

Methane combustion over supported cobalt catalysts

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Abstract

A series of cobalt-based catalysts with different supports have been prepared using impregnation method, and characterised by X-ray diffraction (XRD), laser Raman (LR), and infrared spectroscopy (IR). The catalytic activities for methane combustion were assessed in a micro-reactor. The ZrO₂ and Al₂O₃ supports are themselves active in methane combustion, and ZrO₂ supported cobalt catalyst was found to have the highest activity amongst the TiO₂, Al₂O₃, MgO supported catalysts and bulk Co₃O₄. The Co content has a marked effect on the activity of the ZrO₂ supported catalyst with 1.0 and 15 wt.% of Co having the lowest light-off temperature in methane combustion. In the MgO supported catalyst, Co oxide was highly dispersed over the MgO support surface or enters the lattice of MgO to form a solid solution, whose activity for methane combustion is reasonable. The zirconia supported cobalt catalysts are very active and stable when calcination or reaction temperature is no more than 900°C. Calcining the catalysts at temperatures above 900°C for more than 1 h decreases the catalyst activity. The deactivation of the catalyst probably results from the decrease of the surface area. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Supported cobalt catalyst; Methane combustion; Laser Raman

1. Introduction

Methane is the predominant component of natural gas. The catalytic combustion of methane plays an important role in energy supply using natural gas for industrial as well as domestic applications. The significant advantages of catalytic combustion are the more efficient use of energy sources and minimum pollutant emission as compared to conventional flame combustion [1–3]. However, the combustion catalysts being extensively studied consist of mainly supported palladium and platinum, which are very expensive and

prone to deactivation at high temperatures [4–6] or transition metal-substituted hexaaluminate, which is difficult to prepare [7] and less active at lower temperatures [8–10]. Similarly, there are reports of methane combustion using perovskite-type (ABO₃ structure) oxides [11–13]. However, their low surface area leads to relatively low activity per unit mass of catalyst.

It has been shown that Co₃O₄ is a very active component for methane oxidation [14] and that cobalt-containing catalysts show a good catalytic performance for the combustion of diesel soot [15,16] and for the combustion of methane [17]. However, the effect of supports and the cobalt content on the catalytic activity is still not clear, and little is known on the active centre of the catalyst. In this study, we prepared a series of cobalt-based catalysts supported

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on different metal oxides, and their performance in methane combustion was evaluated using a continuous flow reactor. The supported catalysts were characterised using X-ray diffraction (XRD), laser Raman (LR) and FTIR spectroscopy. The effect of the cobalt content and type of support on the activity of the catalysts was studied.

2. Experimental

The supports used for the catalysts were ZrO₂ (Norton chemical process products, BET surface area: 51 m²/g; pore volume: 0.30 cm³/g; 250–355 μm), MgO (Aldrich Chemical Company, Inc., BET surface area: 22.4 m²/g), TiO₂ (Norton chemical process products, BET surface area: 150 m²/g; pore volume: 0.35 cm³/g; 250–355 μm), and Al₂O₃ (high purity; 250–355 μm; BET surface area: 148.7 m²/g). The powders of TiO₂ and MgO were pressed into pellets and sieved into 250–355 μm particles before supporting the cobalt oxide. The cobalt-based catalysts were prepared by the impregnation method using cobalt nitrate solution. After impregnation the solid was dried at 100°C overnight, followed by calcination in air at 600°C for 4 h. ICP-MS analysis results show that cobalt contents in the zirconia supported catalyst are 0.98, 2.7, 5.45, 9.5 and 13.2 wt.%, respectively for the those denoted as 1.0, 2.8, 5.6, 10, 15 wt.% Co/ZrO₂.

The activity of the catalysts were tested in a fixed bed quartz reactor (i.d. 7 mm), 0.20 g of catalyst was placed in the middle of the tube and plugged with quartz wool in the two ends. The gas flow rate was controlled by a Brooks mass flow meter (Model 5850TR). Before reaction, the furnace temperature was increased to the target temperature in flowing air at a rate of 5°C/min. A thermocouple was fixed to the middle of the catalyst bed to measure the reaction temperature and to control the furnace temperature. A gaseous mixture of CH₄ (1 vol.%) and air (99 vol.%) was continuously supplied at a space velocity of 40,000 h⁻¹. The products were analysed with an on-line gas chromatograph (PE 5880A) using a Porapak T column (20–100 mesh), equipped with and a flame ionisation detector (FID) and thermal conductivity detector (TCD). The conversion of the methane refers to the yield of CO₂ from the combustion.

The surface areas of the catalyst samples were measured in a glass BET apparatus. The XRD pattern of catalysts was recorded on a X-ray diffractometer (Philips PW1710) with Cu Kα X-ray at 40 eV and 30 mA. The samples were mounted on an aluminum plate with a groove cut into it. The Raman spectra were recorded with a resolution of 2 cm⁻¹ in a Yvon Jobin Labram spectrometer, using a 514.5 nm Ar⁺ laser, run in a back scattered confocal arrangement. The scanning range was set from 90 to 3000 cm⁻¹. Infrared (IR) spectra of the catalyst samples were recorded with a Perkin-Elmer Paragon 1000 FTIR as KBr pellets containing ca. 1–2 wt.% of sample powder, using 16 scans at 4 cm⁻¹ resolution.

