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# Highly active and water tolerant $Pt/MFe_2O_4$ (M = Co and Ni) catalysts for low temperature CO oxidation



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Keywords: CO oxidation MFe <sub>2</sub> O <sub>4</sub> composite oxide Pt catalyst Spinel oxide H <sub>2</sub> O tolerant	Pt supported on $CoFe_2O_4$ and $NiFe_2O_4$ spinel oxides were much more active for low temperature CO oxidation compared to those supported on monometallic oxides (i.e. $Co_3O_4$ , $Fe_2O_3$ and NiO). The Pt/CoFe <sub>2</sub> O <sub>4</sub> catalyst gave the best performance, with a turnover frequency of $0.27 \text{ s}^{-1}$ at 50 °C, which was three times as high as that on the Pt/Fe <sub>2</sub> O <sub>3</sub> . The interaction between Pt and the spinel oxide facilitated the activation of the oxygen species as evidenced by the H <sub>2</sub> temperature programmed reduction results, and weakened the adsorption strength of CO on the Pt atoms as revealed by the in situ diffuse reflectance infrared Fourier transform spectroscopy results and kinetic investigation. These facts accounted for the enhanced reactivity. Moreover, the catalysts exhibited excellent water tolerance, which maintained activity even under 10 vol.% water vapor in the feed stock.

Therefore, these catalysts are promising for practical applications.

# 1. Introduction

Catalytic oxidation of CO is a very important reaction because of its essential applications such as automotive exhaust abatement [1] and proton exchange membrane fuel cell (PEMFC) [2]. Also, it is an excellent model reaction to investigate some essential issues in heterogeneous catalysis such as structure-performance relation and the nature of active sites [3]. Noble metal catalysts (Pt, Pd, Au, etc.) have been extensively studied due to their excellent CO low temperature catalytic activity [4–6]. In many cases, the noble metals were supported on support oxides and the supports also take part in the reaction as they may be responsible for the activation of oxygen species. Thus, reducible oxides such as CeO<sub>2</sub> [7], FeO<sub>x</sub> [8,9] and TiO<sub>2</sub> [10,11] have been extensively used as the supports, which not only helps the dispersion of the supported metal species but the reducibility of such oxide promotes the activation of oxygen species to further improve the catalytic performance. Many studies have shown that abundant surface oxygen vacancies in the CeO<sub>2</sub> are vital for the activation of oxygen species and thus the activity for CO oxidation [12,13]. Also, Ma et al. [14] found that the Pt supported on Fe<sub>3</sub>O<sub>4</sub> nanospheres resulted in a synergistic interaction between Pt and Fe<sub>3</sub>O<sub>4</sub> nanospheres, which promoted oxygen activation and thereby enhanced the CO oxidation activity.

Spinel oxides (with a general formula of AB2O4) have broad

application prospects in many fields, among which ferrite (MFe<sub>2</sub>O<sub>4</sub>) has attracted attention due to its unique physical and chemical properties [15–17]. The MFe<sub>2</sub>O<sub>4</sub> spinel oxides could be also used as supports for noble metals. For example, Zheng et al. [18] prepared a Pt/MgFe<sub>2</sub>O<sub>4</sub> catalyst by the colloidal deposition method, which showed high activity for CO oxidation at room temperature. The excellent catalytic performance was related to the undercoordinated oxygen species on the MgFe<sub>2</sub>O<sub>4</sub> support. These oxygen species could react with CO and then recovered in O2 conditions. Generally, normal spinel divalent ions occupy tetrahedral positions, and trivalent ions occupy octahedral positions. However, CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and CuFe<sub>2</sub>O<sub>4</sub> will partially form inverse spinel structure, and the molecular formula can be expressed as:  $(M^{2+}_{1-x}Fe^{3+}_{x})_{td}(M^{2+}_{x}Fe^{3+}_{2-x})_{oh}$  [19,20]. Studies have shown that the inverse spinel structure can improve the ability to activate oxygen. For example, Wu et al. [21] reported that when the structure of CoFe<sub>2</sub>O<sub>4</sub> (a normal spinel) was transformed to CoFeCoO4 (an inverse spinel), its electrocatalytic performance for the oxygen reduction reaction was significantly promoted due to the accelerated the activation and cleavage of O-O bonds via a dissimilarity effect of the distinct metal atoms co-occupying octahedral sites. Moreover, theoretical studies revealed that the Fe ions and Co ions in the octahedral position are mutually polarized due to the difference in electronegativity, so that the octahedral metal positions form a state of cationic and positive charge

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Received 30 January 2021; Received in revised form 11 March 2021; Accepted 4 April 2021 Available online 15 April 2021 0926-860X/© 2021 Elsevier B.V. All rights reserved. separation, which is very conducive to the activation of the O—O bond. Therefore, it seems that the spinel oxides could be promising supports for noble metal catalysts. In addition to the activity, the catalyst stability is of crucial importance in practical applications, particularly when high content of water is presented in the feed gas (which is a typical scenario in practical conditions such as automotive exhaust and PEMFC). In most cases, the presence of water vapor in the reactants cause severe catalyst deactivation due to the competitive adsorption of  $H_2O$  with CO [22,23]. Therefore, it is very challenging to sustain catalyst stability during practical conditions.

