

## Catalytic Combustion of Methane over CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Catalysts Modified by M<sub>x</sub>O<sub>y</sub> (M = Y, Cr, Mg, Ce)

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A series of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts modified by M<sub>x</sub>O<sub>y</sub> (M = Y, Cr, Mg, Ce) have been prepared using sol-gel method. The catalysts have been characterized by BET and XRD techniques and catalytic activity for methane combustion have been investigated. The result of catalytic activity indicates that CuO/Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst has higher catalytic activity and the best thermal stability. The addition of Y<sub>2</sub>O<sub>3</sub> can increase catalytic activity and thermal stability of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst.

**Key Words:** Methane, Catalytic combustion, CuO.

### INTRODUCTION

In the field of methane combustion, the conventional thermal combustion is high temperature reaction. In the process, NO<sub>x</sub> can be produced, which can cause serious environment pollution<sup>1,2</sup>. In addition, the methane can not be completely burning which result in the emission of CO toxic gases and CH<sub>4</sub> greenhouse gases. The catalytic combustion can control and eliminate the harmful gases of NO<sub>x</sub>, CO and not the complete combustion of hydrocarbon compounds<sup>3,4</sup>, but it needs hard reaction conditions and the key problem is the study of the catalyst with high catalytic activity in low-temperature range and stability in high-temperature range<sup>5</sup>. Now, many catalysts have shown excellent low-temperature catalytic activity. However, the problem of the stability of the catalyst in the high temperature range needs to be studied further.

Transition metal oxides have an important promotion for the industrial catalysts and catalytic carriers. For example, ZrO<sub>2</sub>, which not only has favourable chemical properties, but also is p-type semiconductor, easy to produce oxygen vacancies. Zirconium oxide can also generate a strong electronic-interaction with the active component as support and has a greater effect on the properties in the catalytic oxidation, reduction and adsorption process<sup>6</sup>. ZrO<sub>2</sub> is also an excellent high temperature ceramic and high-quality refractory materials<sup>7</sup>. Generally, calcined under different temperature, the ZrO<sub>2</sub> can be existed in three different crystals. Therefore, in order to stabilize the ZrO<sub>2</sub> crystal phase which has high stability under high temperature range, some stabilizer must be added in the ZrO<sub>2</sub>. The CaO, MgO and Y<sub>2</sub>O<sub>3</sub> are preferred because of their similar

crystal structure with the ZrO<sub>2</sub>, which can form a cubic solid solution with ZrO<sub>2</sub> and then stabilize ZrO<sub>2</sub> phase<sup>8</sup>. Then adding rare earth oxides to ZrO<sub>2</sub>, both can improve the thermal stability of ZrO<sub>2</sub> because of stabilizing cubic or tetragonal zirconia within a wide temperature range and can improve zirconia electrical conductivity, mechanical strength and catalytic activity. So the rare earth metal oxide are widely used as a promoter in the field of catalytic combustion, especially the three-ways catalyst for automotive emission control<sup>9</sup>. Despite the exceptional nature in ZrO<sub>2</sub>, it has small surface area and a sharp decline with the high calcination temperature. So, as a catalyst carrier, its application is limited. For the larger specific surface area, better mechanical strength and suitable pore structure *etc.*, γ-Al<sub>2</sub>O<sub>3</sub> is widely used as a catalyst support. However it is not appropriate in the high temperature reaction process. If combining the above two to make the MSZ-γ-Al<sub>2</sub>O<sub>3</sub> (the MSZ are catalyst carrier that ZrO<sub>2</sub> is stabilized by M<sub>x</sub>O<sub>y</sub>, M = Mg, Y, Cr and Ce) carrier, we can obtain a support which has large surface area and good high temperature stability. Zhou and Zheng *et al.*<sup>10</sup> studied Pt/ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalytic activity for CO, Li *et al.*<sup>11</sup> investigated Fe<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> coated on the cordierite and He Xiang-e<sup>12</sup> researched ZrO<sub>2</sub> modified over Pd/Al<sub>2</sub>O<sub>3</sub> for catalytic combustion of methane.

