

Combustion of lean methane mixtures over Pd-Co supported on titanium silicalite zeolite catalyst

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ABSTRACT

Novel Pd-Co supported on TS-1 catalysts were prepared and tested in methane combustion under very lean conditions (<1 %). A strategy for developing a new catalyst is performed by combining three types of material, i.e. palladium, cobalt and titanium silicalite zeolite (TS-1). The high stability of cobalt, together with the high surface area and hydrophobic nature of TS-1 are expected to beneficially influence the combustion properties of Pd-based catalysts. The results show that Pd-based catalysts can fully oxidise methane at reaction temperature below 400 °C. Co loading higher than 5.7 % does not significantly improve the activity of this catalyst, however a decrease in H₂O adsorption intensity is observed upon increasing Co content. These results suggest that higher methane combustion activity and enhanced adsorption capacity are intrinsically linked.

1. Introduction

Flameless combustion technology is a promising option for removal of methane emissions and volatile organic compounds (VOCs) where methane is combusted over a catalytically-active solid surface. During the last few decades, significant resources have been expended to develop this technology. In general, Pd-based catalysts demonstrate outstanding catalytic behaviour [1], but deactivate due to poisoning by water [2], which can reduce the potential for their use in a catalytic combustor. A strategy for improving the stability and activity of Pd-based catalyst is the focus of the current investigation.

Transition metal oxides have been considered as catalysts for total oxidation of methane due to their higher stability and lower cost when compared to noble metals [3]. Earlier work reported the use of single-metal oxides (such as Cr₂O₃, NiO, Mn₂O₃, Co₃O₄, and CuO) and these studies evaluated the activities and deactivation phenomena during lean methane combustion [4]. Among those tested, Co₃O₄ was the most active catalyst but was less stable compared to Mn₂O₃. Preparing different morphologies of cobalt oxide was demonstrated

recently as a strategy for improving the catalytic activity [5]. Enhanced activity and stability was reported for Co_3O_4 nanotube prepared using a morphology-directed technique [6]. A very recent investigation reported that the higher oxygen adsorption capacity of cobalt oxide is strongly related to its superior activity [7].

The titanium silicate-1 (TS-1) materials initially prepared by Taramasso et al. were effectively used as a catalyst for the selective oxidation of alkenes and alcohol substrates using hydrogen peroxide [8-10]. Using photoassisted deposition (PAD) method, nanosize Pd particles was successfully deposited on TS-1 and tested for direct synthesis of H_2O_2 from H_2 and O_2 [11]. Very recently, the preparation of Au-Pd nano-particles supported on hierarchical TS-1 catalysts was evaluated for selective oxidation of benzyl alcohol using in situ generated hydrogen peroxide [12]. It was found that the use of TS-1 support led to better metal dispersion [12]. It is generally agreed that the dispersion of the noble metal is one of the key factors for improving the activity of palladium catalysts for methane oxidation [13]. Moreover, TS-1 zeolite is also known as a more hydrophobic material compared to other zeolites [14]. These properties are thought to improve the long term stability of a combustion catalyst and thus we investigated TS-1 as a support material for palladium catalysts. Our recent investigation showed an excellent stability observed over 1900 h time-on-stream experiment over TS-1 based palladium catalyst, where a constant steady state activity to obtain 90 % conversion was achieved below 500 °C [15].

We report the development of a new catalyst by combining three types of material, i.e. palladium, cobalt and titanium silicalite zeolite (TS-1). The high stability of cobalt, together with the high surface area and hydrophobic nature of TS-1 can beneficially influence the combustion properties of Pd-based catalysts. The physical and chemical properties of Pd/Co-TS-1 catalyst were investigated in order to understand the advantages of this catalyst in comparison with other catalysts.

2. Experimental

Pd/Co-TS-1 catalysts were prepared by incipient wetness method, where a predetermined aliquot of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) impregnated a commercial titanium silicalite (TS-1) support (ENI-Polimeri Europa SpA). The resulting paste was dried at 110 °C for more than 20

h. In order to prepare the palladium catalyst, an aliquot of Pd (II) nitrate solution (10 wt% in 10 wt% nitric acid, Sigma-Aldrich) was used to impregnate the $\text{Co}_3\text{O}_4\text{-TS-1}$, followed by drying in the oven for 24 h. The samples obtained are denoted to Pd/Co_x-TS-1, Pd/Co_y-TS-1, and Pd/Co_z-TS-1 where x, y and z refer to the weight percentage of cobalt. A tubular fixed-bed reactor was employed for the calcination of the dried solid catalyst in air at 500 °C for 2 h followed by purging in helium while slowly cooling the catalyst to desired reaction temperature.

