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Article

Surface density of synthetically tuned spinel oxides of Co^{3+} and Ni^{3+} with enhanced catalytic activity for methane oxidation

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ABSTRACT

Spinel oxides containing Co and Ni are a promising substitute as a noble metal catalyst for methane combustion. Achieving a complete oxidation of methane under 400 °C remains challenging, and whether Ni^{3+} or Co^{3+} is the active center for the catalytic combustion of methane is a controversial issue. Therefore, we designed a series of spinel oxide catalysts by exposing different amounts of Ni^{3+} and Co^{3+} deposited on the surface by hydrothermal and co-precipitation methods in order to study the influence of high oxidation state (Ni^{3+} and Co^{3+}) on surface and catalytic activity. The catalytic performance increased almost linearly with increasing $\text{Ni}^{3+} + \text{Co}^{3+}$ on the surface of the catalyst. Thus, we are convinced that Ni^{3+} and Co^{3+} both act as active centers. The amount of $\text{Ni}^{3+} + \text{Co}^{3+}$ on a hydrothermal 60 h NiCo_2O_4 nanosheet surface is the highest, and reveals the best catalytic performance with T_{50} (50% methane conversion) at about 280 °C. 10 vol% H_2O added to the system has little impact on activity, especially at high space velocities due to the long hydrothermal time with less absorbed oxygen species and crystal defects. Overall, these results help clarify methane activation mechanisms and aid the development of more efficient low-cost catalysts.

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1. Introduction

Natural gas, which contains mostly methane, is abundant in our planet and is widely used in power generation and other heating applications because of its low cost [1–3]. However, unburned CH_4 is a more potent greenhouse gas because its global warming potential is twenty times higher than that of CO_2 ; CH_4 has become a serious environmental problem that has

drawn the attention of many researchers [4–7]. Therefore, the development of catalysts for completely oxidizing unconverted CH_4 at low temperatures has held great promise in the pursuit of highly efficient engine combustion and turbine-based energy devices, prompting the urgent need for low-cost, efficient, and robust catalytic emission control devices [8].

However, it is difficult to initiate oxidation of CH_4 at low temperatures (less than 300 °C) because CH_4 is a typical non-

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polar molecule, and the C–H bond in CH₄ has the highest bond energy (434 kJ/mol) among all organic compounds [7,9]. The activation of a C–H bond is the most critical step for the catalytic combustion of methane (CCM). The activation mechanism of the C–H bond can be summarized as follows: (1) homolytic activation mechanism over precious-metal-based catalysts and (2) heterolytic activation mechanism on oxides [10,11]. Generally speaking, noble metals [12–16] (e.g., Pt, Pd), especially Pd-based catalysts [17,18], can exhibit outstanding catalytic performance and complete oxidation of methane at low temperatures. In order to improve the catalytic efficiency of noble metals, three-dimensionally ordered micro/mesoporous (3-DOM) supported high dispersion noble metal nanoparticles have been reported by Dai's group [19] and Li's group [20]. However, high costs have limited their wide application. Transition metal elements generally have multiple valence states and easily form a redox cycle between the high and low oxidation states, and lattice oxygen can be released and restored [21]. For example, LaMnO₃ with mild citric acid etching showed good catalytic activity due to higher surface area, abundant vacancies, higher surface Mn⁴⁺/Mn³⁺ ratio, and more active oxygen species [22]. Li's group obtained Co₃O₄ nanosheets with exposed high index (112) crystal planes, which showed a high catalytic performance for CCM because the unusually high index crystal planes were more reactive than common planes such as (001) and (011) [23]. Fe-substituted hexaaluminates with superior thermal stability synthesized by a two-step strategy were shown to enhance surface area and show high catalytic activity [24,25]. Other metals oxides, such as Cu, Cr, In, and Sn oxides, have been used as catalysts in the past decades [21,26,27]. However, the catalytic activity of those oxides for complete oxidation of CH₄ above 450 °C occurred at relatively low gas hour space velocity (GHSV). Therefore, efforts to develop non-noble metal oxides catalysts for low temperature methane oxidation become more urgent.

Spinel oxides with catalytic activity even higher than the precious-metal-based catalysts are promising candidates for CCM at low temperature, although relatively little research has been conducted on this catalytic material [21]. Tao's group first reported that NiCo₂O₄ spinel oxides exhibited higher catalytic activity at relatively low temperature. This results from the integration of Ni³⁺, on which methane dissociates to methyl and couples with the surface lattice oxygen atoms to form –CH₃O, and CO₂ forms after dehydrogenation and oxidation [28]. McEwen et al. [29] also presented some evidence that a high oxidation state of Ni is more effective for the first C–H cleavage in methane using both experiments and density functional theory (DFT) calculations. In containing the Co spinel structure, however, most researchers agreed that Co³⁺ association with catalytic activity was essential [23,30]. Lim et al. [3,31] controlled the Co to Ni ratio and used mesoporous silica KIT-6 as the hard template to synthesize ordered mesoporous NiCo₂O₄, which showed higher activity due to the high amount of Co³⁺ and surface oxygen species on the surface. Furthermore, others also reported methane more easily dissociates to methyl on Co cations compared to Ni cations based on results from DFT calculations [8]. Therefore, the relative catalytic activities of Ni³⁺

and Co³⁺ is still a controversial issue.

In order to investigate the relationship between catalytic performance and number of high state valence cations, we designed a series of spinel oxides catalysts by exposing different amounts of Ni³⁺ and Co³⁺ deposited on the surface by hydrothermal method and co-precipitation method. We also focused on preparation methods and the relationship between structure and catalytic properties of spinel oxides [32,33]. Through hydrothermal synthesis, we successfully obtained multiporous spinel oxide nanosheets with high surface area. There are few reports of complete methane oxidation under 350 °C using porous spinel oxides nanosheets. At the same time, these novel porous nanosheets may also be utilized in other systems, such as an electrode material in pseudo capacitors and in oxygen evolution reduction (OER) [33–35].

2. Experimental

2.1. Catalyst preparation

All the chemicals were of analytical grade and used as received without further purification.