However, the effect of Mg, Y, Cr and Ce on high temperature stability of ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> carrier for methane combustion has not been reported. In order to investigate the properties of ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> support in methane combustion, we study the influence oxides of metals on the methane combustion stability of CuO/ZrO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst in this paper.

## EXPERIMENTAL

**Preparation of the catalysts:** The MSZ- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (M = Mg, Y, Cr, Ce) supports were prepared by a sol-gel method. The required amount of ZrOCl<sub>2</sub>·8H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, M(NO<sub>3</sub>)<sub>x</sub> and C<sub>18</sub>H<sub>29</sub>NaO<sub>3</sub>S was dissolved in distilled water. An excess of aqueous solution of NH<sub>4</sub>OH was added to the mixed nitrate solution dropwise and stirring vigorously. The resulting suspension was stirred for 3 h and then kept for 24 h. The obtained gel was washed and dried in supercritical condition (260 °C, 8MP). 10 mol % CuO was incorporated in MSZ- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> through impregnation with copper nitrate. The sample was dried at 120 °C and then calcined at 600 °C for 3 h.

**Tests of the catalytic activities:** Catalytic activity tests were carried out at atmospheric pressure in a fixed-bed quartz microreactor (internal diameter = 12 mm). In each experiment 800 mg of catalysts was used. A mixture containing CH<sub>4</sub> (25 vol.%) and air (75 vol.%) with a flow rate of 30 mL/min was supplied. The catalytic activity was monitored at different temperatures from 25 °C up to 850 °C. A heating rate of 2 °C/min was used in all the experiments. The products were analyzed by on-line gas chromatography with the column of carbon molecular sieve. Every catalyst was evaluated twice under the same experimental conditions.

**Characterization of the catalysts:** X-ray powder diffraction analysis was performed on a D/max-2200 PC X-ray diffractometer. Copper K $\alpha$  radiation was used with power setting at 30 kV and 20 mA. For crystal phase identification, the typical operation parameters were set to a scan rate of 8°/min with 0.08 data interval and the scan range from 10° to 80°.

The BET specific surface areas of the prepared catalysts were evaluated from the linear parts of the BET plot of the N<sub>2</sub> isotherms, using an ASAP 2010 analyzer made by micro-meritics.

## RESULTS AND DISCUSSION

**Catalytic activity and stability:** Methane conversion as a function of reaction temperature are showed in Fig. 1, CuO/M<sub>x</sub>O<sub>y</sub> (M = Y, Cr, Mg, Ce)-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst are prepared after roasting at 600 °C. The temperature corresponding to 10 %, 50 % and 90 % methane conversion and BET surface area are listed in Table-1. CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst shows high catalytic activity for methane combustion and conversion of 90 % for methane is approached at 415 °C. However, the catalyst has bad stability (the difference between T<sub>50 %</sub> of second activity evaluation and T<sub>50 %</sub> of first activity evaluation denotes thermal stability of catalyst<sup>13</sup>,  $\Delta T_{50\%} = 33$  °C), especially at high temperatures. In order to improving thermal stability of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, M metal oxide are added in the catalyst. From Fig. 1, we can find the M modified catalysts have higher thermal stability than that of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. The order of thermal stability for CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> > CuO/CrSZ-Al<sub>2</sub>O<sub>3</sub> > CuO/MgSZ-Al<sub>2</sub>O<sub>3</sub> > CuO/CeSZ-Al<sub>2</sub>O<sub>3</sub> > CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> is best and its  $\Delta T_{50\%} = 9$  °C. All catalysts have similar catalytic activity (T<sub>10%</sub> is located in between 308 °C and 326 °C) for methane combustion than that of unmodified.

