Catalytic combustion of methane over cobalt–magnesium oxide solid solution catalysts

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A series of cobalt–magnesium oxide solid solution catalysts (CoMgO) have been prepared using urea combustion methods, and characterised by X-ray diffraction (XRD) and laser Raman (LR). The catalytic activities for methane combustion have been tested in a continuous-flow microreactor. The Co content has a significant effect on the activity of the cobalt–magnesium oxide solid solution catalysts. The catalysts containing 5 and 10% Co have the lowest light-off temperature in methane combustion. In the preparation of cobalt–magnesium oxide solid solution catalysts, higher urea to metal ratio favors the formation of the catalysts with smaller crystal particles and leads to a better catalytic performance for methane combustion. Addition of lanthanum nitrate to the solution of Co and Mg nitrate depressed the formation of the cobalt–magnesium oxide solid solution and decreased the activity of the catalysts for methane combustion. The cobalt–magnesium oxide solid solution catalysts are very stable when the calcination or reaction temperature is no more than 900 °C. However, the catalytic activity decreases rapidly after high temperature (>1000 °C) calcination, possibly due to sintering of the catalyst and thus decrease of the surface area.

KEY WORDS: cobalt–magnesium oxide solid solution catalyst; methane combustion; laser Raman; XRD

1. Introduction

The catalytic combustion of the methane and volatile compounds represents a family of new technology in air pollution prevention and improvements of energy efficiency. However, the combustion catalysts being extensively studied are mainly supported palladium and platinum, which are very expensive and prone to deactivation at high temperatures [1,2] or transition metal substituted hexaaluminate, which is difficult to prepare and less active at lower temperatures [3–5]. The perovskite-type oxide catalysts show a good catalytic performance in methane combustion [6–8]. However, the low surface area of the catalysts leads to less activity per unit mass catalyst. Recently, it has been reported that the Co/MgO or Co/ZrO_2 catalysts, which are prepared using conventional impregnation methods, exhibit good catalytic activity for the combustion of diesel soot [9,10] and for the combustion of methane [11,12]. It has been pointed out that the activity of these catalysts is directly related to the Co^{2+} sites on the surface of the catalysts. However, the effect of the catalyst preparation method on the Co^{2+} sites on the surface of the catalyst is still not clear. In this study, we have prepared a series of cobalt–magnesium oxide solid solution (CoMgO) catalysts using the urea combustion method [13], and tested their activity in methane combustion. The structures of the catalysts were probed using X-ray diffraction and laser Raman spectroscopy. The effect of the cobalt content and the amount of urea and the lanthanum content (used as a stabiliser) on the catalytic performance of the catalysts has been studied.

2. Experimental

The CoMgO oxide catalysts were prepared as solid solution method using $Co(NO_3)_2\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$. Urea was added to the Co and Mg salts at the desired ratio, and the mixture was stirred at room temperature for 1 h to afford a homogeneous red solution. This solution was then combusted at 650–850 °C for 10–30 min to obtain the CoMgO solid solution catalysts. The composition of the mixture for each catalyst and their marks are shown in table 1.

The activities of the catalysts were tested in a fixed-bed quartz reactor (i.d. 7 mm) containing 0.200 g of catalyst loaded into the middle of the tube, which was plugged with silica wool in the two ends. The gas flow rate was controlled by a Brooks mass flow meter (model 5850TR). Prior to reaction, the furnace temperature was increased to the target temperature in flowing air at a rate of 5 °C/min. A gaseous mixture of CH_4 (1 vol%) and air (99 vol%) was then continuously supplied at a space velocity of $40\,000\ h^{-1}$. The products were analyzed with an on-line gas chromatograph (HP 5880A) using a Porapak T column (20–100 mesh), equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

The X-ray diffraction (XRD) patterns of catalysts were recorded on an X-ray diffractometer (Philips PW1710) with Cu K_α X-ray operated at 40 kV and 30 mA. The samples

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Table 1
A series of cobalt–magnesium oxide solid solution catalysts.