In this work, we prepared several supported  $Pt/MFe_2O_4$  (M = Ni and Co) catalysts and tested them for CO oxidation. It was found that these catalysts were more active than those supported on monometallic oxides (i.e.  $Fe_2O_3$ ,  $Co_3O_4$  and NiO), due to strong interactions between Pt and the spinel oxide. It is also interesting to find that the catalysts showed excellent water tolerance during the reaction, which makes it appealing in practical applications.

# 2. Experimental

#### 2.1. Catalyst preparation

All the chemicals used in this work were purchased from Sinochem. Co. Ltd and were with analytic purity (> 99.5 wt.%), thus they were used as received without further purification.

The supports were prepared by a citric acid-assisted sol-gel method. Taken the preparation of Co-Fe-O mixed oxide as an example, 50 mmol of  $Co(NO_3)_3$ , 100 mmol of  $Fe(NO_3)_3$  and 300 mmol of citric acid were dissolved in deionized water. The solution was stirred at 80 °C in a water bath until a viscous gel was obtained. The gel was then dried at 110 °C for 12 h and calcined in the air at 500 °C for 3 h to obtain the supports, which was denoted as CoFe<sub>2</sub>O<sub>4</sub>. The bimetallic support NiFe<sub>2</sub>O<sub>4</sub> and monometallic supports (Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO) were prepared in a similar manner.

The supported Pt catalysts were prepared by an impregnation method. One gram of the support was immersed in a certain amount of Pt(NO<sub>3</sub>)<sub>2</sub> solution (with a nominal Pt content of 1 wt.%) at room temperature. After 4 h, the suspension was evaporated at 90 °C in a water bath and dried at 100 °C for 12 h, followed by calcination at 300 °C for 2 h in static air. The resulting catalyst was denoted as Pt/MO<sub>x</sub> (MO<sub>x</sub> = CoFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and NiO).

#### 2.2. Catalyst characterizations

The actual contents of Pt in the catalysts were measured by X-ray fluorescence (XRF) analysis on a Shimadzu XRF-1800 spectrometer operated at 70 mA and 40 kV. The Pt dispersion in the catalyst was measured on a BELCAT II chemisorption instrument. Fifty mg of the catalyst was loaded in a quartz reactor. Before the test, the sample was pretreated with pure  $O_2$  (30 mL/min) at 200 °C for 30 min followed by reduction in pure  $H_2$  (30 mL/min) at 200 °C for 1 h. Then the sample was purged with a He flow (30 mL/min) for 30 min. After it was cooled down to 50 °C, pulse of 5% CO in He was injected to the sample until the adsorption was complete. The CO uptake was quantified by calibration of CO pulse with a known volume.

The crystalline structure of the catalyst was determined by powdered X-ray diffraction (XRD) analysis conducted on a Bruker D8 Advance diffractometer, which was operated at 40 kV and 40 mA. Phase analysis was performed using the MDI Jade 6.0 software. Raman spectra were recorded at room temperature using a confocal microprobe Raman system (Renishaw inVia Reflex) with an excitation laser of 532 nm.

The X-ray photoelectron spectroscopies (XPS) of the catalysts were measured on a Thermo - Fisher ESCALAB 250Xi instrument with an Al K $\alpha$  X-ray source of 1486.6 eV. The binding energy of each surface specie was calibrated by the surface deposited carbon at Cls of 284.8 eV. The XPS PEAK41 software was used to analyze the oxidation states and surface concentrations of the species.

The catalyst reducibility was measured by hydrogen temperature program reduction (H2-TPR) on a BELCAT II chemisorption instrument equipped with a thermal conductivity detector (TCD). The catalyst (30 mg) was loaded in the reactor and exposed in a gas mixture of 5% H<sub>2</sub> - 95 % N<sub>2</sub> (30 mL/min), and was heated from room temperature to 700 °C with a heating rate of 10 °C/min. The signal was recorded by the TCD and the H<sub>2</sub> consumption was quantified by calibrating with the reduction of a known weight of CuO powder. Temperature programmed desorption of oxygen (O2-TPD) was conducted on the same instrument. The sample loaded in the reactor was treated with O2 at 300 °C for 30 min and cooled down to room temperature, followed by He purge for 30 min. Then it was heated from room temperature to 650 °C with a heating rate of 10 °C/min, and the desorbed O2 signal was recorded with TCD and its amount was quantified by calibrated O<sub>2</sub> pulse. Temperature programmed desorption of CO (CO-TPD) was conducted on the same instrument, excepted that the signal was monitored by a mass spectrometer (MS, HIDEN QIC-20) instead of TCD. For each test, 50 mg sample loaded in the reactor was pretreated with O2 (30 mL/min) at 300 °C for 30 min, and was then reduced in H<sub>2</sub> (30 mL/min) at 200 °C for 1 h. After that, the sample was cooled to room temperature and purged for 30 min in a He flow (30 mL/min), and 5% CO in He (30 mL/min) was introduced. After adsorption for 30 min, the catalyst was purged with He flow (30 mL/min) for 20 min to remove the free and weakly adsorbed CO. Finally, it was heated to 500 °C at 10 °C/min in the He flow, and CO (m/e = 28) and  $CO_2$  (m/e = 44) signals were recorded by the MS.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO chemisorption was performed on a Thermo - Fisher Nicolet iS50 FTIR spectrometer equipped with a MCT detector and a PIKE DRIFT accessory. A certain amount of catalyst was loaded in the cell and pretreated in pure  $O_2$  (30 mL/min) at 300 °C for 30 min followed by pure  $H_2$  (30 mL/min) at 200 °C for 1 h. After it was cooled down to 30 °C, a mixture of 10 % CO in He (30 mL/min) was introduced for 30 min. After purge with He (30 mL/min) for 30 min, the spectrum was recorded. For the spectra of CO desorption at elevated temperatures, the pre-purged sample was heated from 30 to 200 °C at a rate of 10 °C/min under the He flow, and the spectra were recorded at certain temperature points extracted with corresponding backgrounds.

