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Plasma assisted preparation of cobalt catalysts by sol–gel method for methane combustion

Mu-hua Chen · Wei Chu · Jun-jie Zhu · Lin Dong

Abstract Novel cobalt catalysts were prepared by sol–gel method, and enhanced by plasma treatment, for methane catalytic combustion. These samples were characterized using X-ray diffraction, X-ray photoelactron spectroscopy, UV-vis spectroscopy, Fourier transform infrared spectroscopy, thermal gravimetrical analysis, N_2 Adsorption–desorption, temperature-programmed reduction and hydrogen–oxygen titration technologies. The XPS characterizations suggested that plasma treatment was favorable for the enrichment of surface cobalt, with a value of surface cobalt from 2.2% to 8.5% in mole. The specific surface area of the glow plasma assised sample (Co-Plas-Solgel-2) increased to 320 m^2/g comparing with 305 m^2/g of the conventional sample (Co-Solgel-1). The ignition temperature ($T_{10\%}$) of Co-Plas-Solgel-2 catalyst was about 50 °C lower than that of Co-Solgel-1, and its CH_4 conversion was two times higher than that of Co-Solgel-1 during the whole range of catalytic combustion activity test (340–520 °C). With a better dispersion and more active sites, the plasma assisted sample exhibited significant enhancement in catalytic performances.

Keywords Cobalt Catalyst · Plasma · Sol–gel · Methane catalytic combustion

M. Chen (✉) · W. Chu
Department of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China
e-mail: amoon.mhchen@gmail.com

M. Chen
Department of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, People's Republic of China

J. Zhu · L. Dong
Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

1 Introduction

The application of plasma technology is continuously growing in chemistry, metallurgy, microelectronics, and environmental protection. Compared with the high temperature plasma, low temperature plasma (including thermal quasi-equilibrium plasma and cold non-equilibrium plasma) is more attractive because of its mild generation conditions. As an efficient surface treatment process, low temperature plasma combining with the advantages of the catalysis could obtain interesting and delightful results in catalytic processes [1, 2].

Thermal plasma is known to be excellent in the synthesis of ultrafine particle catalysts and plasma assisted deposition of active compounds on various supports. Vissokov applied plasma-chemical synthesis and regeneration of nanostructured catalysts for various reactions [3]. Phillips et al. created supported metal catalysts from an aerosol containing particles of metal and support employing a microwave frequency plasma torch [4]. Valinčius and co-workers employed atmospheric pressure plasma spray technology for well-adhered CuO and Cr_2O_3 supported catalytic coating with highly developed surface, excellent thermal and mechanical stability and high catalytic activity [5]. Generally, another kind of low temperature plasma, cold gas plasma, is used to modify its properties without affecting the characteristics of the bulk by treating the catalyst surface. Furukawa and co-workers modified H–Y zeolite by a radio-frequency CF_4 plasma, and the hydrophobic character of the zeolite was enhanced by the plasma treatment [6]. Liu et al. reported a glow discharge plasma treatment for Ni–Fe/Al_2O_3 [7] and Pd/HZSM-5 [8, 9]. Such catalysts prepared by plasma technology presented a higher catalytic activity and an enhanced stability than the catalyst without plasma treatment. Legrand used the afterglow of

the microwave plasma for the reduction of zeolite-supported metallic catalysts [10]. Surface treatment by a corona discharge by flowing argon was also effective [11].

From the previous studies,it appears that plasma, composed of highly excited atomic, molecular, ionic and radical species, is a very helpful technique for catalyst synthesis and surface modification [12–14]. Especially, the fundamental properties and scientific rules of plasma treated catalysts have drawn increasing attention owning to the crucial importance of catalyst surface properties in heterogeneous catalytic reactions. It is also known that, owing to low temperature condition, plasma treatment of supported catalyst could modify the dispersion and surface content of catalytically active components, meanwhile, it can avoid the structure collapse and crystalloid transformation. Hence, the treatment process plays an important role in improving catalytic performance. However, the investigation about the effect of plasma treatment on the catalysts prepared by sol–gel method has not been observed within reference works.

Based on our previous investigations [15–17],effects of plasma treatment on the cobalt-based catalyst prepared by sol–gel method, on the properties and the combustion performance, were investigated in this work. The detailed comparisons of the textural, structural and surface chemical properties of two typical catalysts were presented.