3. Results and discussion

3.1. Methane combustion over different supported cobalt catalysts

Fig. 1 shows the results of the catalytic combustion of methane over ZrO₂, MgO, TiO₂, and Al₂O₃ supports. It is interesting to see that there is a large difference in the catalytic performance of the supports for methane combustion. ZrO₂ and Al₂O₃ have the highest activity, over which the light-off temperature of methane combustion is only 500°C. The activity of ZrO₂ increases faster than Al₂O₃ with the temperature, and complete methane conversion to CO₂ occurs at 600°C for Al₂O₃, and 650°C for ZrO₂. This suggests that Al₂O₃ and ZrO₂ themselves are catalytically active for methane combustion. MgO and TiO₂ have a similar activity trend in methane combustion, over which methane starts to convert at 600°C, and the complete conversion of methane occurs at above 700°C. Methane combustion includes free radical and surface catalytic reactions, and is related to the oxygen mobility, acidity and thermal conductivity of the catalyst [18]. Among the four support materials, TiO₂ and MgO have higher oxygen mobility and conductivity, but their acidity is lower than that of Al₂O₃ and ZrO₂. Hence, it is inferred that the acidity of the oxide supports is the prevailing factor in influencing the catalyst performance.

The activity of the supported Co catalysts for methane combustion is shown in Fig. 2. Methane starts to be converted over the ZrO₂ supported cobalt

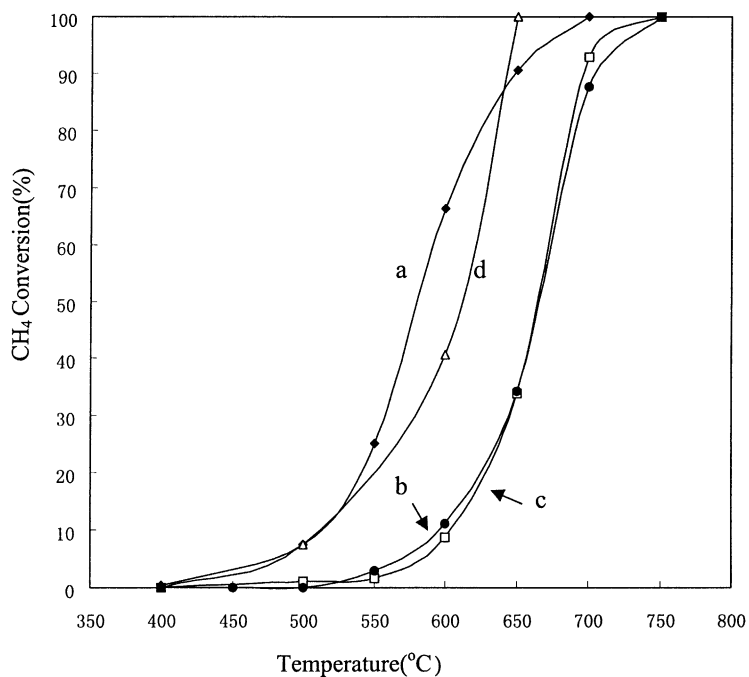


Fig. 1. Activity test for different supports in methane combustion: (a) ZrO₂; (b) MgO; (c) TiO₂; (d) Al₂O₃.

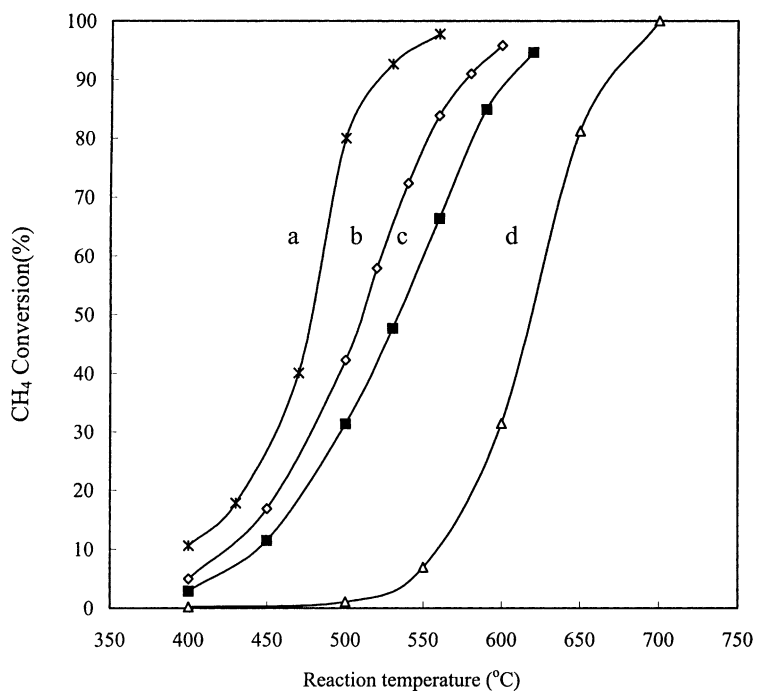


Fig. 2. Activity test for different supported Co catalysts in methane combustion: (a) 10% Co/ZrO₂; (b) 10% Co/MgO; (c) 10% Co/TiO₂; (d) 10% Co/Al₂O₃.