## 2.3. Activity measurement and kinetic study

CO oxidation over the catalysts was performed in a tubular quartz reactor (i.d. = 6 nm) at atmospheric pressure. For a typical test, 50 mg of the catalyst (100–120 mesh) diluted with 100 mg of quartz sand (100–120 mesh) was loaded in the reactor. has been used. The reaction gas consisted of 1% CO + 1%  $O_2$  + 98 %  $N_2$  or 1% CO + 1%  $O_2$  + 10 %  $H_2O$  + 88 %  $N_2$ , with a total flow rate of 100 mL/min (space velocity = 120,000 mL/(g<sub>cat</sub> h). Before the reaction, the catalyst was pretreated with 5%  $H_2$  + 95 % Ar mixture (30 mL/min) at 200 °C for 1 h. Then the catalyst was cooled down to the certain temperature and exposed to the reactor was analyzed by a gas chromatograph (GC1120) equipped with a TCD detector. The CO conversion was calculated using Eq. (1):

$$CO \text{ conversion} = ([CO]_{in} - [CO]_{out})/[CO]_{in}$$
(1)

Where [CO]<sub>in</sub> and [CO]<sub>out</sub> were the CO concentrations in the inlet and outlet of the reactor, respectively.Intrinsic activities (turnover frequencies, *TOF*) of the catalysts were calculated using Eq. (2):

$$TOF\left(s^{-1}\right) = X_{CO}F_{CO}M_{Pt}/(m_{cat}X_{Pt}D_{Pt})$$
<sup>(2)</sup>

Where  $X_{CO}$  was CO conversion,  $F_{CO}$  (mol/s) was the CO gas flow rate,  $M_{Pt}$  was the molar weight of Pt (195.1 g/mol),  $m_{cat}$  was the catalyst weight,  $X_{Pt}$  was weight content in the catalyst, and  $D_{Pt}$  was Pt dispersion in the catalyst (measured by CO chemisorption).

#### Table 1

Pt content, Pt dispersion and Pt particle size of the catalysts, and turnover frequencies (TOFs) at 50 °C.

Catalyst	Pt content / wt.%	CO uptake / umol $g^{-1}$	Pt dispersion <sup>a</sup>	TOF at 50 °C / s <sup><math>-1</math></sup>	
				$1\%CO + 1\%O_2$	$1\%CO + 1\%O_2 + 10\%H_2O$
Pt/CoFe <sub>2</sub> O <sub>4</sub>	0.97	16.4	0.32	0.27	0.22
Pt/NiFe <sub>2</sub> O <sub>4</sub>	0.99	30.1	0.58	0.14	0.12
Pt/Fe <sub>2</sub> O <sub>3</sub>	0.96	9.8	0.19	0.08	0.16
Pt/Co <sub>3</sub> O <sub>4</sub>	1.04	25.9	0.50	0.05	0.10

<sup>a</sup> Determined by CO uptake, assuming the molar ratio of adsorbed CO/surface Pt atoms = 1.



Fig. 1. XRD patterns of various catalysts.

The reaction kinetics study was carried out in the differential reaction mode (CO conversion < 15 %) to eliminate the influence of mass transfer and heat transfer (detailed calculation could be found in Supporting Information). By adjusting the partial pressures of CO and  $O_2$  in the reaction gas, a series of reaction rates were obtained and related kinetic parameters were derived.

# 3. Results and discussion

#### 3.1. Catalyst characterizations

As shown in Table 1, the catalysts contain similar Pt contents (ca. 1 wt.%) as they were prepared by the impregnation method. CO uptakes on the catalysts show that the Pt/NiFe<sub>2</sub>O<sub>4</sub> catalyst has the highest value (30.1  $\mu$ mol/g) while the Pt/Fe<sub>2</sub>O<sub>3</sub> has the lowest (9.8  $\mu$ mol/g), which suggests that metal-support interaction (MSI) greatly influences the morphologies of the Pt species. Consequently, the Pt dispersions of the catalysts significantly vary, as the Pt/NiFe<sub>2</sub>O<sub>4</sub> catalyst has a Pt dispersion of 0.58 while that of the Pt/Fe<sub>2</sub>O<sub>3</sub> is 0.19. Note that such MSI has been well documented in literature. For example, in an early work Enlisch et al. [24] compared the morphologies of Pt/SiO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts (Pt contents of 2 wt.%, prepared by an ion exchange method) and found that the Pt particle size on the Pt/TiO<sub>2</sub> (ca. 1 nm) was much smaller than that on the Pt/SiO<sub>2</sub> (ca. 1.8 nm), which was due to the



Fig. 2. Raman spectra of Pt/NiFe<sub>2</sub>O<sub>4</sub> and Pt/CoFe<sub>2</sub>O<sub>4</sub> catalysts.

different interaction strength between Pt and the supports.