2 Experimental

2.1 Catalyst preparations

The cobalt nitrate, tetraethyl orthosilicate (TEOS) and ethanol were used for the preparation of Co–Si gel. The above mixture containing TEOS was hydrolyzed in the first step with the pre-mixed distilled water solution under the condition of intensive stirring, which contained ethanol and acetic acid. The molar ratio of TEOS : CH_3CH_2OH:H_2O:CH_3COOH was 1:1.2:35:0.12. The solution was stirred continuously at 80 °C until the gel was formed. The final product was an opaque gel of colloidal nature. Subsequently, it was dried at 80 °C in water bath and 110 °C in drying oven, calcined at 470 °C for 4 h in air. The prepared catalyst was labeled as Co-Solgel-1.

As to the plasma-enhanced preparation by a glow discharge, the plasma treatment of the precursor of Co-Solgel-1 took place at ambient temperature or slightly higher one under vacuum. The treated sample was put into the discharging tube and decomposed in nitrogen until its visual color became dark violet from purple. The discharge parameters are as follows: frequency 13.56 MHz, discharge voltage 100 V, anodic current 100 mA, total time of plasma treatment 120 min and a vacuum between 2 and

200 Pa [15, 16]. The sample was then calcined at 470 °C for 4 h,and labeled as Co-Plas-Solgel-2. The initial cobalt content of these two catalysts was 10 wt.%.

2.2 Catalyst characterizations

The nitrogen adsorption–desorption isotherms were measured by nitrogen adsorption at 77 K using a Quantachrome Nova 1000e instrument. Total cobalt contents of the samples before and after plasma treatment were determined by the ICP method using an IRIs Advantage ICP-AES (TJA Solutions). Thermal gravimetrical analysis (TGA) was performed using a Shimadzu model with an operating range from 50 °C to 800 °C at a programmed rate of 15 °C min^{-1}. X-ray powder diffraction(XRD) patterns were recorded by PHILIPS X' Pert pro MPD diffractometer using Cu Kα (40 kV, 40 mA) radiation. The average crystallite size of Co_3O_4 was calculated according to the Scherrer equation using a (311) diffraction peak at $2\theta = 36.8°$. Metallic dispersions were determined by hydrogen–oxygen titration using a conventional volumetric technique. X-ray photoelactron spectroscopy (XPS) spectra were acquired with a ESALAB MK2 spectrometer equipped with an Mg Kα source (hv = 1253.6 eV).

The Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Nicolet 5700 FTIR spectrometer with a spectral resolution of 4 cm^{-1}. UV spectra were recorded by diffuse reflectance on a Shimadzu UV-3600 spectometer. Temperature programmed reduction (TPR) experiments were carried out in a home-made system. It was conducted using 100 mg of catalyst and 6.3 vol% hydrogen in nitrogen (flow rate: 30 ml/min). The temperature was raised up to 600 °C at a heating rate of 10 °C/min.

2.3 Catalytic activity measurement

The catalytic combustion of methane was tested in a continuous fixed-bed quartz micro-reactor. The feed ratio was n(CH_4):n(O_2):n(Ar) = 2:4:4, with a flow rate of 100 ml/min. The weight of catalyst was 150 mg. The reaction gaseous products passed through a condenser, then they were separated in a TDX-01 column and analyzed by gaschromatograph (GC112A) equipped with a TCD detector. The condensate was analyzed using capillary SE30 column and a FID detector.
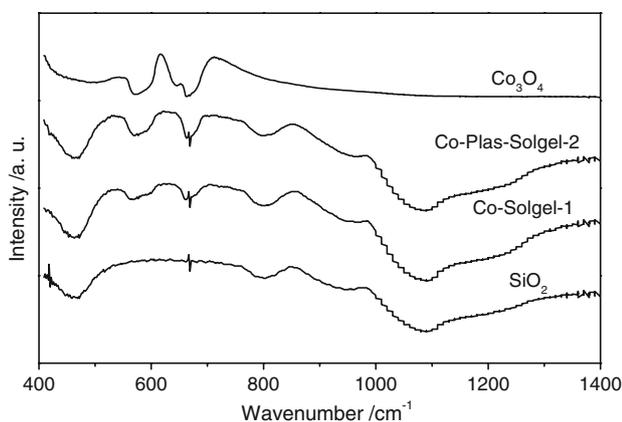
3 Results and discussion