Co(NO₃)₂·6H₂O (10 mmol, 2.91 g), Ni(NO₃)₂·6H₂O (5 mmol, 1.45 g) and urea (100 mmol, 6 g) were physically mixed and completely dissolved in 70 mL deionized water for hydrothermal synthesis of NiCo₂O₄. The obtained solutions were transferred into 100 mL autoclaves with a Teflon liner at 120 °C and kept for 10, 20, 36, 60, and 72 h. The resulting product was centrifuged and washed with deionized water 3 times, was then dried overnight at room temperature, and was finally calcined in air at 350 °C for 2 h. For synthesis of Co₃O₄, Co(NO₃)₂·6H₂O (10 mmol, 2.91 g) and urea (100 mmol, 6 g) were dissolved in 70 mL deionized water. The rest of the synthetic procedure was similar to that used for synthesis of the NiCo₂O₄.

Co(NO₃)₂·6H₂O (10 mmol, 2.91 g) and Ni(NO₃)₂·6H₂O (5 mmol, 1.45 g) were dissolved in 20 mL deionized water under magnetic stirring for 1 h to synthesize NiCo₂O₄ by co-deposition precipitation. Then 50 mL NaOH (1 mol/L) was added to the solution under continuous stirring. The precipitate was collected by centrifuging and washing 3 times, was dried overnight at room temperature, and was finally calcined in air at 350 °C for 2 h. For synthesis of Co₃O₄, the above procedure was used without the added Ni(NO₃)₂·6H₂O.

2.2. Catalyst characterization

The surface areas of the samples were determined from N₂ adsorption isotherms at 197 °C with the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2010 analyzer. Prior to the measurement, the samples were outgassed at 300 °C for 2 h under a reduced pressure of 10^{–5} Torr.

The crystal structure of the catalysts was examined using powder X-ray diffraction (XRD). XRD analysis was carried out on a Bruker D8 Advance with Cu K_α radiation source (λ = 1.5406 Å). A scan rate of 10°/min from 10° to 80° allowed us to

obtain the XRD pattern. The crystal structure parameters of the samples were calculated using the MDI Jade 6.5.

The hydrogen temperature-programmed reduction (H₂-TPR) experiments were performed on a Micromeritics AutoChem 2920 instrument. Prior to reduction, the samples were pretreated at 300 °C for 1 h in an argon flow of 30 mL/min and then cooled down to room temperature. They were then reduced with 10% H₂/Ar until the temperature reached 500 °C at a rate of 3 °C/min.

X-ray photoelectron spectroscopy (XPS) was performed using a VG Thermo ESCALAB 250 spectrometer. The instrument uses a focused monochromatic Al K α X-ray (1486.7 eV) source operated at 120 W and outputs a 500 μ m-diameter beam. The binding energy scale was calibrated using the known standard carbon C 1s line at 284.6 eV. Deconvolution of the XPS peak was performed with XPSPEAK.

Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 with an accelerating voltage of 200 kV. The lattice spacing and lattice planes of the samples were analyzed using DigitalMicrograph.

2.3. Catalytic activity measurements

Methane combustion catalytic activity was measured using a conventional quartz tubular reactor (i.d., 6 mm; length, 300 mm) at atmospheric pressure. The reagent gas mixture (1 %CH₄/air vol%) was flowed over 100 mg catalysts at a gas hourly space velocity (GHSV) of 24000 mL g⁻¹h⁻¹. The reaction of methane combustion was stabilized for 20 min, and activity data were obtained at steady state conditions from 200 °C to 500 °C, with temperature increased in increments of 25 °C. The reactants and reaction products were analyzed by an on-line gas chromatograph. Kinetic studies of complete oxidation of methane were conducted in the kinetics control regime (conversion < 15%). The CCM reaction rates were calculated using Eq. (1):

$$R(\text{mmol h}^{-1} \text{ g}_{\text{cat}}^{-1}) = \frac{X_f GC}{22.4W_{\text{cat}}} \quad (1)$$

X_f is the feed concentration of CH₄ and G is the gas flow rate (mL/h). C is the CH₄ conversion and W_{cat} is the weight of the spinel oxides catalysts (g). The number of (Co³⁺ + Ni³⁺) atoms of surface were calculated using Eq. (2):

$$N(\text{atoms}) = KQ A_{\text{BET}} W_{\text{cat}} \quad (2)$$

Q is the (Ni³⁺ + Co³⁺) to (Ni + Co + O) ratio on the surface obtained from XPS, A_{BET} is the surface area (m²/g) determined from the BET method, and K is the number of atoms per unit area (atom/m²), which we can estimate from the solid surface model (see Figs. S1 and S2 in supporting information)

3. Results and discussion

3.1. Structural properties of the catalysts

Fig. 1 shows the XRD patterns of the samples synthesized at different hydrothermal times. Obviously, the five patterns indicate pure NiCo₂O₄ because all the diffraction peaks can be indexed to NiCo₂O₄ and match well with a cubic crystal struc-

Fig. 1. XRD patterns of NiCo₂O₄ samples formed after different hydrothermal times: (1) 72 h, (2) 60 h, (3) 36 h, (4) 20 h, and (5) 10 h.

ture (JCPDS No. 73-1702). However, the differences, such as in lattice parameters and crystallite sizes, obtained from the Jade refinement of the XRD patterns are listed in Table 1. The lattice parameter decreased with hydrothermal time increasing up to 60 h (8.093 Å). Until the hydrothermal time up to 72 h, the lattice parameter increased to 8.104 Å. The lattice parameter associated with ionic size and ionic radius of Co³⁺ (0.055 nm) is larger than that of Ni³⁺ (0.053 nm), but is smaller than Ni²⁺ (0.069 nm) [3,36]. Previous studies show that Ni ions occupy octahedral sites of the spinel structure, while Co ions occupy both tetrahedral and octahedral sites [37,38], and we can reasonably infer that the large size of Ni²⁺ occupy octahedral sites. Thus, there is a very low amount of Ni³⁺ in the spinel structure at the beginning of the hydrothermal process. The amount of Ni³⁺ in the lattice cell increases with hydrothermal time, and the number of Ni³⁺ is maximum at 60 h hydrothermal time. The XRD patterns of the of NiCo₂O₄ and Co₃O₄ prepared by hydrothermal method and the co-precipitation method are presented in Fig. 2, and the lattice parameter and crystalline size also listed in Table 1. For 60 h hydrothermal NiCo₂O₄, a slight shift in the diffraction peak toward higher angles is observed in comparison to 60 h hydrothermal Co₃O₄. This result matched well with the spinel structure of Co₃O₄ (JCPDS No. 80-1542), resulting in smaller lattice parameter (8.093 Å) than that of 60

Table 1

Lattice parameter (a) and crystalline size (D) of catalysts calculated by fitting the XRD patterns using the Jade program.