Fig. 1 shows the XRD pattern of the catalysts, and the lack of the diffractions of Pt species suggests the high dispersion of these species. The Pt/NiO, Pt/Co<sub>3</sub>O<sub>4</sub> and Pt/Fe<sub>2</sub>O<sub>3</sub> catalysts give diffractions of NiO (JCPDS 44–1159), Co<sub>3</sub>O<sub>4</sub> (JCPDS 43–1003) and Fe<sub>2</sub>O<sub>3</sub> (JCPDS 33–0664), respectively. Diffraction peaks at 20 of 18.3, 30.1, 35.4, 43.1, 57.0, 62.6° are observed on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst, which correspond to (111), (220), (311), (400), (511) and (440) facets of spinel CoFe<sub>2</sub>O<sub>4</sub> oxide (JCPDS 22–1086). The diffractions of the Pt/NiFe<sub>2</sub>O<sub>4</sub> are almost identical to those of the Pt/CoFe<sub>2</sub>O<sub>4</sub>, which are attributed to spinel structure of NiFe<sub>2</sub>O<sub>4</sub> oxide (JCPDS 54–0964). In addition, the lattice parameters of the Pt/CoFe<sub>2</sub>O<sub>4</sub> and Pt/NiFe<sub>2</sub>O<sub>4</sub> catalysts are calculated to be 0.8373 ± 0.001 and 0.8331 ± 0.001 nm, respectively, and the smaller lattice parameter of the NiFe<sub>2</sub>O<sub>4</sub> spinel is due to the smaller ion radius of Ni compared with that of the Co. Therefore, the XRD results indicate that spinel oxides could be successfully synthesized via the sol-gel method.

The structures of the Pt/CoFe<sub>2</sub>O<sub>4</sub> and Pt/NiFe<sub>2</sub>O<sub>4</sub> catalysts were further studied by Raman spectroscopy. Since MFe<sub>2</sub>O<sub>4</sub> ferrite has a cubic spinel structure, it gives five Raman active modes  $(A_{1g}+E_g+3T_{2g})$  which are generated by the vibration of oxygen-metal ions in tetrahedral and octahedral positions [25,26]. Specifically, The A<sub>1g</sub>(1) mode is related to the symmetrical stretching vibration of the FeO<sub>4</sub> tetrahedron [19]. The E<sub>g</sub> mode is related to the symmetrical bending motion of the oxygen



Fig. 3. a) Pt 4f, b) O 1s, c) Fe 2p and d) Co 2p and Ni 2p XPS spectra of the fresh catalysts.

within the AO<sub>4</sub> units (A = di- and tri-valent metal ions). The weak signal at  $T_{2g}(1)$  is related to the translational movement of the BO<sub>6</sub> unit relative to the cation of the A-site [27,28]. The  $T_{2g}(2)$  mode is attributed to the vibration of oxygen atoms and octahedral Fe<sup>3+</sup> [29]. The  $T_{2g}(3)$  mode corresponds to the asymmetric bending vibration of oxygen coordinated with Co<sup>2+</sup> at the tetrahedral position. As shown in Fig. 2, the two catalysts give  $T_{2g}(1)$  (at 182 - 193 cm<sup>-1</sup>),  $E_g$  (at 293 - 318 cm<sup>-1</sup>),  $T_{2g}(2)$  (at

460 - 482 cm<sup>-1</sup>),  $T_{2g}(3)$  (at 554 - 560 cm<sup>-1</sup>),  $A_{1g}(1)$  (at 682 - 695 cm<sup>-1</sup>), which are typical Raman bands of ferrite spinel oxides. Besides, both catalysts give shoulders at 622 - 640 cm<sup>-1</sup> (denoted as  $A_{1g}(2)$ ) due to the replacement of some Fe<sup>3+</sup> cations by Co<sup>2+</sup> or Ni<sup>2+</sup> cations in the tetrahedral site. Therefore, such CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> composite oxides usually contain a mixture of normal spinel and inverse spinel oxides, which give a general formula of  $(M^{2+}_{1-x}Fe^{3+}_{x})_{td}(M^{2+}_{x}Fe^{3+}_{2-x})_{oh}$  (where M refers to Co r Ni, and td refers to tetradehral site and oh refers to octahedral site) [30–33].