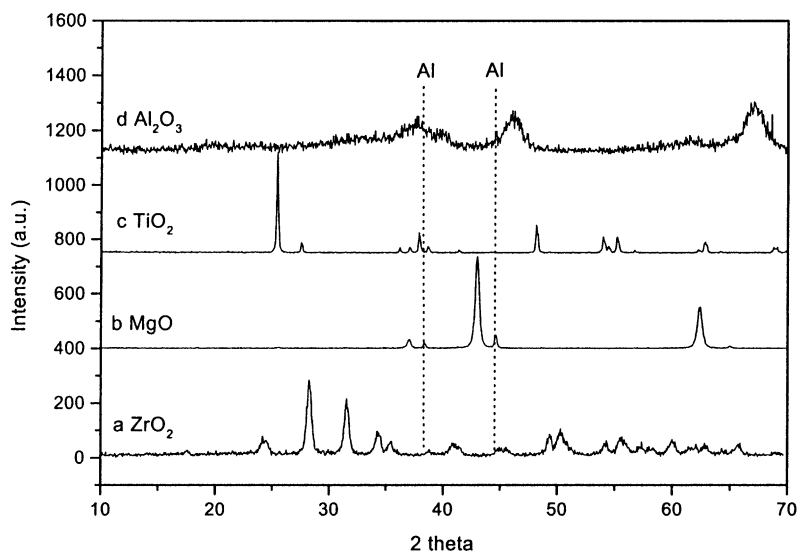


Fig. 3. XRD pattern of the different supports.

catalyst at 400°C, and completely converted to CO₂ at 520°C. This activity is equivalent to the supported noble metal catalysts reported in [19] under similar conditions. The MgO supported Co catalyst is not as active as the ZrO₂ supported materials, but the temperature for methane combustion is lower than that of TiO₂ supported catalyst. The Al₂O₃ supported Co catalyst has the lowest activity among the four supported catalysts, although it has a lower light-off temperature than the Al₂O₃ support itself. This confirms that cobalt oxide is an active component for methane combustion.

The XRD patterns of the supports and their supported cobalt catalysts are given in Figs. 3 and 4. Cobalt is present in the form of Co₃O₄ in the ZrO₂, TiO₂, and Al₂O₃ supported catalysts. However, in the alumina supported cobalt catalyst very strong diffraction peaks attributed to Co₃O₄ are present, suggesting that the Co₃O₄ particles are rather large in this catalyst, and the active component is poorly dispersed. This is probably the reason for the poor activity of alumina supported catalyst for methane combustion. The ZrO₂ and TiO₂ supported cobalt catalysts have a rather weak XRD pattern of Co₃O₄, and the main diffraction peaks were relatively unchanged. This indicates that Co₃O₄ is highly dispersed over the ZrO₂

and TiO₂ supports. Comparison of the XRD patterns of the TiO₂ support and its supported cobalt catalyst reveals that half height width of the TiO₂ supported cobalt catalyst becomes broad, and the absence of some weak diffraction peaks of TiO₂. This probably results from the encapsulation of Co₂O₃ particles in the bulk of TiO₂, and leads to the lattice strain. The diffraction pattern of the MgO supported cobalt catalyst is almost the same as that of MgO. There are two possible reasons for this. One is that the dispersion of cobalt oxide is too high to detect using XRD. Another is that cobalt enters the lattice of MgO, and replaces Mg to form a uniform solid solution. The highly dispersed Co oxide or the Co²⁺ in the lattice of MgO probably forms the active site for methane combustion. The XRD patterns of the catalyst post activity test up to 800°C are the same as those before reaction, suggesting that all the catalysts are stable during the reaction.

The LR spectra of the supports and their supported cobalt catalysts are shown in Figs. 5 and 6. Alumina itself is not Raman active, thus no Raman reflection signal was seen. After 10 wt.% Co is loaded, very strong Raman signals of Co₃O₄ appeared, suggesting that the alumina surface is covered with relatively large Co₃O₄ particles. This result is in agreement with

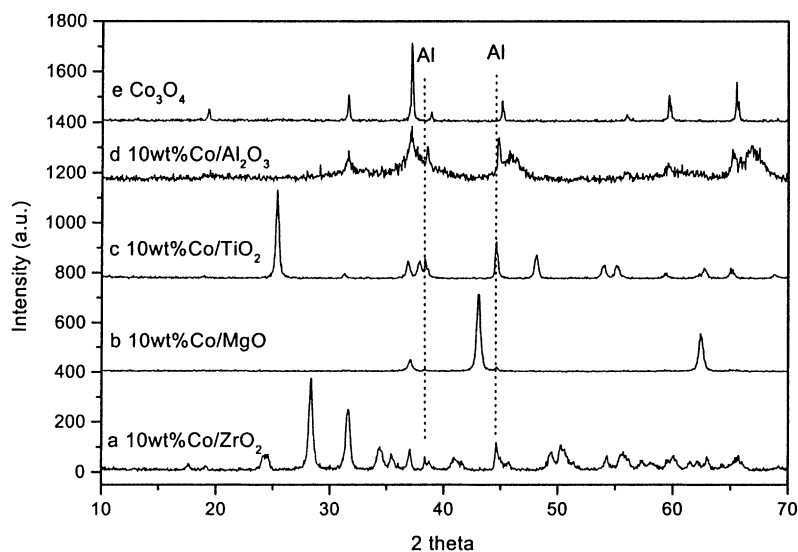


Fig. 4. XRD pattern of the different supported Co catalysts.

the XRD measurements. In the TiO₂ supported cobalt catalyst, the Raman spectrum of Co₃O₄ was not observed, and the Raman bands of TiO₂ became rather broad. However, the weak peak of Co₃O₄ was observed in XRD pattern of the Co/TiO₂ catalyst. This

suggests that Co₃O₄ is present in the bulk but not on the surface of the Co/TiO₂ catalyst, in agreement with the XRD results. Because no Co₃O₄ is present on the surface of Co/TiO₂ catalyst, the catalyst has a poor activity for methane combustion. The LR spec-