Catalyst	a (Å)	D (nm)
JCPDS 73-1702 NiCo ₂ O ₄	8.114	–
hydrothermal 10 h	8.120	9.90
hydrothermal 20 h	8.107	11.5
hydrothermal 36 h	8.099	11.6
hydrothermal 60 h	8.093	12.4
hydrothermal 72 h	8.104	12.9
JCPDS 71-0816 Co ₃ O ₄	8.065	–
Co-precipitation NiCo ₂ O ₄	8.071	15.2
Co-precipitation Co ₃ O ₄	8.064	17.4
JCPDS 80-1542 Co ₃ O ₄	8.110	–
Hydrothermal 60 h Co ₃ O ₄	8.110	12.1

Fig. 2. XRD patterns of the spinel oxides crystals formed by 60 h hydrothermal and co-precipitation method.

h hydrothermal Co_3O_4 (8.110 Å). Some Ni^{3+} ions insert themselves into the Co_3O_4 spinel structure, leading to a decrease in the lattice parameter. For co-precipitation of NiCo_2O_4 , however, the diffraction peak shifted towards low angles compared to co-precipitated Co_3O_4 , which matched with another spinel structure of Co_3O_4 (JCPDS 71-0816) with a larger lattice parameter (8.071 Å) than that of co-precipitated Co_3O_4 (8.064 Å). The reason is that large Ni^{2+} ions occupy the octahedral sites in the Co_3O_4 spinel structure. It is worthy to note that co-precipitation synthesized spinel oxides have relatively small crystalline cells due to the large number of defects in the crystalline cell. The crystal formed by the hydrothermal method tends to crystallize better and form fewer defects [39].

Obviously, the TEM pictures shown in Fig. 3, also demonstrated that 60 h hydrothermal spinel oxides had relatively smaller particles than co-precipitation spinel oxides. The crystalline sizes of 60 h hydrothermal NiCo_2O_4 and 60 h hydrothermal Co_3O_4 almost have the same about of 10–20 nm. There is a good correlation between crystalline size of the hydrothermal spinel oxide samples calculated by XRD and TEM. Generally speaking, the (220) interplanar lattice spacing in the NiCo_2O_4 spinel structure (JCPDS No. 73-1702) is 0.287 nm and (311) is 0.244 nm. However, lattice fringes with an interplanar lattice spacing of 0.281 nm corresponding to the (220) atomic planes and 0.238 nm corresponding to the (311) atomic planes were observed in HRTEM image (Fig. 3(b)), and all the lattice fringe spacings of the 60 h hydrothermal NiCo_2O_4 decrease. One possible cause is that the partial Co^{3+} ions are replaced by smaller Ni^{3+} ions. This indicates consistency with lattice contraction, which leads to a decrease in the lattice parameter by the calculated XRD results. However, there is no obvious change in the lattice fringe spacing of the 60 h hydrothermal Co_3O_4 . Moreover, the selected area fast Fourier transform (FFT) confirms that 60 h hydrothermal NiCo_2O_4 and 60 h hydrothermal Co_3O_4 consist of the single-crystalline particles (insert of Fig. 3(b) and (d)). The angle labeled in the FFT pattern is 65°, which is in agreement with the theoretical angle between the (220) and (311) planes. The set of diffraction spots can be in-

Fig. 3. TEM, HRTEM and FFT (insert) images of 60 h hydrothermal NiCo_2O_4 (a, b), 60 h hydrothermal Co_3O_4 (c, d), co-precipitated NiCo_2O_4 (e) and Co_3O_4 (f).

dexed as the (114), which also indicated dominant exposed planes of 60 h hydrothermal NiCo_2O_4 are (114). Meanwhile, the dominant exposed planes of the Co_3O_4 nanosheets are (112), which is consistent with Li's results [23]. From the above analysis of the exposed planes, we can build up a solid surface model (Fig. S1 and S2) with XPS and H_2 -TPR results to understand the correlation between structure and catalytic activity.

Furthermore, the morphology of samples is clearly visible in the TEM images. Hydrothermal synthesis of spinel oxide nanosheets occurs by assembling by a large number of small particles, resulting in a disordered mesoporous structure, while co-precipitated samples have no definite morphology. SEM images of the 60 h hydrothermal NiCo_2O_4 (Fig. S3(a)) and Co_3O_4 (Fig. S3(b)) samples further confirm their sheet-shaped structures. Generally speaking, the nanosheet has a larger surface area than other nanoshapes. The BET surface area of the samples are summarized in Table 2. Obviously, the hydrothermal samples have larger surface area than the co-precipitated sample, and 60 h hydrothermal NiCo_2O_4 catalysts have the highest surface area among all samples.

3.2. Redox properties of the catalysts

To investigate the reducibility of the Ni and Co species in the spinel oxides catalysts, we performed H_2 -TPR measurements at

Table 2

Summary of the determination and quantitative analysis of surface Co and Ni from XPS results.

Catalyst	Co ³⁺ (%)	Ni ³⁺ (%)	Co ³⁺ + Ni ³⁺ (%)	BET area (m ² /g)	Co ³⁺ + Ni ³⁺ Atoms number (×10 ¹⁸ atoms)
Co-precipitation Co ₃ O ₄	3.00	0.00	3.00	33.1	2.5
Co-precipitation NiCo ₂ O ₄	3.35	3.82	7.17	24.0	4.4
Hydrothermal 10h NiCo ₂ O ₄	8.03	4.61	12.64	45.6	14.9
Hydrothermal 72h NiCo ₂ O ₄	4.90	5.38	10.28	65.0	17.2
Hydrothermal 60h Co ₃ O ₄	18.11	0.00	18.11	39.0	17.8
Hydrothermal 20h NiCo ₂ O ₄	7.49	6.26	13.75	52.2	18.5
Hydrothermal 36h NiCo ₂ O ₄	8.01	6.47	14.48	52.0	19.5
Hydrothermal 60h NiCo ₂ O ₄	6.39	8.22	14.61	70.8	26.7

slow heating rate 3 °C/min. Through slow heating, the Ni³⁺ and Co³⁺ peaks can be obviously distinguished in the H₂-TPR profiles. As shown in Fig. 4(c), there are two reduction peaks both in the 60 h hydrothermal and co-precipitated Co₃O₄, which correspond to stepwise reduction of Co₃O₄. The first peak position at 224 °C is related to the Co³⁺ to Co²⁺ transition, and the second is attributed to full reduction of Co²⁺ to Co⁰. There are a few peaks in the NiCo₂O₄ profile (Fig. 4(a)), which is different

from others previous studies [40,41]. In order to verify the first peak in the 60 h hydrothermal NiCo₂O₄ corresponding to Ni³⁺ reduction, we compared with NiO, where calcination at low temperatures (< 350 °C) can form a few Ni³⁺ on the surface [42]. It is noteworthy that there are two peaks in the case of NiO. The large reduction peak at 224 °C overlaps with the Co³⁺ reduction peak, and a smaller peak at 169 °C is due to a small number of Ni³⁺ on the surface that reduce quickly compared to