Catalytic activity measurements were performed in a tubular stainless steel micro reactor. The reactant mixture was set at 7,000 ppm CH₄ balanced with (dry) air at gas hourly space velocity of 100,000 h⁻¹. The inlet and outlet mixtures were analysed using a gas chromatograph equipped with a thermal conductivity detector (TCD) and concentric packed column (Alltech CTR-I). The reaction temperature was measured with a K-type thermocouple placed into the catalyst bed.

The surface area, pore size and pore volume of the catalyst samples were measured by nitrogen adsorption–desorption at 77 K using a Micromeritics TriStar 3000 physisorption analyzer. Palladium loading was quantified using a Varian 715-ES inductively coupled plasma optical emission spectrometer (ICP-OES). Zeiss Sigma VP FESEM served to capture the Scanning Electron Microscopy (SEM) images of the sample. Bruker light element SSD Energy-dispersive X-ray spectroscopy (EDS) detector allowed the elemental analysis while capturing the SEM images. For surface analysis, ex-situ X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB250Xi (Thermo Scientific, UK). Powder X-ray diffraction (XRD) patterns of catalysts were examined using Cu K α radiation performed by a Philips X'Pert diffractometer. Temperature-programmed desorption (TPD) analyses were performed using a Pfeiffer Prisma quadrupole mass analyser.

3. Results and Discussion

3.1 Catalyst activities

The catalytic performances of Pd/Co-TS-1 catalysts were measured for total combustion of methane. Prior to catalyst testing, the sample was activated in air at 500 °C for 2 h then

cooled to 200 °C in a flow of helium. A feed of reactor 7000 ppm methane in air was passed through the catalyst bed at a GHSV of 100 000 h⁻¹. The experiment was then started by gradually increasing the furnace temperature. A preliminary experiment in absence of catalyst was performed prior to catalytic activity test and confirmed that no methane conversion was observed up to a temperature of 650°C [2].

Figure 1 illustrates the activities of the catalysts examined in this experiment. Note that a TS-1 sample without Pd loading was also tested under similar condition as mentioned above and resulted in no conversion at temperatures as high as 430 °C [15]. It is confirmed that TS-1 zeolite is not an active material for methane oxidation. The deposited palladium and cobalt oxide particles on TS-1 are responsible for converting methane to carbon dioxide. Among those tested, Pd/Co_x-TS-1 catalyst exhibits the highest activity followed by Pd/Co_y-TS-1 and Pd/Co_z-TS-1 catalysts. In contrast, the temperature of Co_z-TS-1 catalyst at 10 % methane conversion level (T_{10}) is 420 °C. While, at this temperature methane can fully be converted to carbon dioxide by using the other catalysts.