Catalyst formula	Composition of catalyst (mol%)	Urea/metal (mole ratio)	Symbol of the catalyst	Surface area (m^2/g)
$Co_{0.05}Mg_{0.95}O$	$5Co(NO_3)_2 + 95Mg(NO_3)_2$	5	CoMgO-1	42.5
$Co_{0.1}Mg_{0.9}O$	$10Co(NO_3)_2 + 90Mg(NO_3)_2$	5	CoMgO-2	31.2
$Co_{0.15}Mg_{0.85}O$	$15Co(NO_3)_2 + 85Mg(NO_3)_2$	5	CoMgO-3	27.4
$Co_{0.2}Mg_{0.8}O$	$20Co(NO_3)_2 + 80Mg(NO_3)_2$	5	CoMgO-4	21.8
$Co_{0.05}Mg_{0.95}O$	$5Co(NO_3)_2 + 95Mg(NO_3)_2$	4	CoMgO-5	38.6
$Co_{0.05}Mg_{0.95}O$	$5Co(NO_3)_2 + 95Mg(NO_3)_2$	3	CoMgO-6	32.2
$Co_{0.05}Mg_{0.95}O$	$5Co(NO_3)_2 + 95Mg(NO_3)_2$	2	CoMgO-7	33.4
$Co_{0.1}La_{0.1}Mg_{0.8}O_{1.05}$	$10Co(NO_3)_2 + 10La(NO_3)_2 + 80Mg(NO_3)_2$	5	CoLaMgO-1	24.8
$Co_{0.1}La_{0.2}Mg_{0.7}O_{1.1}$	$10Co(NO_3)_2 + 20La(NO_3)_2 + 70Mg(NO_3)_2$	5	CoLaMgO-2	19.1
$Co_{0.1}La_{0.3}Mg_{0.6}O_{1.15}$	$10Co(NO_3)_2 + 30La(NO_3)_2 + 60Mg(NO_3)_2$	5	CoLaMgO-3	14.7
$Co_{0.1}La_{0.4}Mg_{0.5}O_{1.2}$	$10Co(NO_3)_2 + 40La(NO_3)_2 + 50Mg(NO_3)_2$	5	CoLaMgO-4	9.2
$Co_{0.20}Mg_{0.80}O$	CoMgO-4 calcined at 1000 °C for 4 h	5	CoMgO-8	3.8

were mounted on an aluminum plate with a groove cut into it. The Raman spectra were recorded with a resolution of 2 cm^{-1} using a Yvon Jobin Labram spectrometer, using a 514.5 nm Ar^+ laser, run in a back scattered confocal arrangement. The scanning range was 90–3000 cm^{-1}. The specific surface area of the catalysts was measured using an ASAP 2010 (Micromeritics Instrument Corporation) using N_2 adsorption method.

3. Results and discussion

3.1. Catalytic combustion of methane over cobalt–magnesium solid solution catalyst with different cobalt contents

Figure 1 shows the results of the catalytic combustion of methane over the cobalt–magnesium oxide solid solution catalysts with different cobalt contents. The performance of the catalysts for methane combustion varies depending on cobalt content. The catalysts with 5 and 10% Co show the best activity for methane combustion among the tested catalysts. The temperatures of the catalysts at 10% methane conversion are 435 and 433 °C, respectively. Increasing Co content to 15 and 20% raises the light-off temperatures of the catalysts to 465 °C. Note, the light-off temperatures of all cobalt–magnesium oxide solid solution catalysts are lower than that for MgO, which is 595 °C, suggesting that the Co component plays an important role in cobalt–magnesium solid solution catalysts for methane combustion.

The XRD patterns of the cobalt–magnesium oxide solid solution catalysts are shown in figure 2. The diffraction peaks at 38.5°, 44.2° and 65.1° are due to the aluminum holder and are labeled with Al in all the figures. For all the catalysts the peaks at 38°, 43° and 62.5° are assigned to the diffraction of MgO. No diffraction peaks due to Co_3O_4 were seen in the cobalt–magnesium oxide solid solution catalysts regardless of the cobalt content. This indicates that the cobalt enters the lattice of MgO forming a uniform solid solution. Hence it is inferred that Co is present in the form of Co^{2+} in these catalysts. The highly dispersed Co^{2+} in the lattice of MgO either forms the active site for methane combustion, or the presence of Co^{2+} in the MgO lattice has synergic effect on the combustion of methane, thus decreasing methane light-off temperatures significantly in the reaction. The XRD patterns of the catalysts after the methane combustion activity test up to 800 °C are the same as those before reaction, suggesting that all the catalysts are stable and undergo no structural change during the activity test. The diffraction peaks become sharper with increasing Co content in the solid solution catalysts, suggesting the particle size of the catalysts become larger, which is confirmed by a decrease in surface area, table 1. Because the catalyst activity depends on the number of active sites, higher dispersion of the catalyst leads to more active sites, hence, the catalytic activity of the catalyst decreases as the cobalt content increases due to a decrease in surface area.