Fig. 3 shows the XPS spectra of the fresh catalysts. It is clear that the fresh catalysts contain oxidized Pt species (Pt<sup>2+</sup> and Pt<sup>4+</sup>, Fig. 3a), which give binding energies (BE) at 72.9 eV ( $4f_{7/2}$  for Pt<sup>2+</sup>) and 74.8 eV ( $4f_{7/2}$ for Pt<sup>4+</sup>) [34,35]. As for the O 1s spectra of the fresh catalysts (Fig. 3b), the peak at BE of 530.1 eV is due to the lattice oxygen (O<sub>lat</sub>) while that at 531.7 eV is due to the adsorbed oxygen (O<sub>ads</sub>) species [36]. Moreover, the concentrations of Oads in the Pt/CoFe2O4 and Pt/NiFe2O4 are relatively higher than that in the Pt/Fe<sub>2</sub>O<sub>3</sub>, suggesting the spinel structures of these two supports may help the formation of surface oxygen species and thus play important roles in CO oxidation [37]. For the Fe 2p spectra of the fresh catalysts (Fig. 3c), it can be seen that  $Fe^{2+}$  and  $Fe^{3+}$  species coexist [38,39]. For the Co 2p spectra (Fig. 3d), BEs at 780.2 and 795.7 eV are attributed to  $Co^{2+}$  in the octahedral position, while BEs at 782.3 and 797.8 eV are attributed to  $Co^{2+}$  in the tetrahedral position [26]. The Ni 2p spectra can also be resolved to Ni<sup>2+</sup> in octahedral position (BE =854.9 eV) and in tetrahedral position (BE =856.4 eV) [38, 40]. Thus, the XPS results suggest that the CoFeO and NiFeO composite oxides consist of a mixture of spinel and inverse spinel oxide, which are in consistent with the Raman spectra (Fig. 2).

Fig. 4a show the H<sub>2</sub>-TPR profiles of the catalysts. The reduction peaks at low temperature range (80-150 °C) could be attributed to the reduction of PtO<sub>x</sub> species in the catalysts, as well as the reduction of the support oxides adjacent to the Pt nanoparticles due to the typical spillover effect. The H<sub>2</sub> consumption values of these low temperature reduction peaks are also listed in the figure. The Pt/CoFe<sub>2</sub>O<sub>4</sub>, Pt/NiFe<sub>2</sub>O, Pt/Fe<sub>2</sub>O<sub>3</sub>, Pt/Co<sub>3</sub>O<sub>4</sub> and Pt/NiO catalysts give H<sub>2</sub> consumptions of 0.23, 0.12, 0.22, 1.12 and 0.05 µmol/g, respectively. The highest H<sub>2</sub> consumption on the Pt/Co<sub>3</sub>O<sub>4</sub> catalyst implies that the amount of oxygen species on the Co<sub>3</sub>O<sub>4</sub> support (including surface oxygen species and/or lattice oxygen) is the highest. Similar finding was also reported by Liu et al. [41] as they found that the low-temperature reduction (lower than 200 °C) on the Pt/Co<sub>3</sub>O<sub>4</sub> was much pronounced than that on the Pt/CeO<sub>2</sub>. Moreover, the temperature for the initial reduction indicates that the Pt/NiFe<sub>2</sub>O<sub>4</sub> catalyst starts reduction at 85 °C, while the Pt/Co<sub>3</sub>O<sub>4</sub> starts reduction at 99 °C. The lower initial reduction



Fig. 4. a) H<sub>2</sub>-TPR, b) O<sub>2</sub>-TPD and c) CO-TPD profiles of various catalysts.



Fig. 5. DRIFTS of a) CO adsorption on  $Pt/Fe_2O_3$ ,  $Pt/CoFe_2O_4$  and  $Pt/NiFe_2O_4$  catalysts; b) CO desorption over  $Pt/Fe_2O_3$  at elevated temperatures and c) CO desorption over  $Pt/CoFe_2O_4$  at elevated temperatures.

temperature suggests more facile activation of the oxygen species in the catalyst, which is related to the catalytic performance in CO oxidation. Close analysis of the low temperature reduction peaks (Fig. S1) also reveals that the rate of  $H_2$  consumption of the catalyst differs much. For example, the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst gives the highest consumption rate (the largest slope of 45.2), while the Pt/NiO gives the lowest rate (the lowest slope of 3.6). The higher  $H_2$  consumption rate reflects easier activation of the oxygen species, which is beneficial to the reaction. At

high temperature range, the reduction peaks are related to the reduction of the support oxides. For example, the peak centered at ca. 280 °C for the Pt/Fe<sub>2</sub>O<sub>3</sub> catalyst is attributed to the reduction of  $Fe_2O_3$  to  $Fe_3O_4$  species [42].

As shown in Fig. 4b, the O<sub>2</sub>-TPD profiles of the catalysts reveal that all the catalysts give desorption peaks in 50–180 °C region assigning to the desorption of surface oxygen species, which are consistent with the H<sub>2</sub>-TPR results (Fig. 4a). The amount of the desorbed O<sub>2</sub> are higher on



Fig. 6. Catalytic results of a) 1% CO + 1% O<sub>2</sub>; b) 1% CO + 1% O<sub>2</sub> + 10 % H<sub>2</sub>O over various catalysts; c) comparison of CO conversions at 80 °C; d) stability of the Pt/NiFe<sub>2</sub>O<sub>4</sub> and Pt/Fe<sub>2</sub>O<sub>3</sub> catalysts at reaction conditions with/without H<sub>2</sub>O.