3.1 FT-IR and UV-vis spectral analysis

Figure 1 shows the UV-vis spectra of prepared samples. The UV-vis spectrums of samples were characterized by
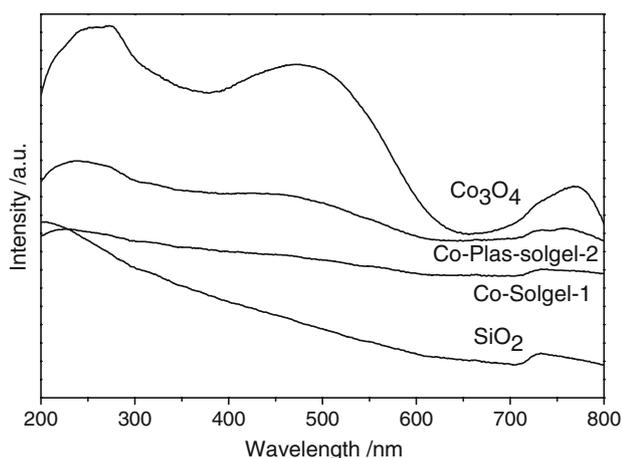
Fig. 1 UV-vis spectra of prepared samples

Fig. 2 FT-IR spectra of prepared samples

two broad bands at 260 nm, 490 nm associated with π–π* and d–d transitions of Co_3O_4 clusters respectively. And it was observed that stronger intensity was obtained over Co-Plas-Solgel-2. The v(Co–O) vibration of Co_3O_4 (570 and 663 cm^{-1}) [18] appear in the FT-IR spectrums of two catalysts (see Fig. 2), suggesting that cobalt was in oxide form. Compared with the reference band of the vibrations of Si–O–Si bonds (around 1,100 cm^{-1}), stronger relative intensity of Co_3O_4 of Co-Plas-Solgel-2 in FT-IR spectra was also observed. It could be inferred that the amount of Co_3O_4 in Co-Plas-Solgel-2 was higher than that in Co-Solgel-1 speculating on the relative intensity changes in these two spectral analyses.

In the case of FT-IR spectrum of containing Si species, bands at approximately 1,200 and 1,100 cm^{-1} correspond to stretching vibrations of Si–O–Si bonds; that at approximately 800 cm^{-1} is attributed to bending vibrations of Si–O–Si bonds, and that at 460 cm^{-1} belongs to bending vibrations of –O–Si–O– bonds [19, 20]. It is worth to point out that the broad band at 946.9 cm^{-1} on SiO_2 is due to the presence of non-bonded oxygen Si–O$^-$ [21, 22]. This band

shifted to around 960 cm^{-1} (956.5 cm^{-1} for Co-Solgel-1 and 962.3 cm^{-1} for Co-Plas-Solgel-2) and promised the formation of new bond (–Si–O–Co–) in these two catalysts. This indicated that a partial breakdown of the framework due to the incorporation of the hetero-element cobalt into the framework [23, 24]. And the relative intensity of this band (taking the vibrations of Si–O–Si bonds as reference band) on plasma treated sample is comparatively weaker, which suggest that fewer –Si–O–Co– bonds were obtained.

These observations supported the fact that Si atom could bond with one or several Co–O bonds to form different network during the gelation process. As a result, there were two kinds of cobalt species in the Co–Si catalysts prepared by sol–gel method in our work. Cobalt species of type A were very difficult to be reduced which entered into the framework of SiO_2 gel and formed the –Si–O–Co– bonds. The cobalt species of type B were the conventional reducible cobalt oxide, which was supported on the gel network. In addition, it was possible that the breakage of the formed –Si–O–Co– bonds took place in ambient temperature owing to the high active species bombardment on treated sample surface during the plasma treatment. In practical terms, there were fewer –Si–O–Co– bonds and a larger proportion of Co_3O_4 in the plasma treated sample than the conventional sol–gel one.