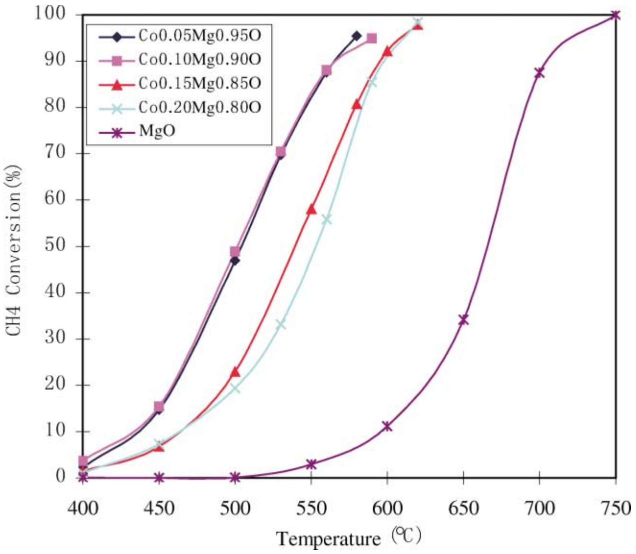

Figure 1. Activity test of the CoMgO catalysts with different Co content.

The laser Raman spectra of the cobalt–magnesium solid solution catalysts are shown in figure 3. The partial replacement of Mg with Co in the lattice of MgO and pure MgO are not Raman active and thus show no Raman peaks. However, in the CoMgO oxide solid solution catalysts, two broad

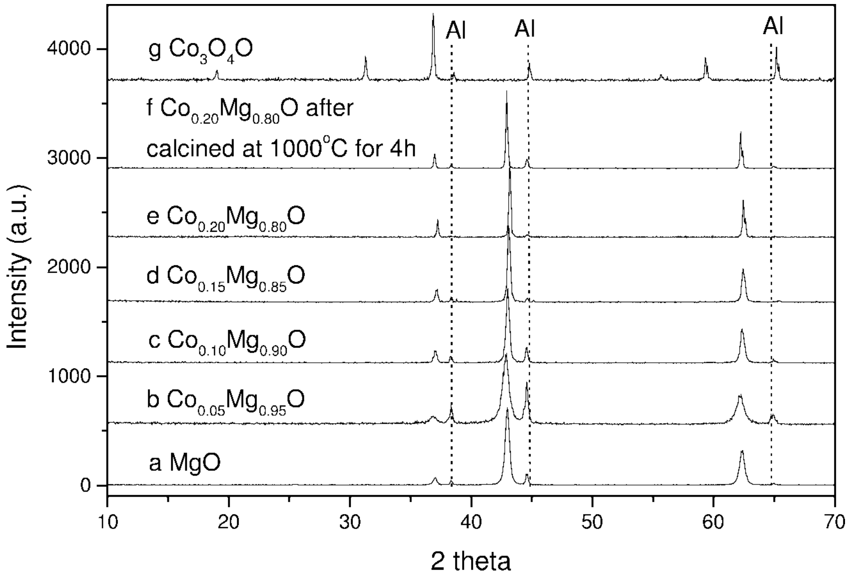

Figure 2. XRD patterns of CoMgO catalysts with different Co content.