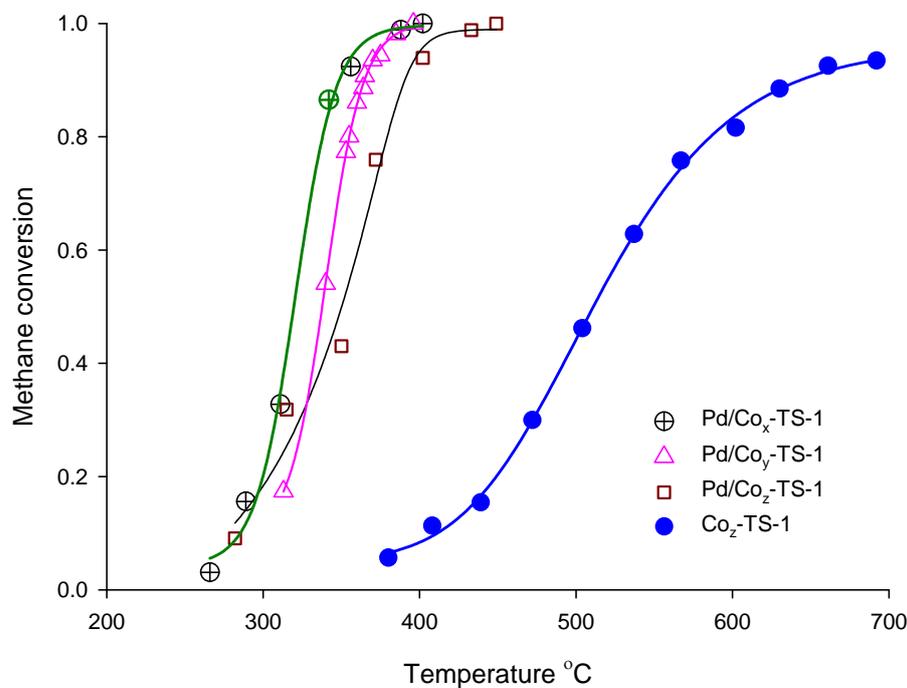


Figure 1 : Methane conversion as a function of reaction temperature of methane oxidation over (⊕) Pd/Co_x-TS-1, (△) Pd/Co_y-TS-1, (□) Pd/Co_z-TS-1 and (●) Co_z-TS-1 catalysts. GHSV = 100,000 h⁻¹, feed: 7,000 ppm CH₄ balance air.

3.1 Catalyst characterization

The adsorption and desorption of nitrogen was performed on pure TS-1 support, Pd/Co_x-TS-1 and Co_z-TS-1 catalysts in order to measure the surface area and the pore sizes. Fig. 2 shows the adsorption-desorption isotherm of Pd/Co_x-TS-1 catalyst. The textural properties of samples are provided in Table 1.

In general, the isotherm adsorption plots of our samples fall into type-I as classified by IUPAC which is typically the behaviour of microporous materials [16]. Interestingly, the desorption curves of Pd/Co_x-TS-1 catalyst is slightly shifted to a higher volume over the pressure range. As reported in the literature, these shifts indicate an improved adsorption over the range of relative pressures which suggests the coexistence of micro and mesopores within these catalysts [17]. As shown in Table 1, the average pore diameter calculated using *Barrett-Joyner-Halenda* (BJH) method results in 30.7 Å, 25.6 Å and 25.3 Å for TS-1, Pd/Co_x-TS-1 and Co_z-TS-1 catalysts, respectively. Unsurprisingly the surface area of Pd/TS-1 catalyst is much higher compared to Pd/Co_x-TS-1 and Co_z-TS-1 catalysts. The surface area estimated by Langmuir method discloses a decrease from 641.9 m²·g⁻¹ to 553.1 m²·g⁻¹ in the presence the Pd and Co nano-particles on TS-1 which confirms the deposition of Pd and Co on TS-1 support. This is further substantiated by ICP-OES, EDS and SEM results below.

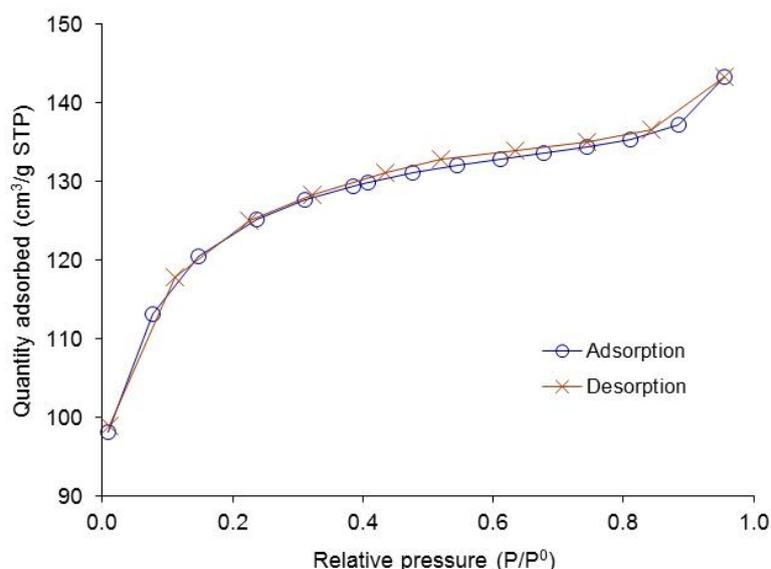


Figure 2 : Nitrogen adsorption-desorption isotherm plot of Pd/Co_x-TS-1 catalyst

Table 1. N₂-physorption calculation results

Parameter	Sample		
	TS-1	Pd/Co _x -TS-1	Co _z -TS-1
Langmuir Surface Area (m ² ·g ⁻¹)	641.9	553.1	485.8
BJH Average Pore Diameter (Å)	30.7	25.6	25.3
BJH Adsorption Pore Volume (cm ³ ·g ⁻¹)	0.07	0.10	0.08

Based on ICP-OES analysis, a nominal loading of 1 wt. % is present on all catalysts. There are 5.7 wt. % of Co loaded on Pd/Co_x-TS-1. For Pd/Co_y-TS-1 and Pd/Co_z-TS-1 catalysts, the loading of Co are 9.0 wt. % and 13.8 wt. %, respectively. The presences of Pd, Co and Ti elements have been confirmed using EDS analysis as shown in Figure 3. This result together with catalytic measurement result suggests that cobalt in limited amount enhances the activity of the catalyst. Adding cobalt on TS-1 support higher than 9 wt. % does not improve the activity of the catalyst.