3.2 Structure and texture analysis

The XRD patterns are shown in Fig. 3. There is no detectable diffraction peak in prepared catalysts besides SiO_2 ($2\theta \approx 24°$) and Co_3O_4 ($2\theta \approx 36°, 59°, 65°$) which indicated that the cobalt species of two catalysts were present mainly in the form of spinel Co_3O_4, in which the Co(II) ions occupy tetrahedral positions and the Co(III) ions occupy octahedral positions in the face-centered cubic oxygen lattice. This was in agreement with that of the UV-vis and FT-IR measurements. In Co-Plas-Solgel-2, a similar peak
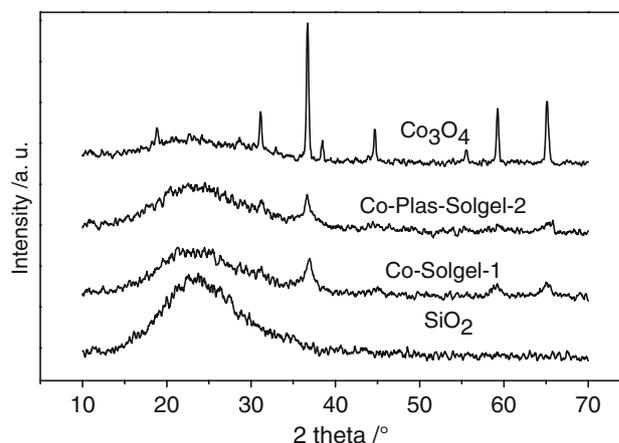
Fig. 3 XRD profiles of the prepared catalysts

Table 1 Textural characteristics of the investigated samples

Sample	BET Surface area m^2/g	Crystallite Size of Co$_3$O$_4$ nm	Cobalt content%
Co-Solgel-1	304.6	12.4	9.74
Co-Plas-Solgel-2	320.1	11.2	9.69
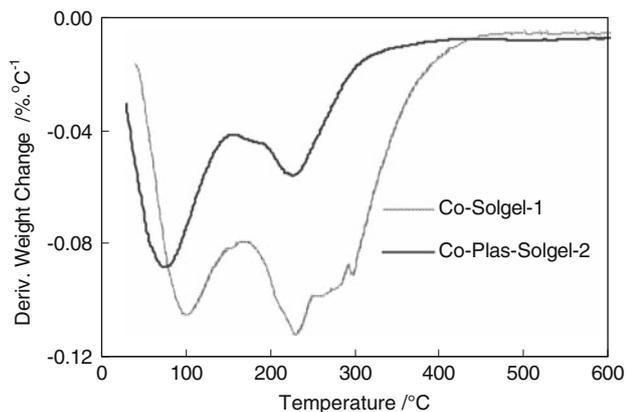
Fig. 4 DTG curve of catalysts prepared by sol-gel method

attributed to Co$_3$O$_4$ (311) and comparative weaker peaks attributed to Co$_3$O$_4$ (511) (440) present, suggesting that the plasma enhanced preparation produces the visible faint impression on the Co$_3$O$_4$ particles. As a result, the average size of Co$_3$O$_4$ crystallites calculated from Scherrer equation was 11.2 nm and 12.4 nm (listed in Table 1), respectively on Co-Plas-Solgel-2 and conventional sample (Co-Solgel-1).

The differential profiles of samples' thermal analysis are shown in Fig. 4. There are two peaks based on the weight decrease, and Co-Plas-Solgel-2 catalyst showed a lower and narrower temperature peak. The first one around 100 °C was attributed to desorption of water adsorbed on the surface, and this peak was at a temperature 80 °C for Co-Plas-Solgel-2; the weight decrease were 10.2% and 8.5% for samples with and without plasma treatment. The second one observed within the range from 230 °C to 290 °C was ascribed to the decomposition of cobalt nitrate and the remaining organic compound; the weight decrease shifted from 17.7% to 7.2% after plasma assisted treatment. It was proved that the decomposition of cobalt nitrate and the removal of the remaining organic compound were partially occurred during the plasma treatment, though the system temperature was much lower than that of calcination.

The total cobalt content by weight in two typical samples obtained by ICP analysis was approximately equal, which was also close to the initial value 10%. The textural properties of catalysts are also listed in Table 1. The specific surface area increased from 304.6 m^2/g of Co-Solgel-1 to 320.1 m^2/g of Co-Plas-Solgel-2, and an appreciable increase in the total pore volume and that of average pore

diameter on plasma assisted catalyst were also observed. The nitrogen adsorption-desorption isotherms of two catalysts were typical for microporous material and their adsorption equilibriums were obtained at relative pressure (P/P$_0$) around 0.4 and over 0.8, respectively. It also could be inferred that the larger pore diameter and the narrow pore distribution were obtained in Co-Plas-Solgel-2. These changes were possibly due to the following two main reasons:first,the removal of water, carbonaceous species from silica gel and the partial decomposition of cobalt nitrate took place during plasma treatment favored the production and broadness of the pores in material;meanwhile,the comparative smaller Co$_3$O$_4$ crystal particles and good dispersion were also beneficial.