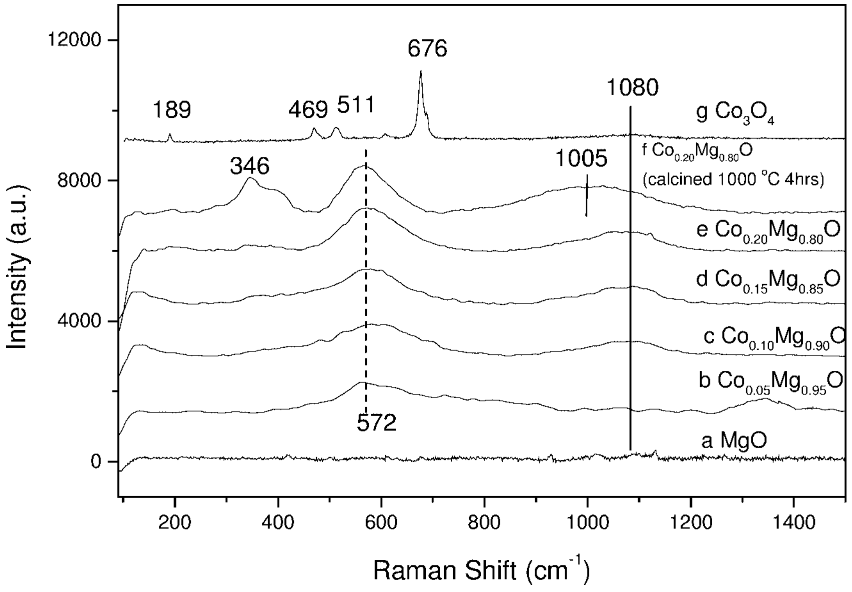

Figure 3. Raman spectra of CoMgO catalysts with different Co content.

Raman peaks at 572 and 1080 cm^{-1} were observed, which increase in intensity with the increase of %Co. These bands are believed to be from the Raman scatter of Co_3O_4 [11]. Although crystalline Co_3O_4 has a spinel structure and is constituted of isolated tetrahedra and interlinked octahedra [14], five Raman active modes (A_{1g}, E_g, $3F_{2g}$) have been identified [15] at 691, 488, 618, 522, and 194 cm^{-1} for a Co_3O_4 single crystal and have been measured at 676, 469, 607, 511, and 189 cm^{-1}, respectively, in Co_3O_4 powder (figure 3). The reason for the Raman spectra of the CoMgO oxide solid solutions being different from that of spinel Co_3O_4 lies in the strong interaction the Co_3O_4 with the support. The broad band at 572 cm^{-1} can be assigned to Co–O stretching mode.

3.2. Effect of urea to metal ratio on the performance of cobalt–magnesium solid solution catalyst

Figure 4 shows the results of the catalytic combustion of methane over the cobalt–magnesium oxide solid solution catalysts containing 5% Co prepared using different urea to metal ratios. For CoMgO-1 (table 1), CoMgO-5, CoMgO-6 and CoMgO-7 catalysts, the temperatures at 10% CH_4 conversion are 440, 451, 445, and 462 °C, respectively, and these at 50% CH_4 conversion are 505, 518, 530, and 560 °C, respectively. The temperatures for complete methane combustion (CH_4 conversion $>90\%$) are 562, 580, 645, and 652 °C, respectively. CoMgO-1 has the highest activity for methane combustion, and the catalytic activity for methane combustion increases with increasing urea to metal ratios.

The XRD patterns of the catalysts with different urea to metal ratios are given in figure 5. The diffraction peaks of all catalysts are similar to that of MgO regardless of the urea to metal ratios and no separated cobalt oxide phases were detected. This indicates that Co^{2+} replaces Mg^{2+} and occupies the lattice positions. The peak width is increasing with the increase of urea to metal ratio, suggesting that the higher ratio of urea to Co and Mg in the preparation of solid solution catalysts leads to finer particles of the catalyst; this is confirmed by the increase in surface area, table 1. The catalytic performance for methane combustion is thus improved. Comparison of the diffraction peak positions of the CoMgO catalysts with MgO shows that the diffraction peaks gradually shift to lower diffraction angles with the increase of urea to metal ratios, suggesting that the cell size of the CoMgO catalysts increase. This can be explained by the incorporation of more Co^{2+} in the lattice of MgO. The shift becomes more with the increase of urea to metal ratio, suggesting that more Co occupy the lattice of MgO.

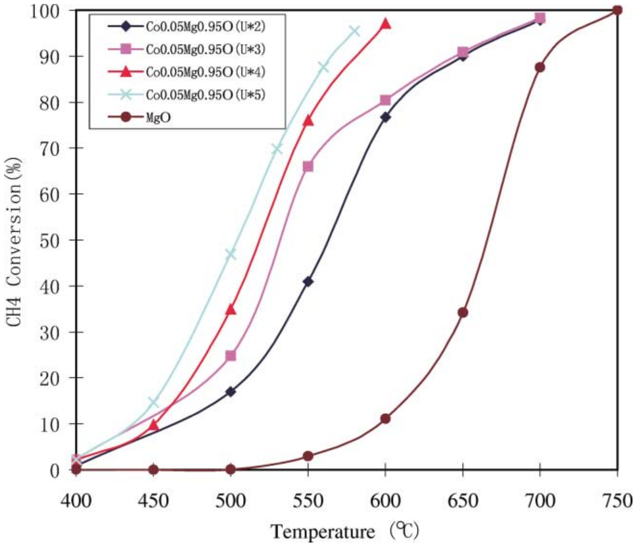

Figure 4. Activity test of CoMgO catalysts prepared using different urea to metal ratios.