the Pt/CoFe<sub>2</sub>O<sub>4</sub> and Pt/NiFe<sub>2</sub>O<sub>4</sub> (0.13 and 0.11 mmol/g, respectively) compared to those on the other catalysts, indicating more abundant surface oxygen species on the former catalysts. In high temperature region (> 300 °C), the desorption signal is due to the release of lattice oxygen. Fig. 4c shows the CO-TPD profiles of the Pt/Fe<sub>2</sub>O<sub>3</sub> and Pt/ CoFe<sub>2</sub>O<sub>4</sub> catalyst. For the Pt/Fe<sub>2</sub>O<sub>3</sub> catalyst, the CO desorption reaches its maximum at about 190 °C, and the CO<sub>2</sub> desorption is maximized at about 130 °C. It should be noted that the catalyst was subjected to different pretreatment (e.g. oxidation at 300 °C in O2 for 30 min and then reduction at 200  $^{\circ}$ C in H<sub>2</sub> for 1 h), thus the decomposition of surface carbonate species and the participation of surface oxygen species in the formation of CO<sub>2</sub> could be safely ruled out because most of the surface carbonates and surface oxygen species were removed during the pretreatment. Therefore, the generation of CO<sub>2</sub> indicates that the lattice oxygen was involved in the reaction. For the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst, the desorption of CO reaches its maximum at lower temperature (ca. 120 °C) compared to that of the Pt/Fe<sub>2</sub>O<sub>3</sub>, suggesting weaker strength of CO adsorption on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst. Also, the CO and CO<sub>2</sub> signals are more intense than those on the Pt/Fe<sub>2</sub>O<sub>3</sub>. The very different CO-TPD profiles on the two catalysts are related to the different features of the Pt species in the catalysts (e.g. dispersion and oxidation states), as revealed by the CO uptake and XPS results. Also, the comparison of the profiles reflect two facts. One is that the strength of CO adsorption on the Pt/NiFe<sub>2</sub>O<sub>4</sub> is weaker than that on the Pt/Fe<sub>2</sub>O<sub>3</sub> as the desorption temperature on the former is ca. 10 °C lower than that on the latter. The other is that the CO uptake is higher on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst and the adsorbed CO can facilely react with the lattice oxygen in the spinel oxide.

The DRIFT spectra of CO chemisorption on the catalysts are shown in Fig. 5a. All the catalysts give asymmetric bands in  $1800-2200 \text{ cm}^{-1}$ . The very weak band at ca. 1850 cm<sup>-1</sup> is assigned to the bridged adsorption of CO on Pt surface atoms. In the region of 2000–2300 cm<sup>-1</sup>, the weak shoulder at 2035 cm<sup>-1</sup> is assigned to linearly adsorbed CO on small  $Pt^{\circ}$  particles, while the band at 2068 cm<sup>-1</sup> is attributed to the linearly adsorbed CO on relatively larger  $Pt^{\circ}$  particles [43,44]. For the  $Pt/NiFe_2O_4$  catalyst, a shoulder at 2080 cm<sup>-1</sup> is also observed, which could be assigned to linear adsorption of CO on  $Pt\delta^+$  [45]. These results imply that the Pt species in the pre-reduced catalysts are dominantly metallic (Pt°). To investigate the adsorption strength of CO on the catalyst, CO desorption experiments at elevated temperatures on the Pt/Fe<sub>2</sub>O<sub>3</sub> and Pt/CoFe<sub>2</sub>O<sub>4</sub> catalysts were conducted and the results are shown in Fig. 5b and 5c. For the Pt/Fe<sub>2</sub>O<sub>3</sub> catalyst (Fig. 5b), the bands at 2035, 2068 and 2080  $\text{cm}^{-1}$  rapidly decrease in intensity, indicating the fast desorption of CO at high temperature, but the bandat 2090 cm<sup>-1</sup> remains until 160 °C, indicating that the CO adsorbed on Pt° is easier to desorb. It may be that CO adsorbed on Pt° is more active and easier to react with lattice oxygen [45]. Similar trends are also observed on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst (Fig. 5c). However, the intensities of the CO bands on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst are much higher than those on the Pt/Fe<sub>2</sub>O<sub>3</sub>, suggesting larger quantity of adsorbed CO on the former. Moreover, the bands completely disappear at 140 °C, imply the adsorption strength on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst is relatively weaker than that on the Pt/Fe<sub>2</sub>O<sub>3</sub>. This finding is in line with the CO-TPD results (Fig. 4c).

#### 3.2. Catalytic activity for CO oxidation

Fig. 6 shows the catalytic activities of the catalysts under different reaction conditions. Under  $CO + O_2$  condition (Fig. 6a), The Pt/CoFe<sub>2</sub>O<sub>4</sub> and Pt/NiFe<sub>2</sub>O<sub>4</sub> catalysts are more active than the Pt/Fe<sub>2</sub>O<sub>3</sub> and Pt/Co<sub>3</sub>O<sub>4</sub>, while the Pt/NiO has the lowest activity. In the presence of 10 % H<sub>2</sub>O in the feed stock (Fig. 6b), it seems that the catalytic activity follows the same order as in the  $CO + O_2$  condition, as the Pt/CoFe<sub>2</sub>O<sub>4</sub> and Pt/NiFe<sub>2</sub>O<sub>4</sub> catalysts are the most active while the Pt/NiO is the least. Moreover, to illustrate the role of H<sub>2</sub>O on the catalytic performance, CO conversions of the catalysts at 80 °C with or without the presence of H<sub>2</sub>O were compared and the results are shown in Fig. 6c. It is found that the



Fig. 7. a) Pt 4f, b) O 1s, c) Fe 2p and d) Co 2p and Ni 2p XPS spectra of the spent catalysts after CO + O\_2 reaction.

