermal stability. A small amount of m-  $ZrO_2$  appears on curve c, which may be related to the low amount of  $Cr_2O_3$  added. Curves e and f have more characteristic diffraction peaks of  $(t+c)-ZrO_2$ after reaction due to the disordered solid solution formed by Ce and Zr. The atoms are subjected to unbalanced forces from all directions at each lattice point at high temperature. The Zr atoms vibrating at the original equilibrium position of the lattice point may escape from the equilibrium position, and a characteristic diffraction peak of  $(t+c)-ZrO_2$  is formed [26].



Fig. 2. XRD patterns of  $M_x$  (= Ni, Ce, Cu) $O_y$  / CrSZ - Al<sub>2</sub>O<sub>3</sub> and  $M_x$  (= Ni, Ce, Cu) $O_y$  / ZrO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub> catalysts Left: new catalysts Right: old catalysts; 1 and a: NiO / CrSZ - Al<sub>2</sub>O<sub>3</sub>, 2 and b: NiO / ZrO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub>, 3 and c: CuO / CrSZ - Al<sub>2</sub>O<sub>3</sub>, 4 and d: CuO / ZrO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub>, 5 and e: CeO<sub>2</sub> / CrSZ - Al<sub>2</sub>O<sub>3</sub>, 6 and f: CeO<sub>2</sub> / ZrO<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub> •: t, c - ZrO<sub>2</sub>, ▼CuO:  $\heartsuit$ : CuAl<sub>2</sub>O<sub>4</sub> and Cu<sub>2</sub>O, ◆: m - ZrO<sub>2</sub>, ★:  $\gamma$  - Al<sub>2</sub>O<sub>3</sub>,  $\overleftrightarrow$ : NiO, $\bigcirc$ : CeO<sub>2</sub>

#### 4.3 SEM characterization of catalyst

Fig. 3 shows the SEM images of  $M_x$  (= Ni, Ce, Cu) $O_y$  / CrSZ –  $Al_2O_3$  catalyst. The shape of the samples is irregular, most of which are below 5 um. Although some large particles are observed, the samples have large specific surface area and good activity. When M= NiO and CuO, the particles are small, which is consistent with the large specific surface area and high activity of the samples. When  $M = CeO_2$ , given that the catalyst has large particle size, the specific surface area is small, and the activity is low.



**Fig. 3.** SEM images of  $M_x$  (= Ni, Ce, Cu) $O_y$  / CrSZ – Al<sub>2</sub>O<sub>3</sub> catalysts

a, b, c: Images of fresh catalysts of  $NiO/CrSZ - Al_2O_3$ ,  $CeO_2/CrSZ - Al_2O_3$ , and  $CuO/CrSZ - Al_2O_3$  calcined at 600 °C, respectively.

## **4.4 Influence of calcination temperature on** *NiO / CrSZ – Al<sub>2</sub>O*<sub>3</sub> catalyst

 $NiO/CrSZ - Al_2O_3$  was selected to explore the influence of calcination temperature on methane catalytic activity, considering activity and stability.

# (1) Test of activity and specific surface area of the catalyst

The data of specific surface area and catalytic activity of  $NiO/CrSZ - Al_2O_3$  catalyst are listed in Table.2. With the increase in calcination temperature, the specific surface area of the catalyst decreases in varying degrees, the activity decreases slowly, and the stability gradually increases. The specific surface area of the catalyst calcined at 1000 °C remains 62.33  $m^2 \cdot g^{-1}$ . The ignition temperature of  $T_{10\%}$  is only 377 °C and 18 °C for  $\Delta T_{50\%}$ .  $NiO/CrSZ - Al_2O_3$  catalyst has good catalytic activity and high-temperature thermal stability.

Sample		$S_{_{BET}} / m^{2.}g^{-1}$	$V_p / cm^{3.}g^{-1}$	$d_p/\!\mathrm{nm}$	<i>T</i> <sub>10%</sub> /°C	<i>T</i> <sub>50%</sub> /°C	<i>T</i> <sub>90%</sub> /°C	${\rm A}T_{50\%}$
$\frac{NiO / CrSZ - Al_2O_3}{(600 ^{\circ}\text{C})}$	(new) (old)	211.12 97.83	0.48 0.41	6.34 14.32	357 401	410 451	451 496	41
$\frac{NiO / CrSZ - Al_2O_3}{(800 ^{\circ}\text{C})}$	(new) (old)	104.99 69.53	0.43 0.35	12.53 25.21	352 397	420 459	465 501	39
$NiO / CrSZ - Al_2O_3$ (1000°C)	(new) (old)	62.33 43.44	0.32 0.29	23.53 27.65	377 395	458 476	516 534	18

**Table 2.** Catalytic activities and specific surface areas of  $NiO/CrSZ - Al_2O_3$  catalysts

Note: Temperature (°C) with methane conversion of 10%, 50%, and 90% denoted as  $T_{10\%}$ ,  $T_{50\%}$ , and  $T_{90\%}$  respectively; (new) indicates first evaluation; (old) indicates second evaluation



Fig. 4. XRD patterns of  $NiO / CrSZ - Al_2O_3$  catalysts

Left: new catalysts, Right: old catalysts; 1, 3, 5:  $NiO / CrSZ - Al_2O_3$  calcined at 600 °C, 800 °C, and 1000 °C  $\blacksquare: t, c - ZrO_2, \forall: NiO, \bigtriangledown: \beta - Al_2O_3, \bullet: m - ZrO_2, \bigstar: \gamma - Al_2O_3, \Box: \alpha - Al_2O_3$ 