**BET surface area:** Table-1 shows BET surface area of the catalysts. CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst modified with M have

lower surface area than that of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, which are because M added hinder partly the total dissolution of ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. But CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts modified with M have higher catalytic activity, it is likely that Y<sub>2</sub>O<sub>3</sub> which are low-valence oxides are added to ZrO<sub>2</sub> can make ZrO<sub>2</sub> in stable fluorite structure, which can conduct oxygen ions at high temperature<sup>7</sup> and then enhance the reaction rate<sup>14</sup> to a large extents. Surface area of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst is the largest, but it decreases from 234.99 to 183.02 m<sup>2</sup> g<sup>-1</sup> after second evaluation, which is consistent with its the worst thermal stability. Catalytic activity of the catalysts modified with M are closely associated with BET surface area. The loss of BET surface area of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> catalyst after second evaluation is smaller than that of other catalysts, so it has the best thermal stability ( $\Delta T_{50\%} = 9$  °C).

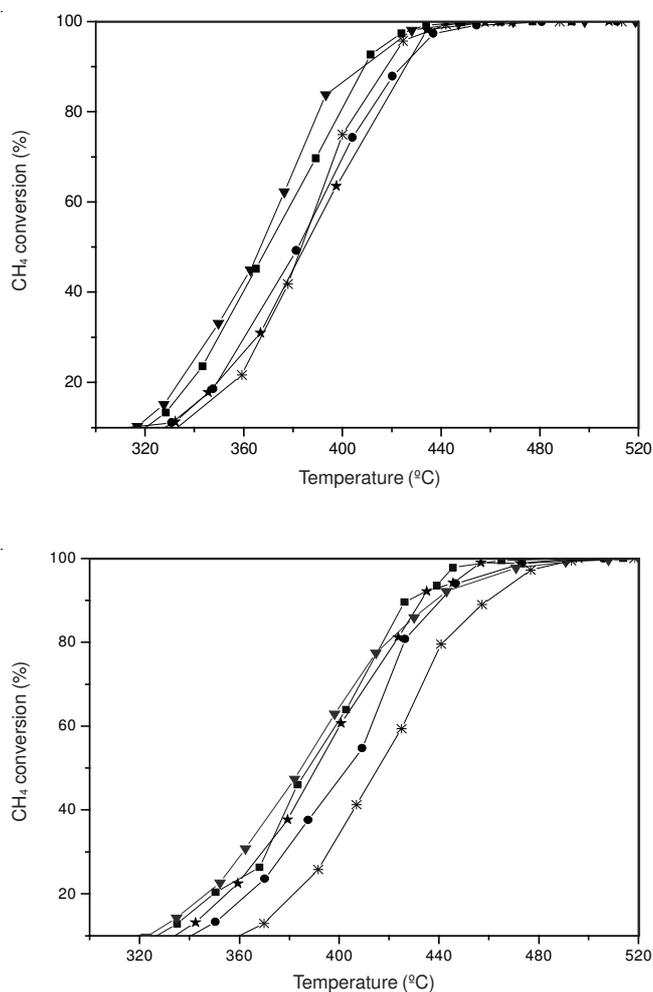


Fig. 1. Conversion of CH<sub>4</sub> over CuO/M<sub>x</sub>O<sub>y</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> samples; Left: first evaluation, Right: second evaluation ★:CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> ●: CuO/CrSZ-Al<sub>2</sub>O<sub>3</sub> ■: CuO/MgSZ-Al<sub>2</sub>O<sub>3</sub> ▼: CuO/CeSZ-Al<sub>2</sub>O<sub>3</sub> \*: CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

**Crystalline phases:** The XRD patterns of fresh CuO/M<sub>x</sub>O<sub>y</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts are shown in Fig. 2 (left). X-ray diffraction analysis does not reveal the presence of M<sub>x</sub>O<sub>y</sub> phases. There are two plausible explanations for this. On the one hand is M<sub>x</sub>O<sub>y</sub> might be dispersed too thin to be detected by XRD. On the other hand, some of M<sub>x</sub>O<sub>y</sub> and ZrO<sub>2</sub> have