activities of the Pt/CoFe<sub>2</sub>O<sub>4</sub> and Pt/NiFe<sub>2</sub>O<sub>4</sub> catalysts do not change significantly with the addition of H<sub>2</sub>O in the feed, which indicates that the two catalysts have excellent tolerance of high content of H<sub>2</sub>O, and thus are very potential in practical applications. Also, it is interesting that the addition of H<sub>2</sub>O in the feed could greatly enhance the activities of the Pt/Fe<sub>2</sub>O<sub>3</sub>, Pt/Co<sub>3</sub>O<sub>4</sub> and Pt/NiO catalysts. According to literature [46], the promotion of  $H_2O$  is due to the dissociation of -OH formed by H<sub>2</sub>O and the rapid reaction of CO with it, thus promoting the reaction activity. Therefore, the excellent water tolerant on the Pt/CoFe2O4 and Pt/NiFe2O4 catalysts could be due to two opposite effects, that is, a positive effect of the new reaction route (reaction between CO and surface -OH group) and a negative effect of the competitive adsorption of H<sub>2</sub>O and CO. Fig. 6d shows the catalyst stability. The Pt/Fe<sub>2</sub>O<sub>3</sub> catalyst suffers quite severe deactivation under both  $CO + O_2$  and  $CO + O_2 + H_2O$  conditions. It has been reported that when traditional oxides are used as supports (such as FeO<sub>x</sub>, TiO<sub>2</sub>, etc.), it is easy to form carbonate species which are difficult to desorb, and then block the active sites, resulting in catalyst deactivation [47]. On the contrary, the Pt/NiFe2O4 catalyst is quite stable under both conditions. The XRD patterns of the spent catalysts (Fig. S2) further confirm that the catalysts remain their structures after reaction.

The obtained reaction rates are comparable to those reported in literature (Table S1), further reflect the advantages of the current catalysts. Also, in order to compare the intrinsic activity of the catalysts, the TOF of each catalyst with or without water vapor at 50 °C was calculated. The results are summarized in Table 1. The TOF of the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst under 1% CO + 1% O<sub>2</sub> reaction conditions is 0.27 s<sup>-1</sup>. After the addition of 10 % H<sub>2</sub>O in the feed, the *TOF* slightly decreases to 0.22 s<sup>-1</sup>, but it still possesses the highest activity among the employed catalysts.

Fig. 7 shows the XPS spectra of the catalysts after  $CO + O_2$  reaction.



Fig. 8. Dependence of reaction rates on partial pressures of CO and  $O_2$  over a1) and a2) Pt/CoFe<sub>2</sub>O<sub>4</sub> and b1) and b2) Pt/Fe<sub>2</sub>O<sub>3</sub> catalysts; Arrhenius plots of CO oxidation over a3) Pt/CoFe<sub>2</sub>O<sub>4</sub> and c3) Pt/Fe<sub>2</sub>O<sub>3</sub> catalysts<sub>o</sub>.

Table 2 Kinetic results of  $Pt/CoFe_2O_4$  and  $Pt/Fe_2O_3$  catalysts under different reaction condition.

Pt/CoFe <sub>2</sub> O <sub>4</sub> @ 70 ℃	$r=k_{app} \; [CO] \; ^a \; [O_2] \; ^b$					
Reaction conditions	$\substack{k_{app \ /} x \\ 10^{-6}}$	а	b	Ea / kJ mol <sup>-1</sup>		
$\begin{array}{c} \text{CO} + \text{O}_2 \\ \text{CO} + \text{O}_2 + 10\% \\ \text{H}_2\text{O} \end{array}$	6.28 6.05	$\begin{array}{c} 0.56\pm0.03\\ 0.63\pm0.02\end{array}$	$\begin{array}{c} -0.01 \pm 0.01 \\ -0.01 \pm 0.01 \end{array}$	$\begin{array}{c} 20.9\pm1.3\\ 22.0\pm1.2 \end{array}$		
Pt/Fe <sub>2</sub> O <sub>3</sub> @ 70 °C	$r = k_{app} \text{ [CO]} \ ^{a} \text{ [O_2]} \ ^{b}$					
Reaction conditions	$\frac{k_{app \ /} \ x}{10^{-6}}$	а	b	Ea / kJ mol <sup>-1</sup>		
$\begin{array}{c} \mathrm{CO} + \mathrm{O}_2 \\ \mathrm{CO} + \mathrm{O}_2 + 10\% \\ \mathrm{H}_2 \mathrm{O} \end{array}$	1.68 4.04	$\begin{array}{c} 0.40 \pm 0.02 \\ 0.51 \pm 0.01 \end{array}$	$-0.01 \pm 0.01 \\ -0.01 \pm 0.01$	$\begin{array}{c} 35.9 \pm 2.2 \\ 28.4 \pm 3.2 \end{array}$		

Several remarks could be made. 1, Considerable amount of metallic Pt species (ca. 30 %) are present in the spent catalysts (Fig. 7a). This is because that the catalyst was pre-reduced before reaction, and the metallic Pt species could sustain even in the oxidative reaction environment. 2, Compared to the fresh catalyst, the spent catalyst contains larger content of adsorbed oxygen species (Fig. 7b), indicating that gaseous  $O_2$  could adsorb on the catalyst surface. 3, The XPS spectra of Fe 2p and Co 2p (or Ni 2p) generally remain unchanged after reaction, suggesting that the surface properties of the support oxides are maintained.