Fig. 4. H₂-TPR profile of spinel oxide samples and first peak analysis. (a) NiCo₂O₄, (b) 60 h hydrothermal spinel oxides and NiO, (c) Co₃O₄, (d) first peak position and initial point.

NiCo_2O_4 . Thus, we confirmed that the first peak is attributed to the reduction of Ni^{3+} to Ni^{2+} . Obviously, the reduction peak intensity at 177 °C for 60 h hydrothermal NiCo_2O_4 is greater than the intensity for co-precipitated NiCo_2O_4 . This indicates that 60 h hydrothermal NiCo_2O_4 possesses a greater quantity of Ni^{3+} . H_2 -TPR spectra from hydrothermal NiCo_2O_4 samples are shown in Fig. S4. The results indicate that the 60 h hydrothermal NiCo_2O_4 contains the largest amount of Co^{2+} among all samples,

and it has the largest amount of Ni^{3+} . This agrees with the XRD and TEM results. In co-precipitated NiCo_2O_4 and Co_3O_4 , the first reduction peak occurs earlier because there are a larger number of adsorbed oxygen species on the solid surface, resulting in very easy reduction, which is consistent with the observed O 1s XPS spectra.

We performed XPS to derive insights into the adsorbed species and metal oxidation states of catalysts, which is an effective

Fig. 5. XPS spectra of spinel oxide samples. (a) Co 2p, (b) O 1s, (c) Ni 2p_{3/2}, (d) summary of determination and quantitative analysis for surface O from the O 1s XPS.

technique to gain surface information [43]. Fig. 5(c) illustrates the XPS results from Ni $2p_{3/2}$ for 60 h hydrothermal NiCo_2O_4 and co-precipitated NiCo_2O_4 (other hydrothermal samples are shown in Fig. S5). The coexistence of Ni(II) and Ni(III) in 60 h hydrothermal and co-precipitated NiCo_2O_4 catalysts is indicated by the shoulder observed on the main peak at 853.6 eV, which is assigned to the Ni(II) species. The higher binding energy (BE) peak at 861.0 eV and its shakeup satellites are due to overlapping Ni(II) and Ni(III) satellites. The surface $\text{Ni}^{3+}/(\text{Ni} + \text{Co} + \text{O})$ molar ratio in 60 h hydrothermal NiCo_2O_4 is approximately 8.22%, which is the largest among all samples. The lowest ratio occurs in the co-precipitated NiCo_2O_4 with 3.82% (Table 2). This result agrees well with the H_2 -TPR results. Co $2p$ XPS spectra of four spinel oxide samples are shown in Fig. 5(a). One should note that the $\text{Co}^{3+}/(\text{Ni} + \text{Co} + \text{O})$ ratio for 60 h hydrothermal Co_3O_4 is the highest in all samples, and the value in the co-precipitated NiCo_2O_4 sample is higher than in the co-precipitated Co_3O_4 sample, which agrees well with results reported by others [31].

In the O 1s XPS spectra (Fig. 5(b)), the broad peaks can be decomposed into four major components by deconvolution. These peaks correspond to lattice oxygen, a surface OH group, defective oxygen, and adsorbed moisture. Quantitative analysis in Fig. 5(d) reveals the lattice oxygen percentage obviously increases for hydrothermal synthesis of spinel oxides compared to the co-precipitation method, and co-precipitated spinel oxides have more adsorbed oxygen species on the surface. Generally speaking, surface oxygen is very important in catalytic oxidation because surface oxygen is more reactive than gaseous oxygen [44]. As is well known, the adsorbed oxygen species increase with increasing oxygen pressure. Therefore, in order to investigate the effect of adsorbed oxygen species on the catalytic reaction, we measured the CH_4 reaction rate under different oxygen pressures, as shown in Fig. 6(a). It suggests that the reaction rate is unaffected by O_2 pressure when O_2

pressure is greater than 15 kPa, which means adsorbed oxygen species are not crucial for the whole catalytic system under catalytic reaction conditions (O_2 pressure about 20 kPa). Moreover, the CH_4 reaction rate is proportional to the CH_4 pressure shown in Fig. 6(b), which is consistent with previous findings that activation and dissociation of the C–H bond is the rate-limiting step [28,44].

3.3. Catalytic activity for methane oxidation

Fig. 7(a) shows the light-off curves for methane combustion in samples with various hydrothermal synthesis times. We can conclude that the catalytic activity improves as hydrothermal time increases, and 60 h hydrothermal synthesis time resulted in 100% methane conversion at 340 °C. From the catalytic activity and XRD results, we can reasonably infer that exposing many high valence state ions on the surfaces of spinel oxide can be attributed to a proper hydrothermal synthesis time, which results in more active centers for CCM. Moreover, as can be seen from Fig. 7(b), the hydrothermal and co-precipitation syntheses of spinel oxides show different light-off curves during CCM. The catalytic performance of hydrothermally synthesized spinel oxides is much better than their co-precipitated counterparts. The co-precipitated sample containing NiCo_2O_4 performs better than co-precipitated Co_3O_4 . This result agrees well with previous studies, where results show that the concentration of surface Ni^{3+} is responsible for high catalytic performance [28]. However, it also should be noted that 60 h hydrothermal NiCo_2O_4 catalytic activity corresponds closely to 60 h hydrothermal Co_3O_4 with 90% methane conversion at 325 °C, which is different from previous reports [3,8,28]. In order to understand the difference, we compared 60 h hydrothermal NiCo_2O_4 with 60 h hydrothermal Co_3O_4 at different GHSV values (Fig. 7(c)). Clearly, when working at relatively high GHSV (e.g., 84000 $\text{mL h}^{-1} \text{g}^{-1}$), hydrothermal NiCo_2O_4 catalytic perfor-

Fig. 6. CH_4 reaction rates as a function of O_2 pressure (a) and CH_4 pressure (b) for 60 h hydrothermal NiCo_2O_4 at 250 °C. The catalyst 20 mg + quartz 500 mg, gas flow rate 100 mL/min, space velocity 300,000 $\text{mL h}^{-1} \text{g}^{-1}$. The CH_4 pressure is fixed at 3 kPa when changing the O_2 pressure. The O_2 pressure is fixed at 10 kPa when changing the CH_4 pressure.