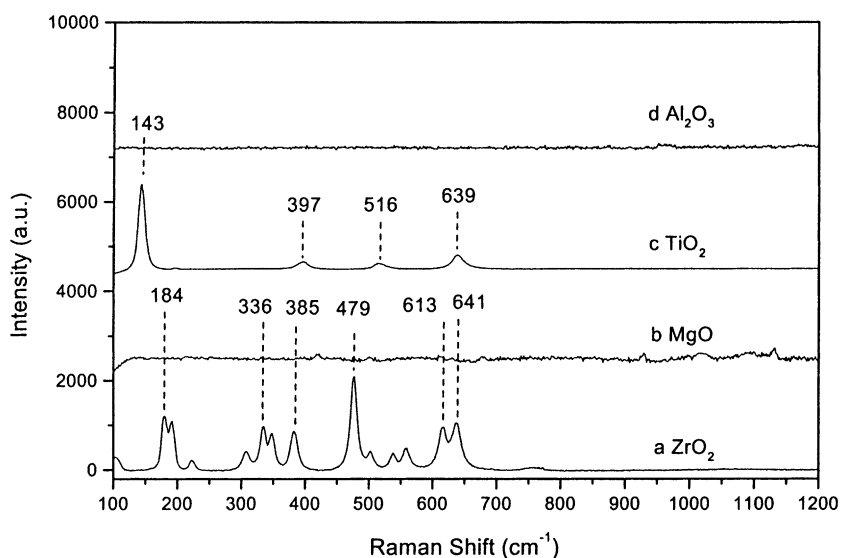


Fig. 5. LR spectra of the different supports.

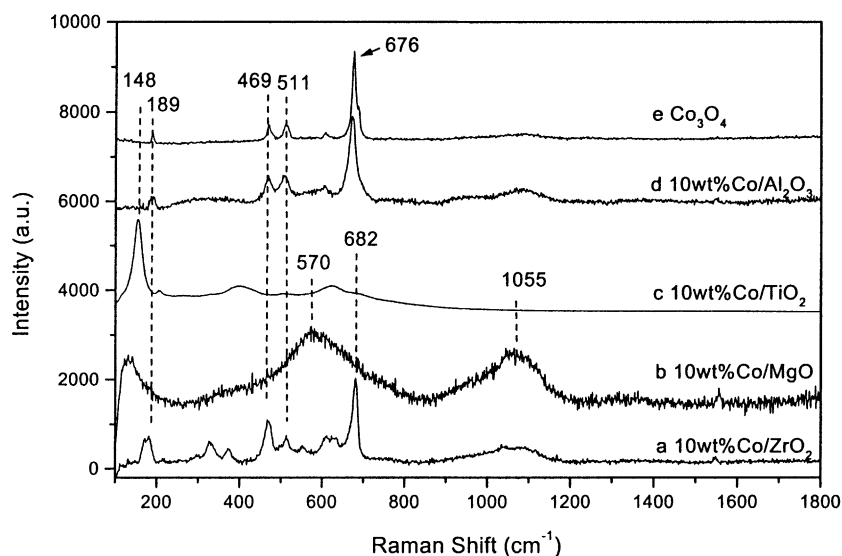


Fig. 6. LR spectra of the different supported Co catalysts.

trum of MgO supported cobalt is different from the Al_2O_3 and TiO_2 supported catalysts. Two broad bands at 570 and 1055 cm^{-1} appeared, which are probably caused by cobalt oxide particles over the supports, however, no Co_3O_4 particles are present in the catalyst surface. Therefore, it is believed that the active site of the MgO supported cobalt catalyst is not Co_3O_4 , but other forms of cobalt oxide. In the Raman spectrum of ZrO_2 supported cobalt catalyst, the bands of Co_3O_4 are clearly observed, and the spectrum of ZrO_2 is changed, all bands were broadened, and the intensity of the band at 479 cm^{-1} is weakened. The changes in the Raman spectrum of ZrO_2 in its supported cobalt catalyst are attributed to the strong interaction of cobalt and zirconia. The ZrO_2 and the highly dispersed Co_3O_4 may have a synergic effect, which leads to the high activity of the catalyst for methane combustion.

Figs. 7 and 8 show the FTIR spectra of the supports and their supported cobalt catalysts. Comparing the two figures, it is seen that the IR bands of the $\nu_{(\text{Co}-\text{O})}$ vibration of Co_3O_4 appear in ZrO_2 , TiO_2 , and Al_2O_3 supported cobalt catalysts. This suggests that cobalt is in oxide form in the catalysts. The IR $\nu_{(\text{Co}-\text{O})}$ of Co–O is not detected in the MgO supported cobalt catalyst. This is probably due to the strong absorption

of MgO or $\text{Mg}(\text{Co})\text{O}$ in the region of 500–800 cm^{-1} , which submerges the Co–O bands at 574 and 663 cm^{-1} .

3.2. Effect of cobalt content on the catalytic performance of ZrO_2 supported catalysts

As shown above, the ZrO_2 supported catalyst with 10 wt.% of cobalt shows the highest activity for methane combustion among the tested catalysts. Hence, in the following we prepared a series of supported cobalt catalysts with different cobalt content, and the effect on catalytic activity was studied. For the catalysts denoted as 1.0, 2.8, 5.6, 10, 15 wt.% Co/ ZrO_2 , the surface areas are 52.3, 51.2, 50.9, 48.5 and 47.0 m^2/g , respectively. This indicates that cobalt content has an effect on the surface area of the zirconia supported catalysts.