#### 3.3. kinetic investigation

Kinetic experiments were carried out on the representative Pt/  $CoFe_2O_4$  and  $Pt/Fe_2O_3$  catalysts, in order to understand the reaction behavior of the catalysts under different reaction conditions. First of all, reaction orders of CO and  $O_2$  under  $CO + O_2$  and  $CO + O_2 + 10 \% H_2O$ conditions and activation energy (Ea) were determined (detailed results are summarized in shown in Table S2-S5), and the results are shown in Fig. 8. It is clear that for both catalysts under different conditions, the reaction rate increases with increasing partial pressure of CO, while it remains constant with increasing partial pressure of O<sub>2</sub>. Based on these results, the kinetic parameters were derived and summarized in Table 2. For the Pt/CoFe<sub>2</sub>O<sub>4</sub>, the power law rate expression under  $CO + O_2$  is  $r = 6.28 \times 10^{-6} [CO]^{0.56} [O_2]^{\circ}$ , while that under  $CO + O_2 + 10 \% H_2O$  is  $r = 6.05 \times 10^{-6}$  [CO]<sup>0.63</sup> [O<sub>2</sub>]°. The parity plots and residual analyses on the catalyst (Fig. S3) further validate the derived the parameters. The addition of H<sub>2</sub>O results in slightly lower apparent reaction constant (kapp) and reaction order of CO, indicating that H2O may competitively adsorb on the catalyst surface with CO and thus decreases the surface coverage of CO. For the Pt/Fe<sub>2</sub>O<sub>3</sub>, the power law rate expression under CO + O\_2 is  $r = 1.68 \times 10^{-6}$  [CO]  $^{0.40}$  [O\_2]  $^{\circ}$  , while that under CO + O\_2 + 10 %  $H_2O$  is  $r = 4.04 \times 10^{-6}$  [CO]<sup>0.51</sup> [O<sub>2</sub>]°. Unlike in the case of Pt/ CoFe<sub>2</sub>O<sub>4</sub>, the addition of H<sub>2</sub>O results in significant enhancement of the kapp. The H<sub>2</sub>O-assisted promotion of CO oxidation has been widely reported various Pt catalysts (i.e. Pt/CeO2 [48], Pt/CrFeO [49]), which is due to the reaction between CO and surface hydroxyl groups (formed by H<sub>2</sub>O and the support oxide). Also, the much lower Ea on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst (20.9-22.0 kJ/mol) under different conditions compared to those on the Pt/Fe<sub>2</sub>O<sub>3</sub> catalyst (28.4–35.9 kJ/mol) further confirm the higher activities of the former.

The above results imply that the CO oxidation over the catalysts may follow a typical Mars van Krevelen (M-K) mechanism, that is, the CO adsorbed on the Pt surface atoms would react with lattice oxygen in the support oxide and the gaseous O2 molecules refill the oxygen vacancies [48,49]. The general rate expression is  $r = kK_{CO}P_{CO}[O]/(1+K_{CO}P_{CO})$ , where k and K<sub>CO</sub> are the rate constant and CO adsorption equilibrium, respectively, and [O] is the surface concentration of lattice oxygen (which is a constant for a given oxide). Thus, the reaction rate depends on the adsorption properties of CO on Pt (i.e. strength and coverage) and the activation of lattice oxygen. In the current case, the reaction order of CO on the Pt/Fe<sub>2</sub>O<sub>3</sub> is lower than that on the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst (0.40 vs. 0.56), suggesting that higher CO coverage on the former catalyst. However, the CO chemisorption results (Fig. 5) indicate that the strength of CO adsorption on the Pt/Fe<sub>2</sub>O<sub>3</sub> is stronger than that on the Pt/CoFe<sub>2</sub>O<sub>4</sub>. This implies that the adsorbed CO on the Pt/Fe<sub>2</sub>O<sub>3</sub> might be difficult to be activated, while the relatively weakly adsorbed CO molecules on the Pt/CoFe<sub>2</sub>O<sub>4</sub> could be easily activated due to metal-support interaction. On the other hand, the H<sub>2</sub>-TPR results (Fig. 3a) clearly show that the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst has much higher initial consumption rate of oxygen than the Pt/Fe<sub>2</sub>O<sub>3</sub>. Therefore, it seems that the enhanced activity of the Pt/CoFe<sub>2</sub>O<sub>4</sub> catalyst is closely related to the synergistic effects of weakened CO adsorption strength and facile activation of the lattice oxygen species.

## 4. Conclusions

This work demonstrates that the Pt supported on spinel  $CoFe_2O_4$  and  $NiFe_2O_4$  oxides are very active for CO oxidation. Compared to the monometallic oxides, the interaction between Pt and the spinel oxides results in weakened CO adsorption and facile activation of the lattice oxygen, which accounts for the enhanced activity. More importantly, these catalysts maintain their performance even under high concentration of water vapor in the feed, thus making these catalysts promising in practical applications. These findings provide some new information on the design of highly efficient catalyst system for CO oxidation, particularly under practical conditions.

#### CRediT authorship contribution statement

M.T.Z. synthesized the catalysts and performed performed the catalytic tests; K.F.Z., W.P.D. and A.P.J. carried out the characterization measurements and analyzed the data; M.F.L. and J.Q.L. supervised the project and wrote the manuscript. All authors discussed the results and contributed to the final manuscript.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118142.

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