Figure 6 shows the laser Raman spectra of the catalysts prepared with different urea to metal ratios. The Raman band at 572 cm^{-1} in the CoMgO catalyst was present, which was attributed to highly dispersed Co_3O_4. The peak intensity decreases with the increase of urea to metal ratio, suggesting that less Co_3O_4 is present on the surface of the CoMgO. This is in agreement with the XRD measurements in figure 5. As shown in figure 4, the activity of the CoMgO increases with the urea to metal ratio, and CoMgO-1 has the highest activity for methane combustion, which can be explained by the more inclusion of Co^{2+} in the MgO lattice forming more active centres.

Surface area measurements show that the CoMgO-1, prepared using the urea to metal ratio at 5, has the highest surface area, *ca.* 42.5 m^2/g. The CoMgO-5, -6 and -7, prepared with urea to metal ratios of 4, 3, and 2, have surface areas of 38.6, 32.2 and 33.4 m^2/g, respectively. This shows that higher urea to metal ratio in the oxide solid solution catalyst preparation leads to increase in the catalyst surface area. This may contribute to the higher activity of CoMgO catalyst prepared with increasing more urea to metal ratio. However, the difference in surface area among the catalysts is only small, and therefore entirely, in this case to be the minor factor controlling activity of the catalysts.

3.3. Effect of lanthanum contents on the catalytic performance of the cobalt–magnesium solid solution catalyst

Rare earth oxides are often thought to be stabilisers for the high temperature combustion of methane, improving the stability of the supports. In this work, we introduced lanthanum to CoMgO oxide solid solutions by combusting a mixture of lanthanum nitrate, cobalt nitrate, mag-

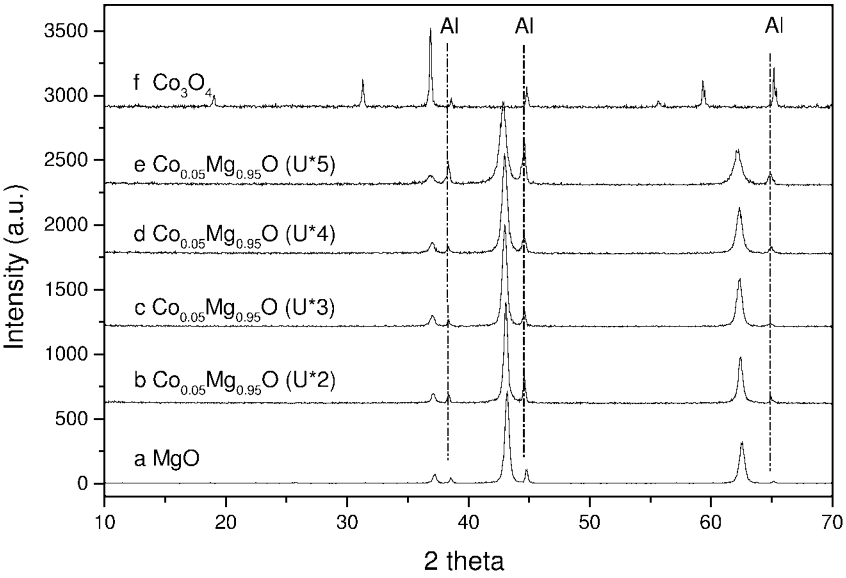

Figure 5. XRD patterns of CoMgO catalysts prepared using different urea to metal ratios. (Al refers to peaks from the aluminum sample holder.)