Fig. 9 shows the effect of cobalt content on the activity of the ZrO_2 supported catalysts for methane combustion. It is interesting to see that the light-off temperature of catalyst with 1.0 wt.% Co at 10% methane conversion is only 400°C, the same as the catalysts with 10 and 15 wt.% Co, and lower than the catalysts containing 2.8 and 5.6 wt.% Co. The temperature at 50% methane conversion was found to

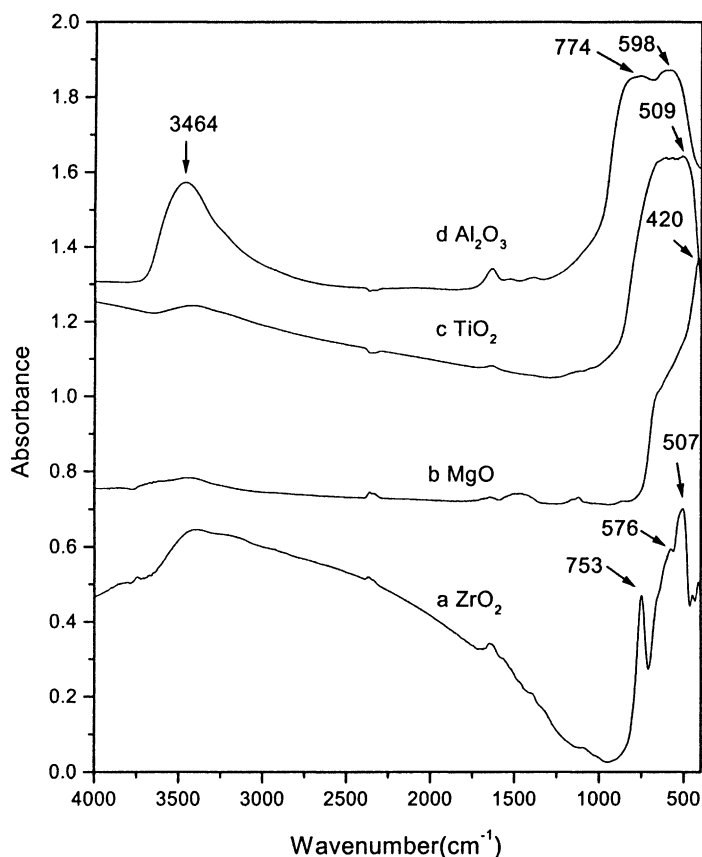


Fig. 7. FTIR spectra of the different supports.

be 460°C for 1.0 wt.% Co/ZrO₂, 470°C for 15 wt.% Co/ZrO₂, 475°C for 2.8 wt.% Co/ZrO₂, 480°C for 10 wt.% Co/ZrO₂ and 483°C for 5.6 wt.% Co/ZrO₂. Hence, the catalyst of 1.0 wt.% Co/ZrO₂ has the highest activity for methane combustion. This suggests that although Co₃O₄ is proved to be the active component for methane combustion, high content of Co₃O₄ can be detrimental for methane combustion. The synergism between Co₃O₄ and ZrO₂ may play a more important role in the catalytic process.

Bulk Co₃O₄ is not detected in the 1.0 wt.% Co/ZrO₂ catalyst (Fig. 10), revealing that cobalt oxide is highly dispersed in the support. This is probably the main reason for the high activity of the catalyst. In the XRD patterns of the catalysts containing 2.7, 5.45, 9.5 and 13.2 wt.% cobalt, the diffraction peaks of Co₃O₄

become more and more intense with increasing cobalt content.

The LR spectra of zirconia supported catalysts containing different amount of cobalt are shown in Fig. 11. The 1.0 wt.% Co/ZrO₂ has the bands of zirconia as well as weak bands attributed to Co₃O₄, suggesting that the surface of ZrO₂ is partly covered with Co₃O₄, although no bulk Co₃O₄ is detected by XRD. In the zirconia supported catalysts containing 2.6, 5.6, 10 and 15 wt.% Co, the Raman bands corresponding to ZrO₂ become weaker and those of Co₃O₄ become more intense. This suggests that more of zirconia surface is covered with Co₃O₄.

IR spectra of the zirconia supported cobalt catalysts are shown in Fig. 12. It is seen that zirconia has IR bands at 507 cm⁻¹ (strong), 574 cm⁻¹ (weak) and 753 cm⁻¹ (strong). In the supported cobalt catalyst,

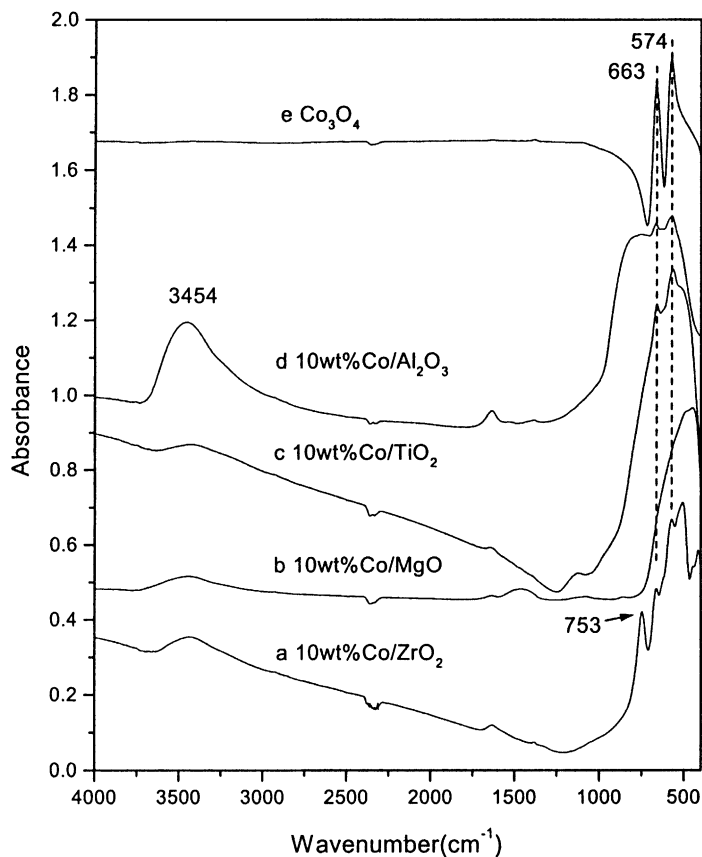


Fig. 8. FTIR spectra of the different supported Co catalysts.