TABLE-1  
CATALYTIC PERFORMANCE AND SPECIFIC SURFACE AREA OF THE CATALYSTS

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$dp$ (nm)	$T_{10\%}$ ( $^{\circ}\text{C}$ )	$T_{50\%}$ ( $^{\circ}\text{C}$ )	$T_{90\%}$ ( $^{\circ}\text{C}$ )
CuO/ ZrO <sub>2</sub> - Al <sub>2</sub> O <sub>3</sub> (I)	234.99	0.45	7.63	332	382	415
(II)	51.97	0.34	24.42	361	415	459
CuO /YSZ- Al <sub>2</sub> O <sub>3</sub> (I)	168.72	0.37	9.21	326	380	423
(II)	48.96	0.33	25.6	333	389	432
CuO /CrSZ- Al <sub>2</sub> O <sub>3</sub> (I)	166.97	0.34	8.24	317	380	421
(II)	41.54	0.29	27.79	339	396	439
CuO /MgSZ- Al <sub>2</sub> O <sub>3</sub> (I)	183.33	0.36	7.77	320	369	408
(II)	35.37	0.26	29.48	339	388	426
CuO /CeSZ- Al <sub>2</sub> O <sub>3</sub> (I)	192.84	0.31	6.51	315	366	408
(II)	40.72	0.24	23.14	324	386	438

Note: Temperature ( $^{\circ}\text{C}$ ) with methane conversion of 10 %, 50 %, 90 % denoted as  $T_{10\%}$ ,  $T_{50\%}$ ,  $T_{90\%}$  respectively; (I) means first evaluation; (II) means second evaluation

similar structures, they can completely miscible and form an ideal solid solution or complex, which change crystal internal structure and form metastable tetragonal phase and stable cubic phase ((t+c)-ZrO<sub>2</sub>)<sup>15</sup>. Under high temperature, CuO can be transferred into brown CuAl<sub>2</sub>O<sub>4</sub> spinel, which has lower catalytic activity for methane combustion. XRD patterns of the catalysts except Mg and Ce modified samples show CuAl<sub>2</sub>O<sub>4</sub> spinel peaks. For Cr and Mg modified catalyst samples, zirconium exists in amorphous phase, may be because ionic radius of Cr and Mg are similar with that of Zr and solubility of their oxides in ZrO<sub>2</sub> are large. Thus they can form substitutional solid solution with ZrO<sub>2</sub> and stabilize tetragonal phase and cubic phase [(t+c)-ZrO<sub>2</sub>]. Further, the different amount of stabilizer can stabilize all or partially zirconia<sup>16</sup>. Ionic radius of Y and Ce are larger than that of Zr. Then they can form filled solid solution with ZrO<sub>2</sub><sup>17</sup>. From the curve 1 and 5 in Fig. 2 (left), it can be seen that ZrO<sub>2</sub> appears in stabilized zirconia. For the Y modified catalyst sample, it does not appear the peak of yttria. However, the four diffraction peaks of Zr<sub>0.86</sub>Y<sub>0.14</sub>O<sub>1.93</sub> are observed at  $2\theta=30.34^{\circ}$ ,  $35.45^{\circ}$ ,  $50.61^{\circ}$  and  $59.53^{\circ}$  respectively, which shows Y<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> form filled solid solution which is benefit to forming stable high-temperature phase of ZrO<sub>2</sub>. For Ce modified sample, also it does not appear the peak of cerium oxide and the four diffraction peaks of Zr<sub>0.85</sub>Ce<sub>0.15</sub>O<sub>2</sub> are observed at  $2\theta=30.34^{\circ}$ ,  $35.45^{\circ}$ ,  $50.61^{\circ}$  and  $59.53^{\circ}$  respectively, which also indicates that CeO<sub>2</sub> and ZrO<sub>2</sub> form filled solid solution who can stable high-temperature phase of ZrO<sub>2</sub>. For non-modified catalyst calcined under 600  $^{\circ}\text{C}$ , zirconia exists in (t+c)-ZrO<sub>2</sub>, which indicates the phase of ZrO<sub>2</sub> is stable in the range of low temperature.