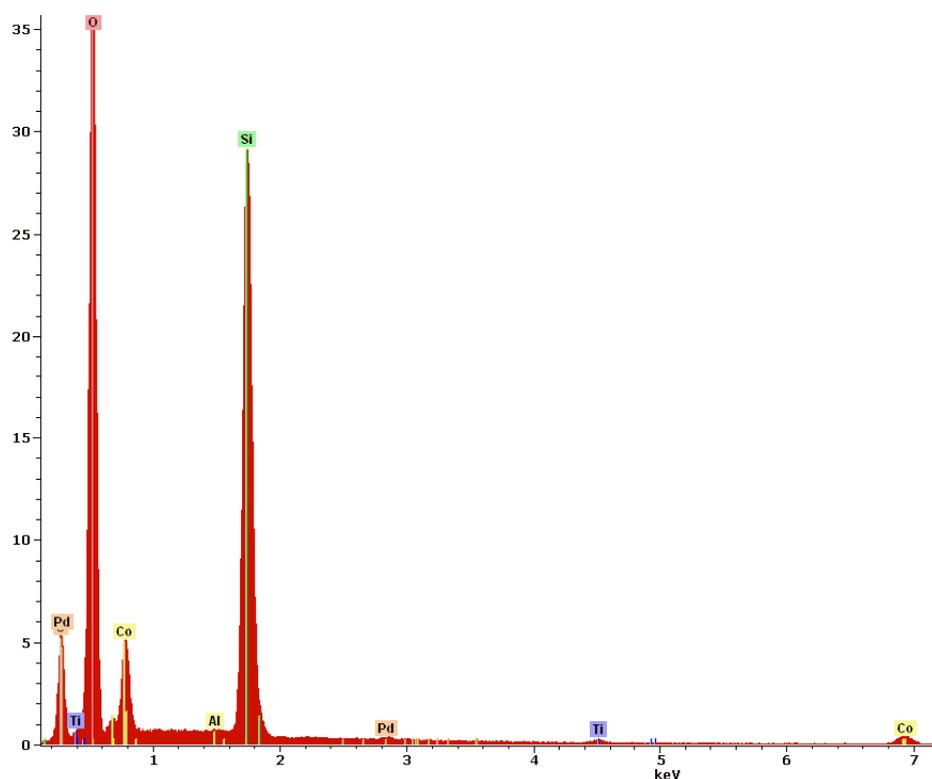


Figure 3 : EDS spectra of Pd/Co_x-TS-1catalyst

The observation of a possibility in morphological transformation during catalyst preparation and methane oxidation was carried out using scanning electron microscopy (SEM). Fig. 4 shows SEM images of TS-1 zeolite, $\text{Co}_x\text{-TS}$ and $\text{Pd/Co}_x\text{-TS-1}$ catalysts. The topography of un-modified TS-1 zeolite was captured by a secondary electron (SE) detector and shown at different magnification in Fig. 4a and 4b. Representation of surface features of $\text{Co}_x\text{-TS}$ and $\text{Pd/Co}_x\text{-TS-1}$ samples are respectively shown in Fig. 4c and 4d.