3.3 Surface analysis by X-photoelectron spectroscopy and hydrogen oxygen titration

X-photoelectron spectroscopy was used in an attempt to obtain more information insight into the surface composition of Co–Si catalysts. The Co 2p spectrums showed the shake-up satellites with low intensity and the main peak at BE = 780.0 eV,which is typical for Co^{2+}/Co^{3+} ions in the Co$_3$O$_4$ spinel phase. The position of XPS Co 2p peak shifted to the lower region of binding energies on plasma treated catalyst slightly. Thus, Co$_3$O$_4$ was likely to be the predominant phase present on the outer surface of catalysts. Table 2 provides the elemental composition on the surface of cobalt-based catalysts prepared with and without plasma treatment. The cobalt surface composition of Co-Plas-Solgel-2 sample was nearly 3.8 times higher than that of Co-Solgel-1 catalyst. The intensity ration of Co/Si of the plasma treated sample (0.32) was also obviously higher than that of untreated sample (0.07). And the Cobalt surface density of Co-Plas-Solgel-2 was 159.9 Co/nm^2, while that of Co-Solgel-1 was 43.5 Co/nm^2. The similar results had been reported by Liu et al. [10, 11]. According to the correlative results of XRD, the augment of the amount of cobalt atom on the surface did not produce the grow-up of the catalytically active Co$_3$O$_4$ crystallites, the good dispersion was obtained on Co-Plas-Solgel-2.

Hydrogen consumption (HC) in hydrogen oxygen titration was calculated after the experiment. HC for Co-Plas-

Table 2 Comparison of surface atomic compositions from XPS analysis

| Atom	Atom ratio			Dispersion %
	Co2p	O 1s	Si 2p	
Calculated value	3.4	66.0	30.6	–
Co-Solgel-1	2.2	66.5	31.3	0.19
Co-Plas-Solgel-2	8.5	65.3	26.2	0.65

Solgel-2 and conventional sample was 20.3 μmol/g and 5.8 μmol/g, respectively. Owing to the sol–gel method, cobalt species would be dispersed in the bulk mostly. The dispersion of metallic cobalt was 0.65%, and the calculated metallic active surface area was 0.33 m^2/g for the plasma assisted sample, which was about 3.4 times more than that of Co-Solgel-1. These results were coincident with the results of XPS analysis; it was indicated that the plasma assisted sol–gel catalyst could gave a better dispersion, higher active surface area and more active sites compared with those of the conventional sample.