The XRD patterns of CuO/M<sub>x</sub>O<sub>y</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts after second evaluation are shown in Fig. 2 (right). The diffraction peaks of the catalysts after second activity test are stronger than that of the fresh ones, which indicates that the catalyst particles after the second evaluation are larger than that of the fresh ones. This result is in agreement with the data of BET measurement and catalytic activity and stability. For M = Y, Cr and Ce modified catalyst samples, the intensity of monoclinic phase (m-ZrO<sub>2</sub>) peak are low. In particular, the catalyst modified by Y remains (t+c)-ZrO<sub>2</sub> after high-temperature reaction, which is consistent with the smallest change in surface area and the best stability under high reaction temperature. A little amount of m-ZrO<sub>2</sub> appears probably because of adding too little stabilizer to sufficiently stabilize CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

The diffraction peak of CuO at  $2\theta = 38.78^{\circ}$  disappear, probably because of generating the low-activity CuAl<sub>2</sub>O<sub>4</sub> with Al<sub>2</sub>O<sub>3</sub>. The new peak at  $2\theta = 62.65^{\circ}$  of ZrO<sub>2</sub> appears in the catalysts. This is the result of because amorphous ZrO<sub>2</sub> converting into (t+c)-ZrO<sub>2</sub> by overcoming smaller lattice distortion energy. For the M = Mg sample, characteristic diffraction peaks of m-ZrO<sub>2</sub> at  $2\theta = 24.28^{\circ}$ ,  $28.35^{\circ}$ ,  $31.43^{\circ}$ ,  $34.31^{\circ}$  and  $41.20^{\circ}$  are found. The peak intensity clearly increases after second evaluation because a large part of a morphous in the unreacted turn into m-ZrO<sub>2</sub>. This is evident from bigger change of the surface area, which is consistent with the surface area down intensely to minimum value of  $35.37 \text{ m}^2 \cdot \text{g}^{-1}$  after second evaluation and its stability is worse. May be due to Mg<sup>2+</sup> whose radius is smaller ( $r_{\text{Mg}^{2+}} = 65 \text{ pm}$ ) in ZrO<sub>2</sub> ( $r_{\text{Zr}^{4+}} = 84 \text{ pm}$ ) lattice is easy to move, so serious de-fused and poor resistance to heat and shock<sup>18</sup>. Curve 6 is the spectra of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, it can be seen the peak shape changes significantly after secondary evaluation, a large part of m-ZrO<sub>2</sub> appears due to t-ZrO<sub>2</sub> after evaluation at high temperature turns into m-ZrO<sub>2</sub> in the cooling process, which is consistent with its worst thermal stability.

**Effect of the catalyst calcination temperature:** In view of the activity and stability of catalyst, CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> and CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts are selected as specimen and calcined at 600, 800 and 1000  $^{\circ}\text{C}$  respectively, to study roasting temperature influence on catalyst performance. The evaluation results of catalytic activity at different roasting temperature of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> and CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst are showed in Fig. 3.

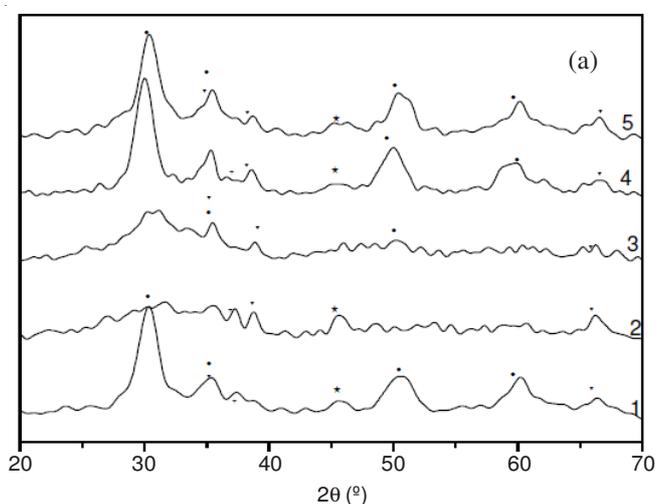


TABLE-2  
CATALYTIC ACTIVITIES AND SPECIFIC SURFACE AREAS OF CuO/YSZr-Al<sub>2</sub>O<sub>3</sub>, CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> CATALYSTS