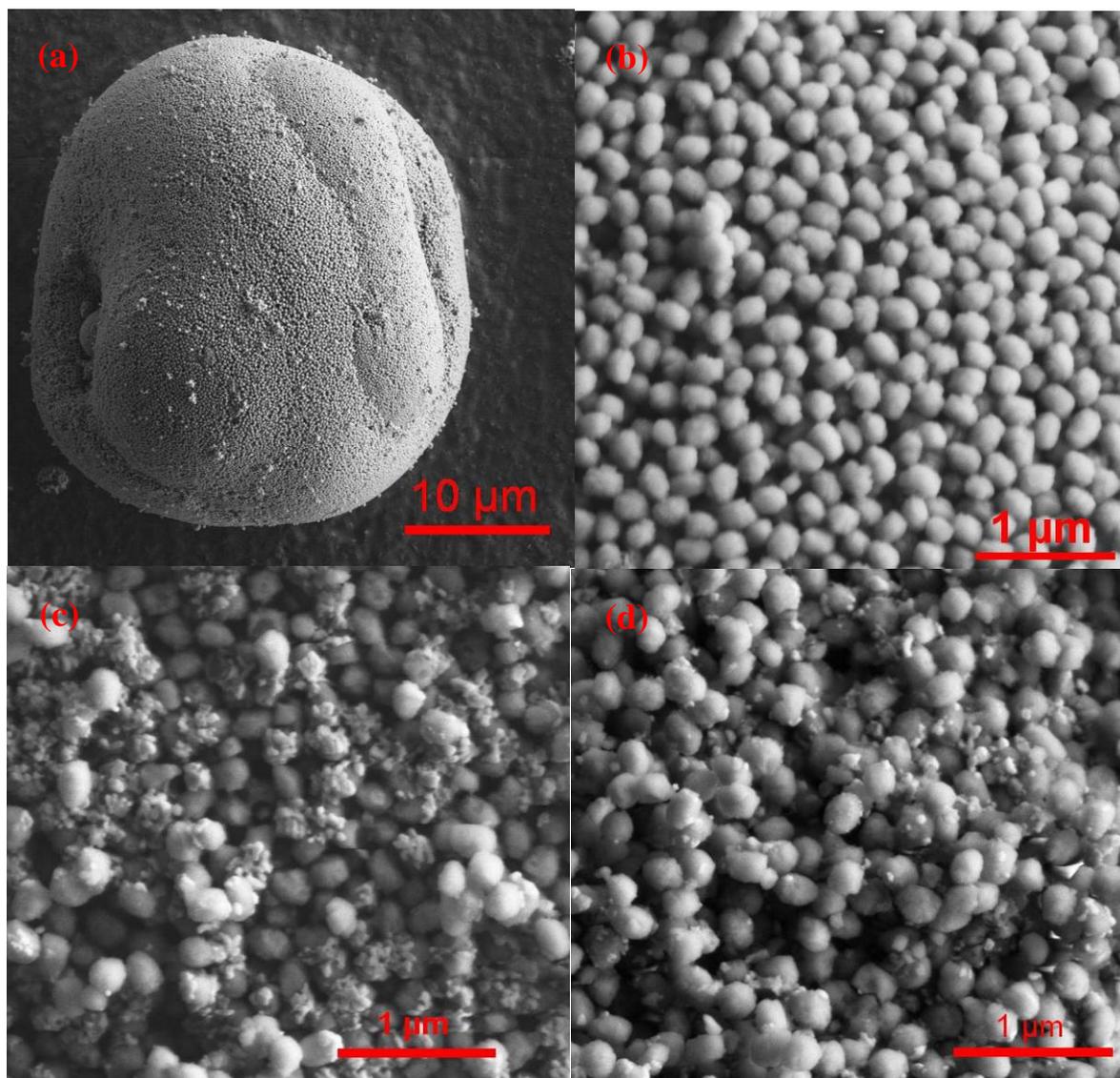


Figure 4 : SEM images of (a) un-modified TS-1, (b) un-modified TS-1 at higher magnification, (c) $\text{Co}_x\text{-TS}$ catalyst and (d) $\text{Pd/Co}_x\text{-TS-1}$ catalyst.

Using backscattered electron (BE) detector, the images of Pd/Co_x-TS-1 catalyst was captured as shown in Fig. 5. In this image, SEM micrograph reveals small brighter particles distributed over the whole area of TS-1 surface which are interpreted as signal from cobalt oxide particles. In this image, the cobalt oxide particle is recognized as the brighter particle due to its higher atomic weight (see the arrows). This has been confirmed by Energy Dispersive Spectroscopy (EDS) which was performed during analysis. The existence of palladium particle was not detected in this images due to its extremely small size. These images suggest that the nature of TS-1 support helps in establishing a better palladium and cobalt oxide particles distribution. This is in a good agreement to what has been reported in the literature that the morphology and microstructure of nano-sized Pd particle is affected by the nature of its support [18].