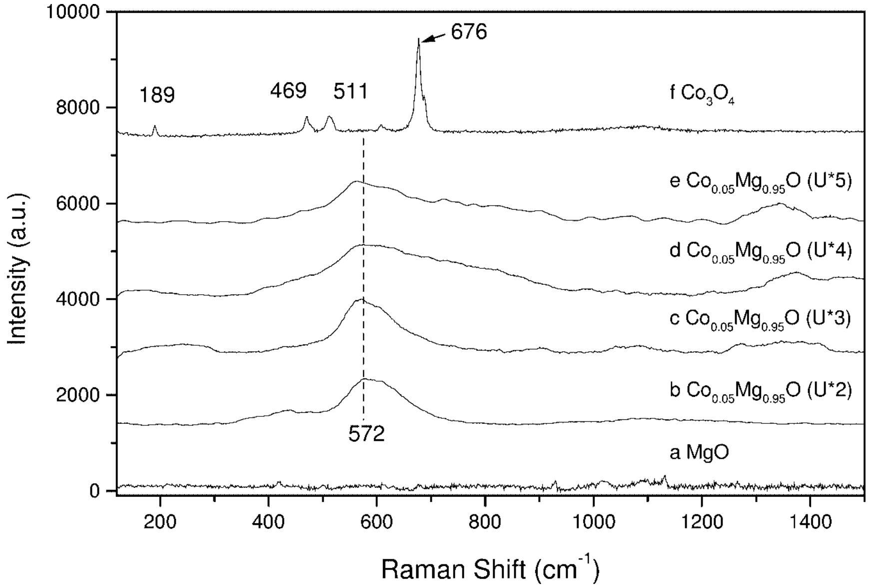

Figure 6. Raman spectra of CoMgO catalysts prepared using different urea to metal ratios.

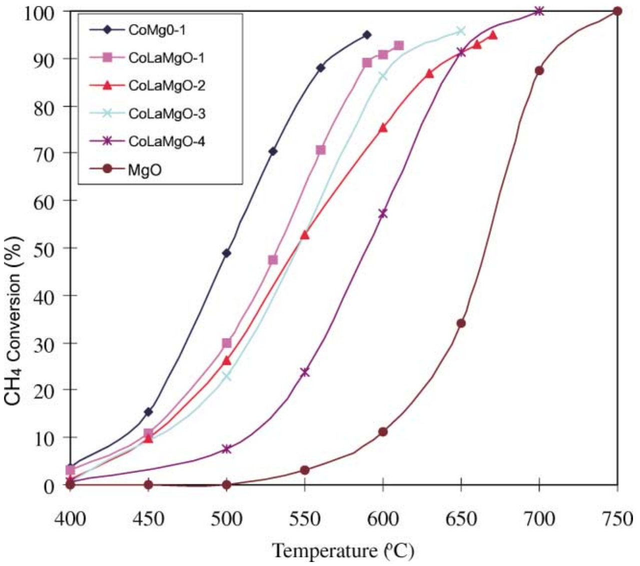

Figure 7. Catalytic activity of CoMgO catalysts containing different amount of lanthanum.

nesium nitrate, and urea. The activities of the resultant cobalt–magnesium solid solution catalysts with different lanthanum contents are shown in figure 7. The temperatures for CH_4 conversion to CO_2 become higher with increasing lanthanum content in the catalysts. The CoLaMgO-4 catalyst has the highest light-off temperature for CH_4 conversion. Only 10% CH_4 is converted at 510 °C and 50% CH_4 is converted at 570 °C. Complete combustion of CH_4 occurs at 630 °C, which is 80 °C higher than for CoMgO-2 containing no lanthanum. This indicates that the addition of lanthanum to the cobalt–magnesium oxide solid solution catalysts does not improve the catalytic activity. In contrast, it decreases the catalytic activity as the lanthanum content increases in the catalysts.

The XRD patterns of the cobalt–magnesium solid solution catalysts containing different amounts of lanthanum are given in figure 8. The diffraction pattern of $Co_{0.1}Mg_{0.9}O$ is the same as that of MgO, suggesting they have the same structure. In the XRD pattern of CoLaMgO-1, two broad peaks at 23.3 and 33.3° are observed, attributed to the diffraction of $LaCoO_3$ [16], while the peaks corresponding to CoMgO oxide solid solution decrease in intensity. This suggests that addition of lanthanum in the catalyst preparation depresses the oxide solid solution formation, and that lanthanum is present in a separated phase of $LaCoO_3$. In the XRD patterns of CoLaMgO-2, -3 and -4 catalysts, diffraction peaks of $LaCoO_3$ did not increase linearly with the increase of lanthanum in the samples, but new peaks at 26.4°, 29.1° and 30.2° appear, with the strongest peak at 30.2°. These peaks are due to the diffraction of a La_2O_3 phase [17]. The amount of La_2O_3 increases with lanthanum content in the catalyst, suggesting that lanthanum does not enter the lattice of MgO. When the lanthanum amount is continuously increased in the catalyst, a separated phase of La_2O_3 can be identified. The surface area of the CoLaMgO series catalysts was also found to decrease from 19.1 to 9.2 m^2/g with the increase of lanthanum content in the catalysts. The presence of $LaCoO_3$ and La_2O_3 in the catalysts may cover the active sites or even remove Co to form $LaCoO_3$ and thus decreasing the catalysts activity.