Sample	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> ·g <sup>-1</sup> )	dp (nm)	T <sub>10%</sub> (°C)	T <sub>50%</sub> (°C)	T <sub>90%</sub> (°C)	
CuO/ZrO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	600 °C	(I)	234.99	0.45	7.63	332	417
		(II)	51.97	0.34	24.42	361	459
	800 °C	(I)	94.23	0.36	15.32	344	433
		(II)	34.76	0.27	30.72	353	478
	1000 °C	(I)	17.0	0.12	27.28	397	530
		(II)	12.1	0.10	28.36	398	541
CuO/YSZ-Al <sub>2</sub> O <sub>3</sub>	600 °C	(I)	168.72	0.37	9.21	326	423
		(II)	48.96	0.33	25.6	333	432
	800 °C	(I)	78.38	0.32	16.56	322	415
		(II)	45.3	0.28	25.21	322	433
	1000 °C	(I)	31.3	0.21	27.53	356	495
		(II)	30.44	0.20	27.65	361	505

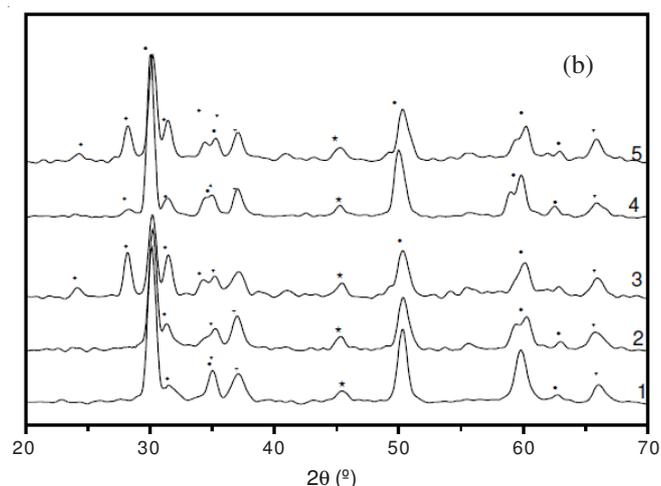


Fig. 2. XRD patterns of CuO/M<sub>x</sub>O<sub>y</sub>-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts (a) fresh catalysts, (b) old catalysts; 1: CuO/YSZ-Al<sub>2</sub>O<sub>3</sub>, 2: CuO/CrSZ-Al<sub>2</sub>O<sub>3</sub>, 3: CuO/MgSZ-Al<sub>2</sub>O<sub>3</sub>, 4: CuO/CeSZ-Al<sub>2</sub>O<sub>3</sub>, 5: CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; ●: t.c.-ZrO<sub>2</sub>, ▼: CuO, □: CuAl<sub>2</sub>O<sub>4</sub> and Cu<sub>2</sub>O, ◆: m-ZrO<sub>2</sub>, ☆: γ-Al<sub>2</sub>O<sub>3</sub>

It can be seen from Fig. 3, the catalyst modified by Y calcined at 800 °C has the best catalytic activity and better thermal stability, The T<sub>50%</sub> and T<sub>10%</sub> of the catalyst is 5 °C and 322 °C, respectively. The catalyst activity calcined at 1000 °C significantly decrease, especially that the catalyst modified without Y reduce more significantly, whose T<sub>10%</sub> is 397 °C, but T<sub>10%</sub> of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> catalyst is only 356 °C, which shows the great role of Y. In addition, the activity of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> calcined at 1000 °C also falls more, which may be related to too little amount of Y added.

Table-2 shows the specific surface area of catalysts which are calcined under different calcination temperature. This phenomenon is more obvious on CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst sample, which is consistent with its poor activity. This may be associated with the catalyst which is sintered partly who lead to decrease of the pore volume and larger of the particles. After calcined at 1000 °C, surface area of the catalyst is only 17.0 m<sup>2</sup>·g<sup>-1</sup>, but the surface area of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> catalyst is able to maintain at 31.3 m<sup>2</sup>·g<sup>-1</sup>, clearly showing the stabilizing effect of Y<sub>2</sub>O<sub>3</sub>.