Fig. 7. Methane conversion over spinel oxide catalysts: (a) NiCo₂O₄ with different hydrothermal times and GHSV 24000 mL h⁻¹ g⁻¹; (b) Spinel oxides with hydrothermal and co-precipitation methods and GHSV 24000 mL h⁻¹ g⁻¹; (c) Hydrothermal spinel oxide tests at different GHSV values; (d) Stability test for hydrothermal spinel oxides.

mance is higher than that of Co₃O₄. We try to use previous studies on Co³⁺ or Ni³⁺ as an active center for CCM to explain our experimental results. If Co³⁺ ions of the spinel oxides surface were active centers, 60 h hydrothermal Co₃O₄ and co-precipitated Co₃O₄ both would have better catalytic performance than NiCo₂O₄. If the active sites were Ni³⁺, co-precipitated NiCo₂O₄ would be superior to 60 h hydrothermal Co₃O₄. Therefore, we infer that Co³⁺ and Ni³⁺ maybe both are active sites in the spinel structure. Then we calculated the (Ni³⁺ + Co³⁺) to (Ni + Co + O) ratio on the surface from the XPS spectra. Table 2 clearly indicates that the (Ni³⁺ + Co³⁺) to (Ni + Co + O) ratio in the 60 h hydrothermal Co₃O₄ is the highest among all samples. It seems that 60 h hydrothermal Co₃O₄ would have the best catalytic activity. However, this was not the case. While we take the surface area and crystal plane into account to calculate the number of (Ni³⁺ + Co³⁺) ions on the surface, the methane combustion light-off curves give a relatively rational explanation. As indicated in Fig. 8(b), as the (Ni³⁺ + Co³⁺) content increases on the surface, the reaction rate also increases. Thus, this is direct evidence that Ni³⁺ and Co³⁺ both serve as active centers on the surface of spinel oxides. The ap-

parent activation energy of all the samples are very similar in Fig. 8(a), which indicate they have similar activation modes and the same active center [45]. This indirect evidence also supports our conclusion that Ni³⁺ and Co³⁺ both serve as active centers.

Our catalysts are compared with some previously reported catalysts, including noble metal catalysts, as summarized in Table 3. To examine the catalytic performance of NiCo₂O₄ in the complete oxidation of CH₄ from the exhaust of a natural gas engine, we measured the catalytic performance of complete CH₄ oxidation on NiCo₂O₄ in two different gas mixtures (Fig. 9). First, 1% CH₄ and 10% H₂O balanced with air at a flow rate 40 mL/min (Fig. 9(a)) is used to evaluate the influence of H₂O in the catalytic system. It is clear that the addition of H₂O causes the *T*₉₀ to lag behind about 50 °C compared to the case without H₂O. We also noted that the initial activity starts at a low temperature of about 200 °C, which indicates the added H₂O will not cover the active sites and maybe only take more heat from the catalyst surface, resulting in a slight increase in complete oxidation temperature at relatively low GHSV. Second, results with 0.2% CH₄, 5% O₂, 10% H₂O, and 15% CO₂ balanced with

Fig. 8. (a) Arrhenius plots for the reaction kinetics; (b) The relationship between the reaction rate and number of $\text{Co}^{3+} + \text{Ni}^{3+}$ atoms on the surface.

Table 3
Overview of catalytic activities for our samples and the samples reported in the literature.

Catalyst	Reaction condition	T_{50} (°C)	Ref.
Hydrothermal 60 h Co_3O_4	1% CH_4 ; 99% Air; 24000 $\text{mL h}^{-1} \text{ g}^{-1}$	283	This work
Hydrothermal 60 h Co_3O_4	1% CH_4 ; 99% Air; 60000 $\text{mL h}^{-1} \text{ g}^{-1}$	348	This work
Hydrothermal 60 h NiCo_2O_4	0.2% CH_4 ; 5% O_2 ; 10% H_2O ; 15% CO_2 ; 60000 $\text{mL h}^{-1} \text{ g}^{-1}$	335	This work
Hydrothermal 60 h NiCo_2O_4	1% CH_4 ; 99% Air; 84000 $\text{mL h}^{-1} \text{ g}^{-1}$	360	This work
Hydrothermal 60 h NiCo_2O_4	1% CH_4 ; 4% O_2 ; 78000 $\text{mL h}^{-1} \text{ g}^{-1}$	361	This work
Co_3O_4	1% CH_4 ; 10% O_2 ; 36000 $\text{mL h}^{-1} \text{ g}^{-1}$	597	[50]
Co_3O_4	2% CH_4 ; 98% Air; 12000 $\text{mL h}^{-1} \text{ g}^{-1}$	297	[50]
Co_3O_4	1% CH_4 ; 10% O_2 ; 18000 $\text{mL h}^{-1} \text{ g}^{-1}$	303	[23]
$3\text{Co}_3\text{O}_4\text{-SnO}_2$	1% CH_4 ; 10% O_2 ; 48000 $\text{mL h}^{-1} \text{ g}^{-1}$	410	[26]
MgCr_2O_4	4% CH_4 ; 25% O_2 ; 6000 $\text{mL h}^{-1} \text{ g}^{-1}$	565	[51]
NiCo_2O_4	1% CH_4 ; 22% O_2 ; 17000 $\text{mL h}^{-1} \text{ g}^{-1}$	295	[28]
NiO-NaOH	1% CH_4 ; 99% Air; 60000 $\text{mL h}^{-1} \text{ g}^{-1}$	335	[52]
$\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ nanocubes	1% CH_4 ; 22% O_2 ; 17000 $\text{mL h}^{-1} \text{ g}^{-1}$	450	[53]
$0.5\text{Pd/Al}_2\text{O}_3$	0.5% CH_4 ; 2% O_2 ; 200000 $\text{mL h}^{-1} \text{ g}^{-1}$	325	[52]
$\text{Pd@CeO}_2/\text{H-Al}_2\text{O}_3$	2.5% CH_4 ; 20% O_2 ; 10% H_2O ; 20000 $\text{mL h}^{-1} \text{ g}^{-1}$	280	[6]
$1.97\text{Au}_{0.45}\text{Pd/meso-Co}_3\text{O}_4$	1.5% CH_4 ; 98.5% Air; 80000 h^{-1}	300	[54]
$1\%\text{Pd-0.2\%Pt/Ce/Al}_2\text{O}_3$	1% CH_4 ; 99% Air; 48000 h^{-1}	340	[13]
$1.1\%\text{Pd/Al}_2\text{O}_3$	2% CH_4 ; 20% O_2 ; 30000 $\text{mL h}^{-1} \text{ g}^{-1}$	420	[55]
$1.1\%\text{Pt/3DOM CYZ}$		434	[56]