no IR bands of cobalt oxide were observed when Co content is 1.0 wt.%. However, when the cobalt content is increased, the IR bands of Co_3O_4 become stronger, suggesting that more Co_3O_4 particle is present in the catalysts. This is in agreement with XRD results.

The results of XRD, LR, IR results and the activity test suggest that the active site for the low-content Co catalyst is the highly dispersed Co_3O_4 promoted by ZrO_2 , and the active site for the high-content Co are the bulk Co_3O_4 particles.

3.3. Effect of calcination temperature on the activity of the catalysts

During methane combustion in turbine engines, the reaction temperature often varies from 300 to 1000°C , therefore, the catalyst ability to resist the

high temperature is especially important. In this work, the $\text{CoO}_x/\text{ZrO}_2$ (Co content: 10 wt.%) was calcined at 1000°C for 4 h, and its activity tested for methane combustion at lower temperature. The results are shown in Fig. 13. Methane starts to react at 550°C , and is completely converted to CO_2 at 750°C . The background activity of methane combustion in the absence of catalyst under the same conditions was also determined, and found to have a similar temperature profile with Fig. 13c. The combustion reaction in the absence of catalyst is regarded as a free radical reaction. Hence, it is concluded that the methane combustion over the 1000°C calcined Co/ZrO_2 catalyst is due mainly to the uncatalyzed radical reaction. This suggests that the calcined catalyst has a very poor activity for methane combustion, and whose activity is much lower than the catalyst without high

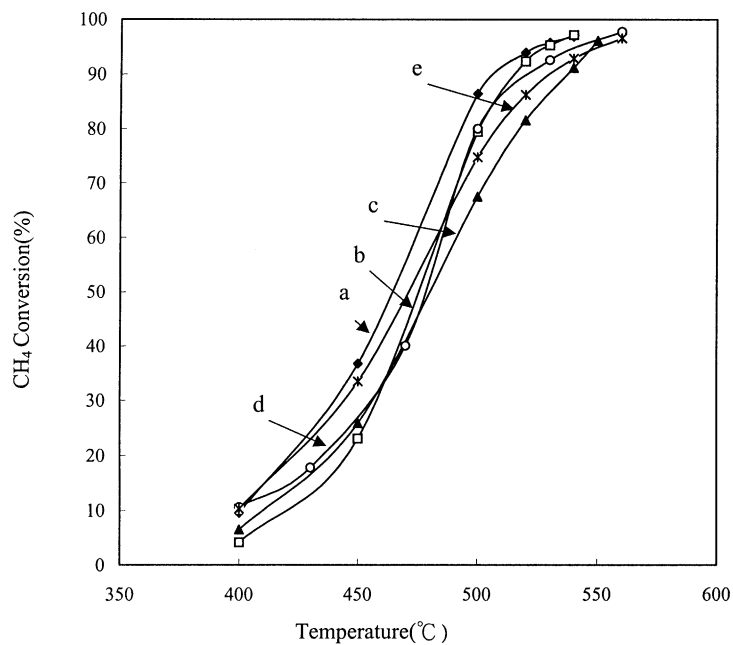


Fig. 9. Activity test for ZrO_2 supported Co catalysts for methane combustion: (a) 1.0 wt.% Co/ ZrO_2 ; (b) 2.8 wt.% Co/ ZrO_2 ; (c) 5.6 wt.% Co/ ZrO_2 ; (d) 10 wt.% Co/ ZrO_2 ; (e) 15 wt.% Co/ ZrO_2 .

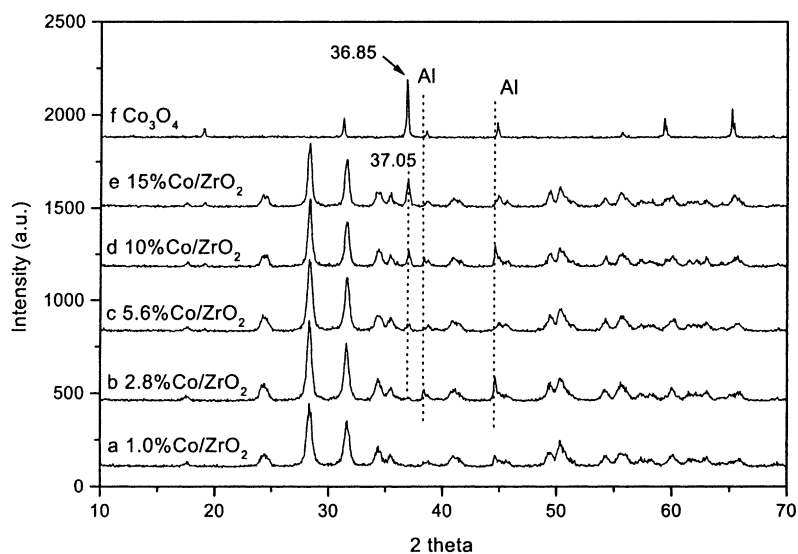


Fig. 10. XRD pattern of ZrO_2 supported Co catalysts with different Co content.