Figure 9 shows the laser Raman spectra of the catalysts with different lanthanum contents. The two bands at 572 and 1080 cm^{-1} due to surface Co_3O_4 on MgO or CoMgO oxide solid solutions were identified in CoLaMgO-1, but show lower intensity and are more broad than in CoMgO-2, suggesting that less Co_3O_4 is present on the surface of CoLaMgO-1. However, a strong band at 388 cm^{-1} appears in the Raman spectra of the CoLaMgO-1 catalyst, which is due to the presence of La_2O_3 [18]. With in-

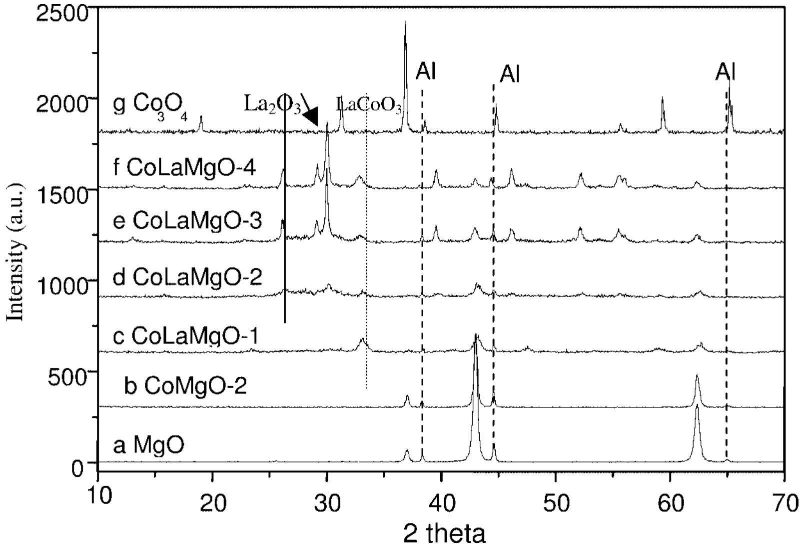

Figure 8. XRD pattern of CoMgO catalysts containing different amount of lanthanum. (Al refers to the peaks from aluminum sample holder.)

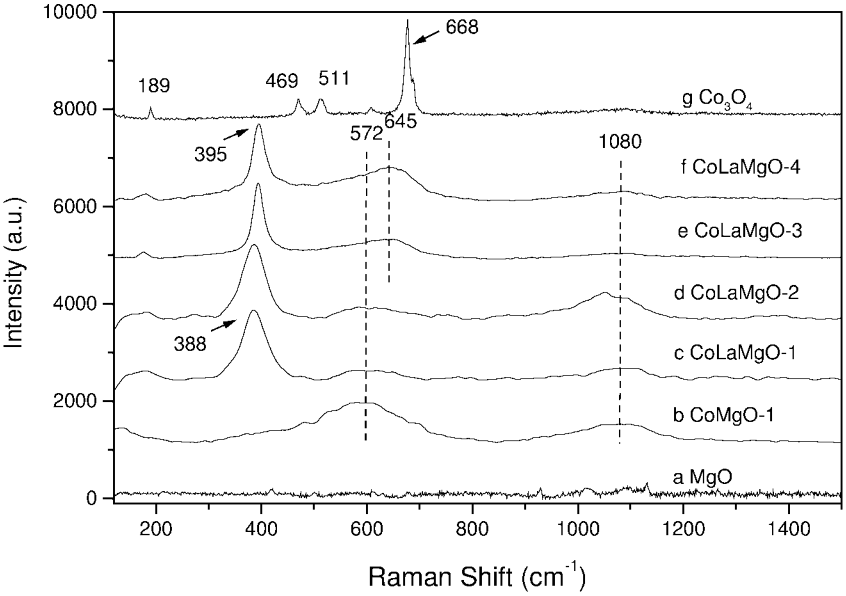

Figure 9. Raman spectra of CoMgO catalysts containing different amount of lanthanum.

creasing lanthanum content, the band at 388 cm^{-1} shifts to 395 cm^{-1} and becomes sharper indicating that more La_2O_3 is present on the catalyst surface. This further supports the XRD and surface area measurements, revealing that the surface of the catalyst is covered with La_2O_3 particles.