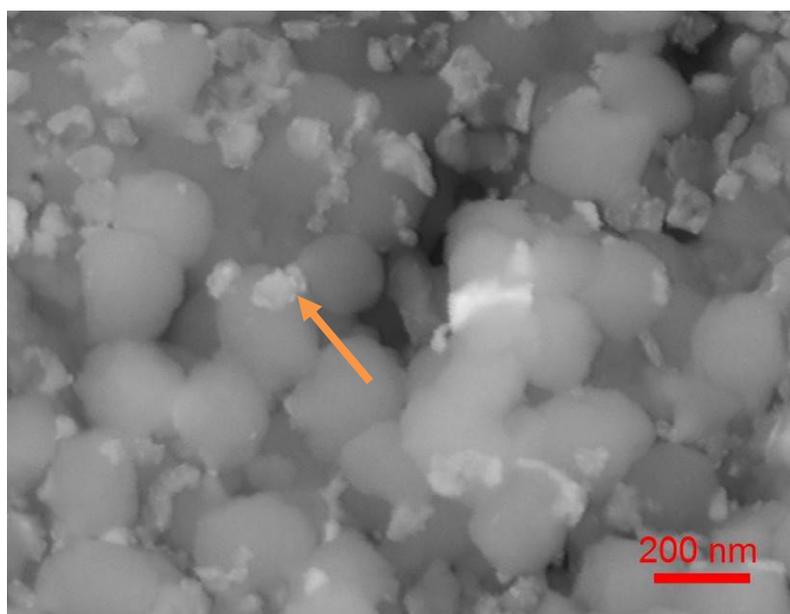


Figure 5 : SEM images of Pd/Co_x-TS-1 catalyst captured by backscattered electron detector

The effect of water on palladium and cobalt oxide supported on TS-1 catalyst was investigated using TPD analysis. Water has been selected as an adsorbate with the purpose of investigating the interactions between water, active sites and the support material. Before adsorption, both samples were pre-heated for 1 h at 500 °C with a heating rate of 5 °C·min⁻¹ to remove any pre-adsorbed compounds. Water was adsorbed at 110 °C to avoid any weakly bound adsorbate retained on the sample.

Figure 6 shows TPD spectra of H₂O desorption ($m/e = 18$) of Pd/Co_x-TS-1, Pd/Co_y-TS-1 and Pd/Co_z-TS-1 catalysts. The intensity of H₂O adsorption was normalized to the mass of sample. Interestingly, a lower intensity of water desorption was observed when Co loading was increased.

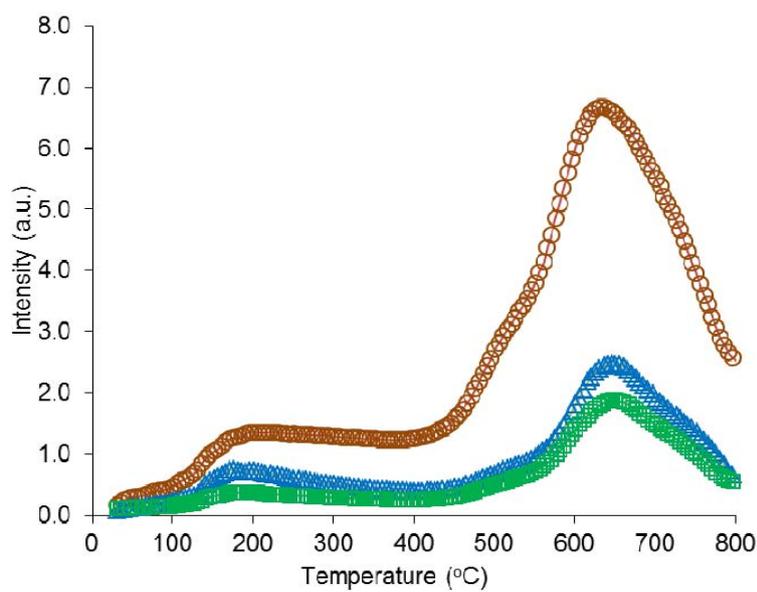


Figure 6: TPD curves of water desorption from (○) Pd/Co_x-TS-1, (△) Pd/Co_y-TS-1, (□)Pd/Co_z-TS-1 catalysts. Water was adsorbed at 110 °C. Heating ramp = 5 °C·min⁻¹.

4. Conclusion

Pd-Co supported-on TS-1 catalysts have been prepared and studied in order to explore a new strategy for improving the stability and activity of catalyst. The Pd-based catalysts can fully oxidise methane at reaction temperature below 400 °C. Co loading higher than 5.7 % does not significantly improve the activity of this catalyst, however a decrease in H₂O adsorption intensity is observed upon increasing Co content. These results suggest that higher methane combustion activity and enhanced adsorption capacity are intrinsically linked.

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