#### (2) Phase analysis of the catalyst

XRD Fig. 4 shows the patterns of  $NiO/CrSZ - Al_2O_3$  catalysts calcined at different temperatures. The diffraction peaks tend to be complete and sharp with the increase in calcination temperature, and more  $(t+c) - ZrO_2$  are transformed into  $m - ZrO_2$ . Especially for the catalyst calcined at 1000 °C, ZrO2 mainly exists in the form of m-  $ZrO_2$ . This finding may be because the addition amount of  $Cr_2O_3$  is insufficient or  $Cr^{3+}$  with small radius is large specific surface area and good activity. After calcination at different temperatures, the particle size of the catalyst almost does not change, indicating its strong antisintering ability and good high-temperature thermal stability. This finding is consistent with the activity evaluation data. After calcination at 1000 °C, the particle size of  $NiO/CrSZ - Al_2O_3$  catalyst increases slightly and no evident agglomeration is observed. Although the XRD of the catalyst shows evident crystal phase change, the high dispersion of NiO on the support is not influenced. Therefore, the catalytic ability of the catalyst for methane combustion is unaffected, and the catalyst still has good catalytic activity for methane.

precipitated from the solid solution at high temperature.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> appears after the second evaluation. This result is consistent with the decrease in the specific surface area of the catalyst. However, the activity of the catalyst does not decrease evidently probably because of the dispersion of active component NiO on the support.

#### (3) SEM test of the catalyst

Fig. 5 shows the SEM images of  $NiO/CrSZ - Al_2O_3$  catalysts calcined at different temperatures. The particle size of most catalysts is below 5 um, which is consistent with the



Fig. 5. SEM images of  $NiO / CrSZ - Al_2O_3$  catalysts

a, b, and c: Fresh catalyst  $NiO/CrSZ - Al_2O_3$  calcined at 600 °C, 800 °C, and 1000 °C, respectively



## (4) Test of thermal stability of NiO / CrSZ – Al<sub>2</sub>O<sub>3</sub>

**Fig. 6.** Cycling run tests of  $NiO/CrSZ - Al_2O_3$  catalyst calcined at 1000 °C.

Fig. 6 shows the 10-time continuous activity evaluation diagram of  $NiO / CrSZ - Al_2O_3$  catalyst calcined at 1000 °C.  $\Delta T_{90\%}$  of the catalyst has little fluctuation, indicating its good stability. The comparative result of the XRD characteristic spectrum of  $NiO / CrSZ - Al_2O_3$  catalyst after 10-time activity evaluation and the fresh catalyst indicates that the peak positions are completely consistent, with slight enhancement of the peak intensity of  $m - ZrO_2$ , which may be related to the small addition amount of  $Cr_2O_3$  promoter.

## 5. Conclusion

 $M_{\chi}O_{\gamma} / Al_2O_3 - ZrO_2$  catalyst was prepared using sol-gel method to obtain methane combustion catalyst with high activity at low temperature and good stability at high temperature. Activity evaluation, BET, SEM, XRD, and aging test were carried out to explore the modification effect of  $M_{\chi}O_{\gamma} / Al_2O_3 - ZrO_2$  catalysts. The following conclusions could be drawn:

(1) The results show that the catalyst  $M_XO_Y / Al_2O_3 - ZrO_2$  has high catalytic activity, but its stability is poor. Adding  $Cr_2O_3$  can improve the stability and activity of the catalyst. The results of activity evaluation,

BET, SEM, and XRD analysis indicate that CuO has the best activity, but its thermal stability is poor. With the increase in the reaction temperature, CuO reacts with support  $Al_2O_3$ , and  $CuAl_2O_4$  with low activity is generated, thereby leading to sintering phenomenon of the catalyst. When the active component is NiO, the modification effect is evident, and the catalyst shows good activity and stability.  $Cr_2O_3$  can inhibit the phase transition of  $ZrO_2 - Al_2O_3$  at high temperature and obtain highly dispersed active component NiO.

(2) With the increase in the calcination temperature, the specific surface area and activity of  $NiO/CrSZ - Al_2O_3$  catalyst decrease slowly, showing good activity and stability. The structure of  $NiO/CrSZ - Al_2O_3$  catalyst calcined at 1000 °C changes greatly, but the catalyst still has good activity. Moreover, its specific surface area is up to 62.33  $m^2 \cdot g^{-1}$ , and no evident sintering phenomenon is found in SEM test. The aging test results show that  $\Delta T_{90\%}$  is approximately 10 °C, indicating that NiO is highly dispersed on such supports. The antisintering ability of the catalyst stabilized by  $Cr_2O_3$  is enhanced.

This study analyzed the influence of  $Cr_2O_3$  on the catalytic performance of  $M_xO_y / Al_2O_3 - ZrO_2$  catalyst for methane. Adding  $Cr_2O_3$  could not only inhibit the high-temperature phase transition of  $ZrO_2 - Al_2O_3$ , but also cause NiO to be highly dispersed on the support, thereby greatly improving the activity and stability of the catalyst. A good catalyst promoter was provided for methane catalytic combustion. However, the structure of  $NiO / CrSZ - Al_2O_3$  catalyst calcined at 1000 °C changed greatly. This condition may be because the addition amount of  $Cr_2O_3$  is too little or  $Cr^{3+}$  with small radius is likely to be precipitated from  $Zr^{4+}$  at high temperature. This finding needs to be further verified.

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