N_2 at high GHSV (60000 $\text{mL h}^{-1} \text{ g}^{-1}$) (Fig. 9(b)) show that H_2O has a minor impact on catalytic performance, especially for 60 h hydrothermal Co_3O_4 , and CH_4 can be completely oxidized to CO_2 and H_2O at 450 °C. Generally, H_2O is easily adsorbed on the catalyst surface, which tends to reduce catalytic activity. However, it is worth noting that the activity of 60 h hydrothermal NiCo_2O_4 and Co_3O_4 , the first C–H cleavage remains at 200 °C, which means H_2O cannot completely cover the active sites. On the other hand, our catalysts prepared by long hydrothermal treatments showed a very low content of adsorbed moisture on the catalyst surface, as indicated by the O 1s XPS results. This means that H_2O is weakly adsorbed on the catalyst surface, especially at high temperature. These gas compositions are typically used in the evaluation of catalytic performance of Pd- and Pt-based catalysts for complete oxidation of CH_4 in the exhaust of natural gas engines [46–48]. Thus, it is evident that

60 h hydrothermal spinel oxide catalysts show higher activity than some noble metal catalysts.

Furthermore, the stability performance shown in Fig. 7(d) indicates that both 60 h hydrothermal NiCo_2O_4 and Co_3O_4 are able to completely oxidize CH_4 to CO_2 , and catalytic activity does not obviously decline for 12 h under feed gas including 10 vol% H_2O at 425 °C (GHSV = 24000 $\text{mL h}^{-1} \text{ g}^{-1}$). On the other hand, our catalysts were repeatedly used several times at different GHSV and different feed gas compositions, which also exhibit good stability. We can confirm that the stability of spinel oxides improves as the extensive hydrothermal time results in highly crystalline structures. This is supported by the appearance of a larger lattice oxygen peak in the O 1s XPS spectra.

The correlation between structure and catalytic activity is established for 60 h hydrothermal spinel oxides by combining the activity measurements with the characterization results. As

Fig. 9. Catalytic performance of 60 h hydrothermal spinel oxides in exhaust gases from natural gas engines. (a) CH₄ 1%, H₂O 10%, Air 79%, flow rate of the mixture 40 mL/min, catalyst 100 mg; (b) CH₄ 0.2%, O₂ 5%, H₂O 10%, CO₂ 15%, N₂ 69.8%, flow rate of the mixture 100 mL/min, catalyst 100 mg.

observed in TEM, the 60 h hydrothermal spinel oxides investigated here both exhibit disordered nanosheet structure due to their disordered assembly from small nanoparticles. 60 h hydrothermal NiCo₂O₄ have higher surface area as confirmed with BET measurements. In general, a high surface area often results in greater catalytic activity because more active sites are exposed during the catalytic reaction [49]. For hydrothermal synthesis of spinel oxides, both have high valence ion content on the surface based on analysis of the XPS, H₂-TPR, XRD, and TEM results, as well as the solid surface model (Fig. S1 and S2), which leads to excellent catalytic performance. It can be concluded that a strong correlation exists between activity and structure and, more significantly, that a high concentration of valence ions and high surface area are responsible for high methane combustion activity.

4. Conclusions

In summary, we synthesized a series of spinel oxide catalysts with different amounts of Ni³⁺ and Co³⁺ cations by hydrothermal and co-precipitation methods. As the amount of (Ni³⁺ + Co³⁺) on the surface increases, the catalytic activity for methane combustion also increases. The (Ni³⁺ + Co³⁺) content on the 60 h hydrothermal NiCo₂O₄ surface is the highest among all samples, thus it exhibits the best catalytic performance and results in complete CH₄ conversion at 340 °C. Therefore, we are convinced that Co³⁺ and Ni³⁺ can both function as active sites on the surface of spinel oxides. Moreover, multiporous spinel oxide nanosheets without any surfactants and templates were obtained from hydrothermal synthesis and were nearly unaffected by water in low-temperature methane combustion. This occurred because the long hydrothermal treatment results in less adsorbed oxygen on spinel oxides. Finally, multiporous nanosheet spinel oxides with high surface areas and our conclusion that both Co³⁺ and Ni³⁺ function as active sites may be applicable in other catalytic oxidation systems in the future.