Fig. 4 show the XRD patterns of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> and CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts calcined under different temperature. Diffraction peak width become narrow and the crystal line phase of catalysts tend to be in complete with increasing of roasting temperatures. Curve 4 and 6 still don't appear

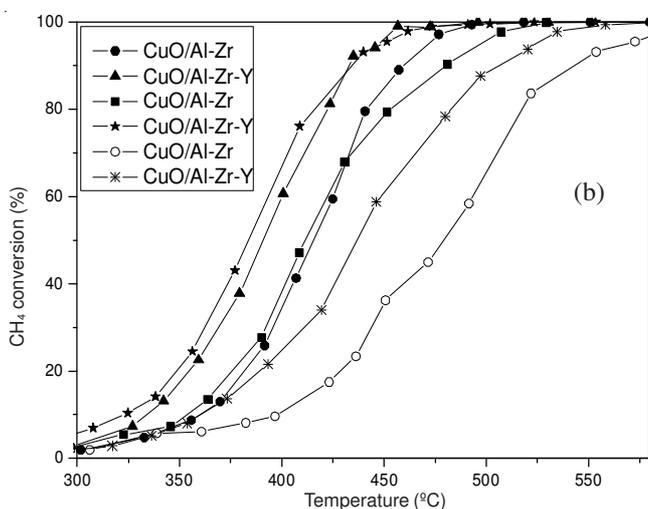
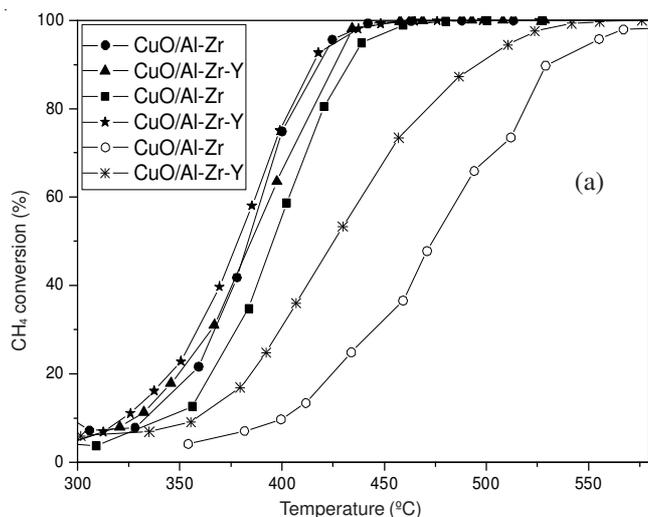


Fig. 3. Conversion of CH<sub>4</sub> over CuO/YSZ-Al<sub>2</sub>O<sub>3</sub>, CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> samples (a) means first evaluation; (b) means second evaluation ● and ▲: 600 °C; ■ and □: 800 °C; ○ and ☆: 1000 °C

diffraction peaks of Y<sub>2</sub>O<sub>3</sub>, which confirms that ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> form solid solution formation. And nor appear diffraction peak of α-Al<sub>2</sub>O<sub>3</sub>, which shows ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> both can stabilize γ-Al<sub>2</sub>O<sub>3</sub> to a certain extent<sup>11</sup>. These make the catalyst remains specific surface area and good catalytic activity at 1000 °C, but activity of the catalyst decreases more, which may be related to Y added is too little to can fully prevent CuO and γ-Al<sub>2</sub>O<sub>3</sub> generate CuAl<sub>2</sub>O<sub>4</sub>. CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst calcined

above 800 °C all appear the peak of *m*-ZrO<sub>2</sub>. The curve 5 shows the XRD pattern of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 1000 °C, which shows a large number of *m*-ZrO<sub>2</sub> appear and the strongest peak of *t,c*-ZrO<sub>2</sub> is very weak, indicating that most of the ZrO<sub>2</sub> turn into *m*-ZrO<sub>2</sub>. At the same time, γ-Al<sub>2</sub>O<sub>3</sub> of this catalyst partially convert into the low activity of α-Al<sub>2</sub>O<sub>3</sub>, which makes specific surface area of the catalyst sharply declines to 17.0 m<sup>2</sup>.g<sup>-1</sup> after calcined at 1000 °C, the thermal stability and activity of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> decrease significantly.