3.4. Stability of the cobalt–magnesium oxide solid solution catalyst

We have shown that the cobalt–magnesium oxide solid solution catalyst is very active for methane combustion. However, in practical applications such as engines, the reaction temperature is often up to 1000 °C and a high stability of the catalyst under such conditions is required. Hence in our experiment, the catalyst CoMgO-4 (20% Co content) was calcined at 1000 °C for 4 h, and the activity of the calcined catalyst tested for methane combustion. The results are shown in figure 10. Over this catalyst, the methane started to combust to CO_2 at 660 °C and complete methane conversion occurs at 745 °C. This is almost identical to the gas phase reaction without catalyst. Thus it is inferred that the high temperature calcination causes a dramatic loss in the catalytic activity.

XRD measurement of the calcined cobalt–magnesium solid solution catalyst (figure 2(f)) shows that the diffraction pattern of the high temperature calcined catalyst is similar to that of the uncalcined sample. No diffraction peaks due to Co_3O_4 or other separate phases were detected. This indicates that the bulk structure of the cobalt–magnesium solid

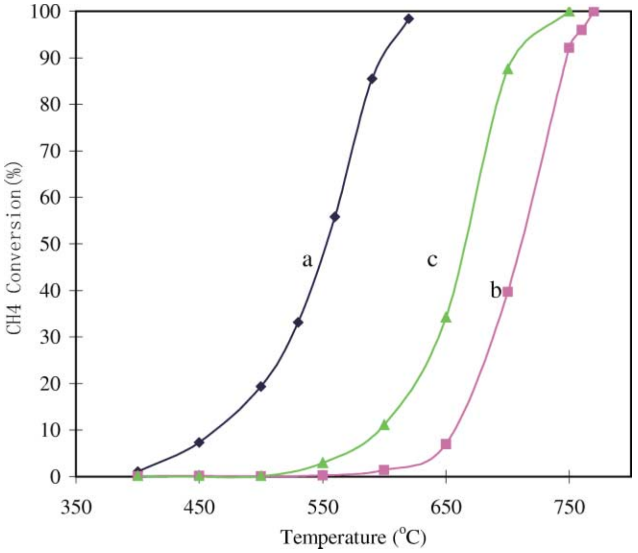

Figure 10. Activity test of CoMgO catalysts for methane combustion: (a) $Co_{0.20}Mg_{0.80}O$, (b) $Co_{0.20}Mg_{0.80}O$ after being calcined at 1000 °C for 4 h, and (c) MgO.

solution catalysts remains stable after exposure to high temperatures.

Laser Raman spectra of the calcined cobalt–magnesium solid solution catalyst (figure 3(f)) shows two strong bands at 346 and 572 cm^{-1} and a broad and weak band at 1005 cm^{-1}, which are tentatively assigned to Co_2O_3 on the catalyst surface. The Co_2O_3 is not an active component for methane combustion but it covers the catalyst centres, so the catalyst activity is lowered after the high temperature calcination. Table 1 shows that after the high temperature calcination, the surface area of the catalyst decreases from 21.8 to 3.8 m^2/g. The dramatic decrease of the catalyst surface area is believed to be the main reason for the catalyst deactivation.

4. Conclusions

Cobalt–magnesium oxide solid solution catalysts have been prepared using the urea combustion method. The active sites of the catalysts for methane combustion are Co^{2+} ions substituted into MgO lattice. With increasing Co content, the catalyst particles become larger, and the surface area of the catalyst decreases and thus causes a drop in catalytic activity. In the preparation of the cobalt–magnesium oxide solid solution catalysts, increasing the urea to metal ratio affords smaller catalyst particles, and increases the surface area of the catalyst, thus promoting the catalyst performance for methane combustion. Addition of lanthanum nitrate to the solution of Co and Mg nitrate during catalyst preparation suppresses the formation of the cobalt–magnesium oxide solid solution and decreases the activity of the catalysts for methane combustion. Lanthanum is present in the form of La_2O_3 and $LaCoO_3$ in the catalysts, which are believed to cover the active centres of the catalysts. Similarly, the cobalt–magnesium oxide solid solution catalyst is deactivated for methane combustion after high temperature (>1000 °C) calcination, due to a dramatic decrease in surface area and the change of the surface structure.

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