References

- [1] Z. H. Li, G. B. Hoflund, *React. Kinet. Catal. Lett.*, **1999**, 66, 367–374.
- [2] P. Goyal, *Atmos. Environ.*, **2003**, 37, 5423–5431.
- [3] T. H. Lim, S. J. Cho, H. S. Yang, M. H. Engelhard, D. H. Kim, *Appl. Catal. A*, **2015**, 505, 62–69.
- [4] R. Burch, P. K. Loader, *Appl. Catal. B*, **1994**, 5, 149–164.
- [5] P. Glin, M. Primet, *Appl. Catal. B*, **2002**, 39, 1–37.
- [6] M. Cargnello, J. J. D. Jan, J. C. H. Garrido, K. Bakhmutsky, T. Montini, J. J. C. Gmez, R. J. Gorte, P. Fornasiero, *Science*, **2012**, 337, 713–717.
- [7] X. X. Chen, Y. P. Li, X. Y. Pan, D. Cortie, X. T. Huang, Z. G. Yi, *Nat. Commun.*, **2016**, 7, 12273.
- [8] Z. Ren, V. Botu, S. B. Wang, Y. T. Meng, W. Q. Song, Y. B. Guo, R. Ramprasad, S. L. Suib, P. X. Gao, *Angew. Chem. Int. Ed.*, **2014**, 53, 7223–7227.
- [9] R. J. Farrauto, *Science*, **2012**, 337, 659–660.
- [10] D. Dissanayake, J. H. Lunsford, M. P. Rosynek, *J. Catal.*, **1994**, 146, 613–615.
- [11] Y. H. Chin, C. Buda, M. Neurock, E. Iglesia, *J. Am. Chem. Soc.*, **2013**, 135, 15425–15442.
- [12] G. H. Zhu, J. Y. Han, D. Y. Zemlyanov, F. H. Ribeiro, *J. Am. Chem. Soc.*, **2004**, 126, 9896–9897.
- [13] X. Fan, F. Wang, T. L. Zhu, H. He, *J. Environ. Sci.*, **2012**, 24, 507–511.
- [14] M. Hoffmann, S. Kreft, G. Georgi, G. Fulda, M. M. Pohl, D. Seeburg, C. Berger-Karin, E. V. Kondratenko, S. Wohlrab, *Appl. Catal. B*, **2015**, 179, 313–320.
- [15] J. Shen, R. E. Hayes, X. X. Wu, N. Semagina, *ACS Catal.*, **2015**, 5, 2916–2920.
- [16] X. L. Zou, Z. B. Rui, S. Q. Song, H. B. Ji, *J. Catal.*, **2016**, 338, 192–201.
- [17] R. Gholami, M. Alyani, K. Smith, *Catalysts*, **2015**, 5, 561–594.
- [18] X. Q. Pan, Y. B. Zhang, Z. Z. Miao, X. G. Yang, *J. Energy Chem.*, **2013**, 22, 610–616.
- [19] H. Arandiyn, H. X. Dai, K. M. Ji, H. Y. Sun, J. H. Li, *ACS Catal.*, **2015**, 5, 1781–1793.
- [20] S. H. Xie, Y. X. Liu, J. G. Deng, S. M. Zang, Z. H. Zhang, H. Arandiyn, H. X. Dai, *Environ. Sci. Technol.*, **2017**, 51, 2271–2279.

Graphical Abstract

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Surface density of synthetically tuned spinel oxides of Co³⁺ and Ni³⁺ with enhanced catalytic activity for methane oxidation

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The catalytic activity for complete methane oxidation positively correlates with the amount of high valence metal cations on the spinel oxide surface. The 60 h hydrothermal NiCo_2O_4 porous nanosheets have the best catalytic performance with $T_{90} = 325^\circ\text{C}$.

- [21] J. H. Chen, H. Arandiyana, X. Gao, J. H. Li, *Catal. Surv. Asia*, **2015**, 19, 140–171.
- [22] Y. Ding, S. Wang, L. Zhang, Z. P. Chen, M. Z. Wang, S. D. Wang, *Catal. Commun.*, **2017**, 97, 88–92.
- [23] L. H. Hu, Q. Peng, Y. D. Li, *J. Am. Chem. Soc.*, **2008**, 130, 16136–16137.
- [24] F. Huang, X. D. Wang, A. Q. Wang, J. M. Xu, T. Zhang, *Catal. Sci. Technol.*, **2016**, 6, 4962–4969.
- [25] M. Tian, X. D. Wang, X. Liu, A. Q. Wang, T. Zhang, *AIChE J.*, **2016**, 62, 792–801.
- [26] X. F. Tang, J. M. Hao, J. H. Li, *Front. Environ. Sci. Engin. China*, **2009**, 3, 265–270.
- [27] Y. E. Zheng, K. Z. Li, H. Wang, D. Tian, Y. H. Wang, X. Zhu, Y. G. Wei, M. Zheng, Y. M. Luo, *Appl. Catal. B*, **2017**, 202, 51–63.
- [28] F. F. Tao, J. J. Shan, L. Nguyen, Z. Y. Wang, S. R. Zhang, L. Zhang, Z. L. Wu, W. X. Huang, S. B. Zeng, P. Hu, *Nat. Commun.*, **2015**, 6, 7798.
- [29] F. L. Che, S. Ha, J. S. McEwen, *Angew. Chem. Int. Ed.*, **2017**, 56, 3557–3561.
- [30] Q. Wang, Y. Peng, J. Fu, G. Z. Kyzas, S. M. R. Billah, S. Q. An, *Appl. Catal. B*, **2015**, 168–169, 42–50.
- [31] T. H. Lim, S. B. Park, J. M. Kim, D. H. Kim, *J. Mol. Catal. A*, **2017**, 426, 68–74.
- [32] P. Boldrin, A. K. Hebb, A. A. Chaudhry, L. Otley, B. Thiebaut, P. Bishop, J. A. Darr, *Ind. Eng. Chem. Res.*, **2007**, 46, 4830–4838.
- [33] J. Bao, X. D. Zhang, B. Fan, J. J. Zhang, M. Zhou, W. L. Yang, X. Hu, H. Wang, B. C. Pan, Y. Xie, *Angew. Chem. Int. Ed.*, **2015**, 54, 7399–7404.
- [34] G. Q. Zhang, X. W. D. Lou, *Adv. Mater.*, **2013**, 25, 976–979.
- [35] X. H. Gao, H. X. Zhang, Q. G. Li, X. G. Yu, Z. L. Hong, X. W. Zhang, C. D. Liang, Z. Lin, *Angew. Chem. Int. Ed.*, **2016**, 55, 6290–6294.
- [36] Y. J. Wei, K. B. Kim, G. Chen, *Electrochim. Acta*, **2006**, 51, 3365–3373.
- [37] P. D. Battle, A. K. Cheetham, J. B. Goodenough, *Mater. Res. Bull.*, **1979**, 14, 1013–1024.
- [38] Y. E. Roginskaya, O. V. Morozova, E. N. Lubnin, Y. E. Ulitina, G. V. Lopukhova, S. Trasatti, *Langmuir*, **1997**, 13, 4621–4627.
- [39] M. Yoshimura, K. Byrappa, *J. Mater. Sci.*, **2007**, 43, 2085–2103.
- [40] Y. Liu, J. Xu, H. R. Li, S. X. Cai, H. Hu, C. Fang, L. Y. Shi, D. S. Zhang, *J. Mater. Chem. A*, **2015**, 3, 11543–11553.
- [41] X. Y. Wang, W. Wen, J. X. Mi, X. X. Li, R. H. Wang, *Appl. Catal. B*, **2015**, 176–177, 454–463.
- [42] G. El. Shobaky, P. C. Gravelle, S. J. Teichner, *J. Catal.*, **1969**, 14, 4–22.
- [43] J. Yang, C. Yu, S. X. Liang, S. F. Li, H. W. Huang, X. T. Han, C. T. Zhao, X. D. Song, C. Hao, P. M. Ajayan, J. S. Qiu, *Chem. Mater.*, **2016**, 28, 5855–5863.
- [44] Y. J. Xie, Y. L. Guo, Y. Guo, L. Wang, W. C. Zhan, Y. S. Wang, X. Q. Gong, G. Z. Lu, *Catal. Sci. Technol.*, **2016**, 6, 8222–8233.
- [45] X. W. Xie, Y. Li, Z. Q. Liu, M. Haruta, W. J. Shen, *Nature*, **2009**, 458, 746–749.
- [46] M. Honkanen, M. Kärkkäinen, V. Viitanen, H. Jiang, K. Kallinen, M. Huuhtanen, M. Vippola, J. Lahtinen, R. Keiski, T. Lepistö, *Top. Catal.*, **2013**, 56, 576–585.
- [47] T. Maillet, C. Solleau, J. Barbier Jr, D. Duprez, *Appl. Catal. B*, **1997**, 14, 85–95.
- [48] P. Gélin, L. Urfels, M. Primet, E. Tena, *Catal. Today*, **2003**, 83, 45–57.
- [49] B. Y. Bai, H. Arandiyana, J. H. Li, *Appl. Catal. B*, **2013**, 143, 677–683.
- [50] N. van Vegten, T. Baidya, F. Krumeich, W. Kleist, A. Baiker, *Appl. Catal. B*, **2010**, 97, 398–406.
- [51] J. N. Hu, W. Y. Zhao, R. S. Hu, G. Y. Chang, C. Li, L. J. Wang, *Mater. Res. Bull.*, **2014**, 57, 268–273.
- [52] F. Yu, X. L. Xu, H. G. Peng, H. J. Yu, Y. F. Dai, W. M. Liu, J. W. Ying, Q. Sun, X. Wang, *Appl. Catal. A*, **2015**, 507, 109–118.