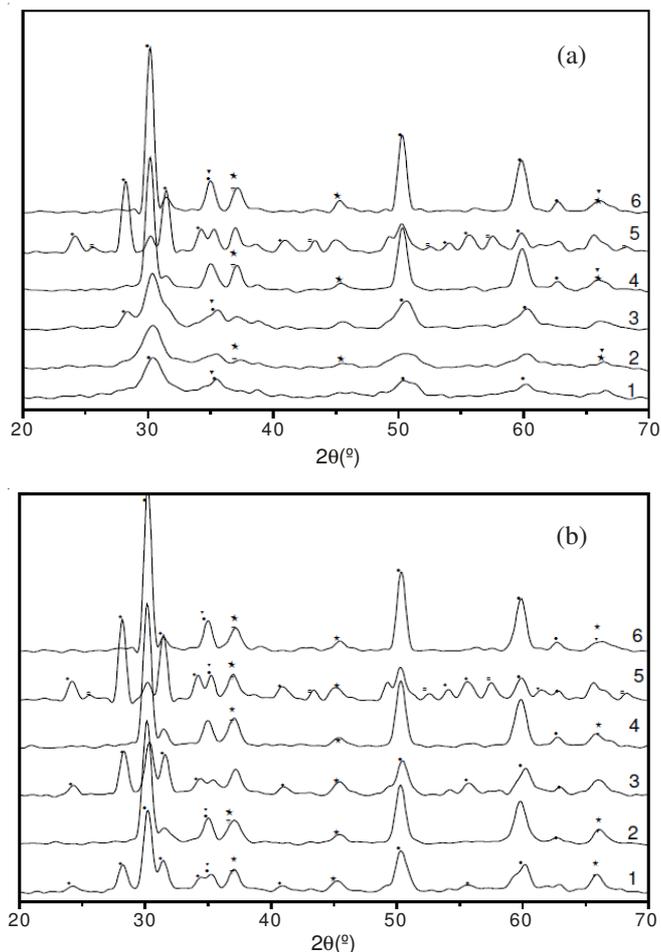


Fig. 4. XRD patterns of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub>, CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts (a) fresh catalysts, (b) old catalysts; 1,3,5: CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; 2,4,6: CuO/YSZ-Al<sub>2</sub>O<sub>3</sub>; 1 and 2: 600 °C; 3 and 4: 800 °C; 5 and 6: 1000 °C ●: *t,c*-ZrO<sub>2</sub>, ▼: CuO; ▽: CuAl<sub>2</sub>O<sub>4</sub> and Cu<sub>2</sub>O, ◆: *m*-ZrO<sub>2</sub>, ★: γ-Al<sub>2</sub>O<sub>3</sub>, □: α-Al<sub>2</sub>O<sub>3</sub>

## Conclusion

The M (= Y, Cr, Mg and Ce) modified CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst show high catalytic activity and thermal stability under

reaction temperature. The CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts modified by Cr and Mg show the best methane combustion activity and better thermal stability and the catalyst structure has greatly changed after the second evaluation, which demonstrates that Cr and Mg are not suitable for modification of ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support. The CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst modified by Y shows the best thermal stability and excellent methane combustion activity. The results of BET and XRD analysis show that Y<sub>2</sub>O<sub>3</sub> has a significant stabilizing effect on high temperature phase of ZrO<sub>2</sub> and high activity of γ-Al<sub>2</sub>O<sub>3</sub>, because there are complex interactions between the different proportions of Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which need to be further explored.

With increasing in calcination temperature, performance of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> is superior to that of CuO/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> calcined at 800 °C is an excellent catalyst which have the best methane combustion catalytic activity and thermal stability. With increasing calcine temperature, thermal stability of CuO/YSZ-Al<sub>2</sub>O<sub>3</sub> catalyst rises gradually, but its activity declines clearly, which may be related to Y added is too little to can sufficiently stabilize high temperature phase of ZrO<sub>2</sub> and high activity γ-Al<sub>2</sub>O<sub>3</sub>.

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