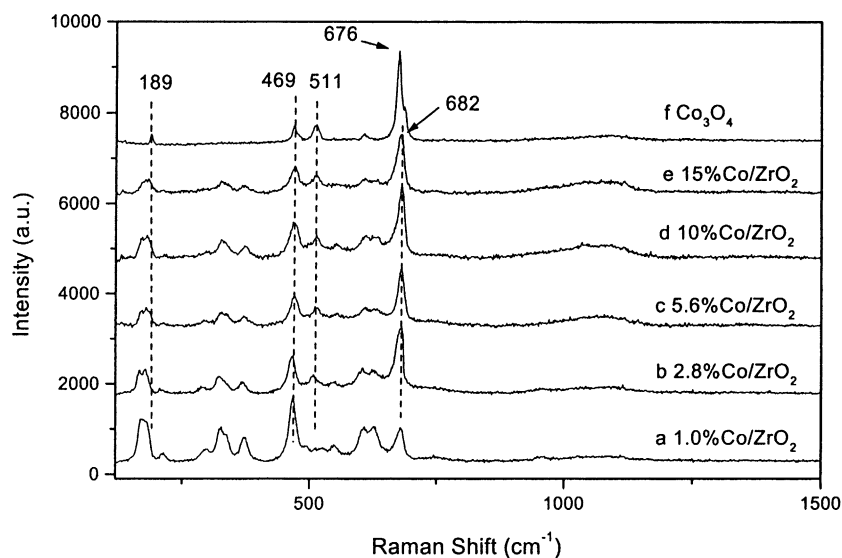


Fig. 11. LR spectra of ZrO_2 supported Co catalysts with different Co content.

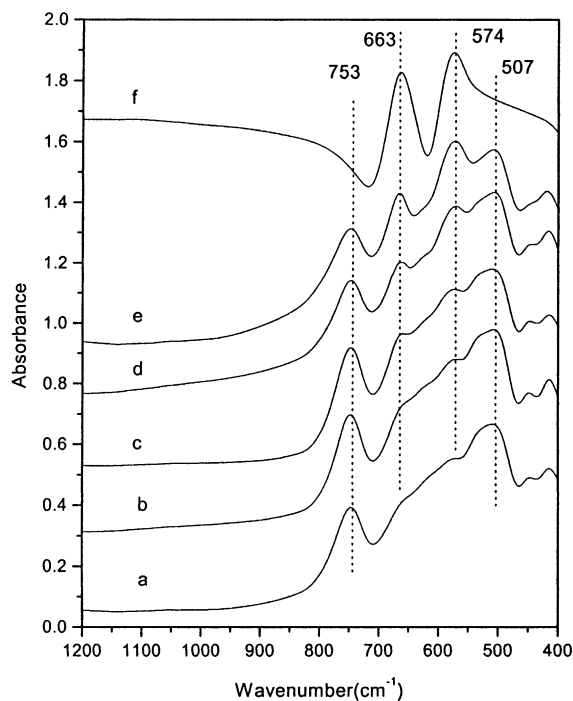


Fig. 12. FTIR spectra of ZrO_2 supported Co catalysts with different Co content: (a) 1.0 wt.% Co/ZrO_2 ; (b) 2.8 wt.% Co/ZrO_2 ; (c) 5.6 wt.% Co/ZrO_2 ; (d) 10 wt.% Co/ZrO_2 ; (e) 15 wt.% Co/ZrO_2 ; (f) Co_3O_4 .

temperature calcination and the pure ZrO_2 support. Hence, it is expected that the ZrO_2 supported cobalt catalyst is not stable in high temperature reaction. Further work is underway to stabilise the catalyst at high temperature.

The XRD pattern of the calcined zirconia supported cobalt catalyst is shown in Fig. 14. The diffraction peaks of ZrO_2 become much sharper, and some of them split. This suggests that the zirconia particle becomes large after high temperature calcination. The split may result from the sintering of ZrO_2 support, or the formation of a new phase of ZrO_2 . Because the zirconia particle becomes large, the surface area of the catalyst is greatly decreased, as confirmed by BET measurement. The surface area of the catalyst changed from 51.5 to 1.5 m^2/g after calcination. Meanwhile, the diffraction intensity of Co_3O_4 decreases. The decrease of Co_3O_4 and loss of the surface area are probably the main reasons for the decrease in the catalytic activity.

LR measurements show no obvious differences between the zirconia supported catalysts before and after high temperature calcination (Fig. 15), suggesting that the surface state of the catalyst is not changed during the calcination. Hence, it is concluded that the loss of the activity of the catalyst is due to the decrease in the surface area.