- [53] S. H. Liang, T. G. Xu, F. Teng, R. L. Zong, Y. F. Zhu, *Appl. Catal. B*, **2010**, 96, 267–275.
- [54] Z. X. Wu, J. G. Deng, Y. X. Liu, S. H. Xie, Y. Jiang, X. T. Zhao, J. Yang, H. Arandiyán, G. S. Guo, H. X. Dai, *J. Catal.*, **2015**, 33, 13–24.
- [55] H. Widjaja, K. Sekizawa, K. Eguchi, H. Arai, *Catal. Today*, **1997**, 47, 95–101.
- [56] H. Arandiyán, H. X. Dai, K. M. Ji, H. Y. Sun, Y. Y. Zhao, J. H. Li, *Small*, **2015**, 11, 2366–2371.

调控尖晶石 Co^{3+} 和 Ni^{3+} 表面密度来提高催化甲烷氧化活性

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摘要: 天然气资源丰富、价格低廉, 因而被广泛用作燃料。天然气的主要成分是甲烷, 未燃烧完的甲烷所产生的温室效应是二氧化碳的 21 倍, 所带来的环境问题引起越来越多的研究者关注。但甲烷是最稳定的非极性有机小分子, C–H 键能高达 434 kJ/mol, 大多数催化剂很难将其在很低的温度下完全转化。C–H 键的活化解离是催化甲烷燃烧最关键的一步, 而活化 C–H 键方式主要有两大类: (1) 均裂活化机制, 一般用在贵金属催化剂上; (2) 异裂活化机制, 往往发生在过渡金属氧化物上。比较而言, 贵金属催化剂, 尤其是 Pd, 往往具有更优异的低温催化活性, 但价格昂贵, 从而限制了其广泛使用。因此, 开发更加高效的非贵金属催化剂用于废气中未转化的甲烷完全氧化是亟待解决的问题。

含有 Co 和 Ni 的尖晶石氧化物具有良好的催化甲烷燃烧活性, 有望代替贵金属催化剂, 但要求在低于 400 °C 完全转化, 仍具有一定挑战。另一方面, Ni^{3+} 和 Co^{3+} 哪个是活性中心, 还具有一定争议。因此, 我们通过水热法和共沉淀法合成一系列表面暴露不同数目的 Ni^{3+} 和 Co^{3+} 来探究表面高氧化态 Co 和 Ni 跟活性之间的关系。

XRD 和 TEM 结果表明, 相比于水热法合成的 Co_3O_4 , 水热法合成的 NiCo_2O_4 发生明显的晶格收缩现象, 这是由于在尖晶石体相中大量小半径 Ni^{3+} (0.053 nm) 取代了大半径 Co^{3+} (0.055 nm) 所致。同时还发现, 水热合成的尖晶石具有多孔纳米片层结构, 相比于共沉淀法合成的尖晶石具有更大的比表面积, 催化活性也更高。XPS 分析发现, 催化甲烷燃烧的活性随着表面 ($\text{Ni}^{3+} + \text{Co}^{3+}$) 含量增加而提高。结合文献分析和本文的实验结果推测, 表面的 Ni^{3+} 和 Co^{3+} 都可作为解离 C–H 键的活性中心。水热 60 小时合成的 NiCo_2O_4 纳米片表面 $\text{Ni}^{3+} + \text{Co}^{3+}$ 的数量最多, 所以具有最优异的催化性能, 大约在 280 °C 甲烷转化 50%。当加入 10% (体积比) 的水, 在高空速工况下对催化活性影响不大, 主要是因为长时间水热合成的尖晶石表面缺陷少, 对水的吸附弱, 这可通过 O 1s 图谱得到印证。总之, 这些研究结果能够给甲烷活化和开发更加高效和低成本催化剂一些启示。

关键词: 尖晶石氧化物; 催化甲烷燃烧; 多孔纳米片; 活性中心; 水热稳定性

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