3.4 Reduction properties

These two typical cobalt-based catalysts were measured by Temperature Programmed Reduction (TPR-H$_2$). The typical TPR curves are shown in Figs. 5 and 6. Both the two curves exhibited one hydrogen consuming signal around 360 °C attributing to the reduction of Co$_3$O$_4$ species to metallic cobalt directly. The slight shift of TPR peak from 357.9 °C to 362.1 °C after plasma assisted preparation was observed. And the H$_2$ consumption value of two catalysts
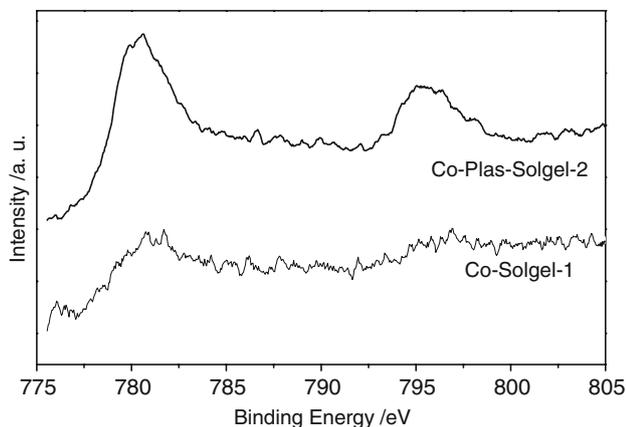
Fig. 5 Co2p X-ray photoelectron spectra of the prepared samples
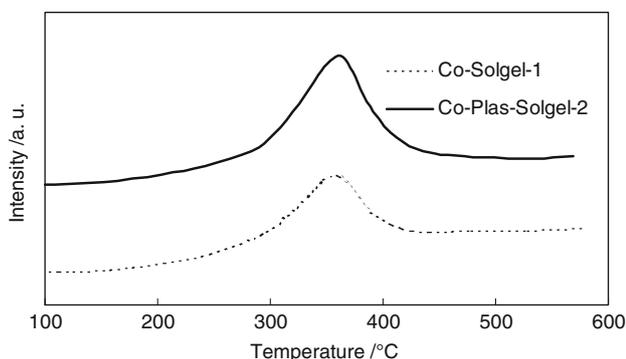
Fig. 6 TPR spectra of samples prepared by sol-gel method and plasma enhancement
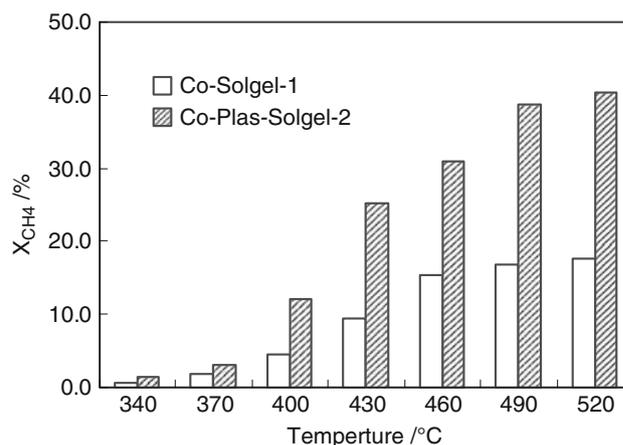
Fig. 7 Influence of plasma treatment on catalytic performance. Conditions: M$_{cat.}$ = 150 mg, n(CH$_4$):n(O$_2$):n(Ar) = 2:4:4

was rather lower than the theoretic one. According to the TPR results, the extent of reduction was 16.3% of Co-Solgel-1 and 28.3% of Co-Plas-Solgel-2, respectively. This indicated that most of cobalt in prepared sol–gel catalyst was present in the form of non-reducible oxides and plasma discharge treatment on the catalyst surface was benefit for the formation of reducible Co$_3$O$_4$ phase, which was in agree with the conclusions from FT-IR and UV-vis results.

3.5 Catalytic combustion of methane

These typical catalysts were tested in catalytic combustion of methane. Selectivity to carbon dioxide was about 100% for both samples in our work. It could be seen from the results (shown in Fig. 7) that the plasma treatment of catalyst had significant influence on its catalytic performance, especially at lower reaction temperature. With the increase of reaction temperature from 340 °C to 520 °C, the methane conversion shifted from 0.5% to 17.6% on Co-Solgel-1, while it was improved from 1.5% to 40.4% on Co-Plas-Solgel-2. In addition, T$_{10\%}$ value of Co-Plas-Solgel-2 was also 48 °C lower than that of Co-Solgel-1 (437 °C).

Supported by the above characterizations, plasma treatment was in favor of the good dispersion of Co$_3$O$_4$ and the significant enrichment on the catalyst surface. The more active sites and less-perfect crystal lattice with a large number of vacancies for the gaseous reactants to be adsorbed and activated, were the main reasons for the quite high reaction rate provided by Co-Plas-Solgel-2.

4 Conclusions

Small crystal diffraction peaks of Co$_3$O$_4$ were detected in these two typical catalysts, confirmed by XRD results. Owing to the bombardment of high active species on the

surface during plasma treatment, the removal of water, carbonaceous species from silica gel and the partial decomposition of cobalt nitrate took place at lower temperature than that of conventional sol–gel one, and the specific surface area increased from 305 m^2/g to 320 m^2/g. Moreover, these bombardments lead to the breakage of formed –Si–O–Co– bonds and the formation of Co$_3$O$_4$. The discharge plasma treatment of samples prepared by sol–gel method induced a better generation of active cobalt species. The hydrogen consumption in TPR experiment was more in Co-Plas-Solgel-2, compared with that of the conventional sol–gel sample. The CH$_4$ conversion was nearly twice of that of Co-Solgel-1, at each temperature during the whole catalytic combustion test (340–520 °C). From XPS and HOT characterizations of catalysts, the significant enrichment of Co on catalyst surface was confirmed, and a higher dispersion was obtained for plasma assisted sample.

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