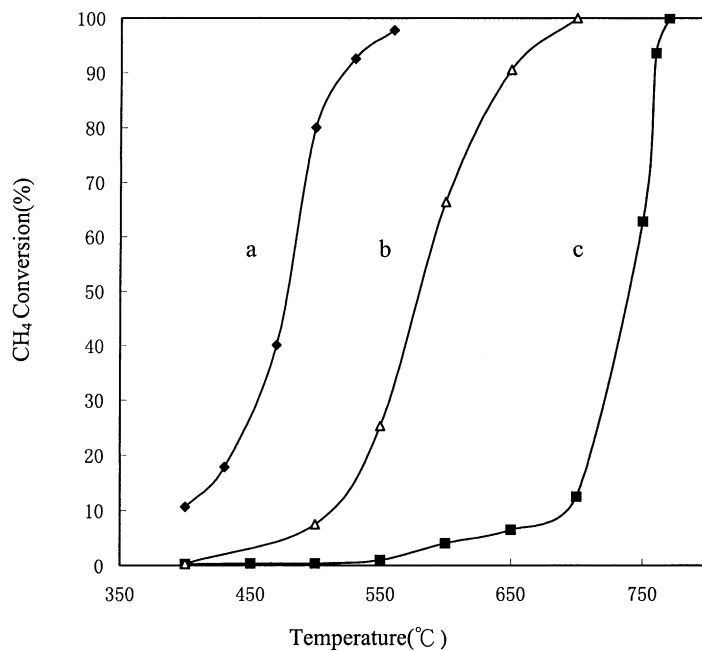


Fig. 13. Activity test for ZrO₂ support and supported Co catalysts for methane combustion: (a) 10 wt.% Co/ZrO₂; (b) ZrO₂ support; (c) 10 wt.% Co/ZrO₂ calcined at 1000°C for 4 h.

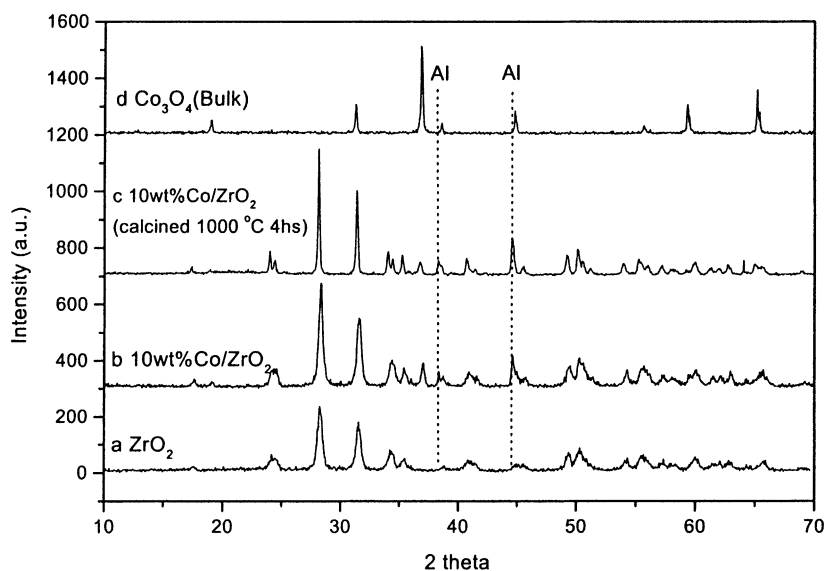


Fig. 14. XRD pattern of ZrO₂ supported Co catalysts calcined at 1000°C.

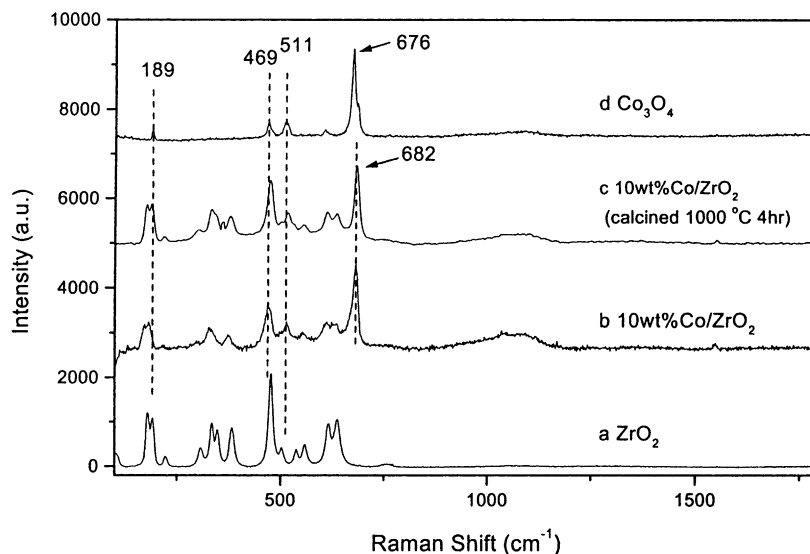


Fig. 15. LR spectra of ZrO_2 supported Co catalysts calcined at 1000°C .

4. Conclusion

ZrO_2 and Al_2O_3 supports are themselves active in methane combustion, while MgO and TiO_2 are not as active. Zirconia supported cobalt catalyst shows the highest activity among the supported catalysts, because of its special interaction with the active component, e.g. Co_3O_4 . In titania supported cobalt catalyst, Co_3O_4 exists in bulk and not on the surface of the catalysts, thus, leads to the poor activity of the catalyst. A solid solution is formed in the MgO supported cobalt catalyst, in which the active component is probably Co^{2+} clusters. In alumina supported catalyst, Co_3O_4 is poorly dispersed, which leads a lower activity of the catalyst for methane combustion.

Although Co_3O_4 is identified as the active component for methane combustion, the activity is not increased with Co_3O_4 content in the zirconia supported catalysts. The catalyst containing 1.0% Co shows the highest activity. Hence, it is inferred that a synergic effect between Co_3O_4 and ZrO_2 exists in the catalyst, and the active centre is Co_3O_4 promoted by zirconia.

Unfortunately, the zirconia supported cobalt catalyst is not stable to high temperatures ($>1000^\circ\text{C}$). The activity for methane combustion decreases dramatically for catalysts exposed to 1000°C for 4 h. The drop of

the catalyst activity is mainly due to the loss of the surface area.

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