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Investigation on Fe-Ni mixed oxide catalysts for NO reduction by CO: Physicochemical

properties and catalytic performance

Xuexun Du^a, Tian-Liang Yao^b, Qinglian Wei^a, Hao Zhang^a, Yongmin Huang^a*

Abstract: A series of Fe-Ni mixed oxide catalysts were synthesized through a sol-gel method for NO reduction by CO. Compared to monometallic catalysts prepared using the same method, Fe-Ni mixed oxide catalysts revealed a tremendous enhancement in catalytic performance. The effects of Fe/Ni molar ratio and calcination temperature on catalytic activity were examined. The physicochemical properties of catalysts were characterized by XRD, Raman, N₂ adsorption-desorption, H₂-TPR, NO-TPD and XPS. The results indicated that the reduction behavior, surface oxygen species and surface chemical valence states of Fe and Ni in catalysts are the key factors for NO elimination. The Fe_{0.5}Ni_{0.5}O_x sample calcined at 250 °C exhibited an excellent catalytic activity of 100% NO conversion at 130 °C and lifetime more than 40 h. A possible mechanism for NO reduction by CO over Fe-Ni mixed oxide catalysts was proposed based on the XPS and in-situ DRIFTS analyses.

Introduction

Although renewable energy source, such as solar and wind energy, have been developing rapidly, fossil fuels are still the essential energy source for industrial application and daily life. Nitric oxide (NO) derived from fossil fuel combustion process is one of the major air pollutions, which causes environmental problems such as greenhouse effect and photochemical smog.^[1] For decades, NO abatement has gained more attention owing to the rigorous environmental regulations. NO reduction by different reducing agents (NH₃, hydrocarbon, CO and H₂) is an effective strategy to eliminate NO.^[2-5] Among the various de-NO_x technologies, NO reduction by CO is likely to be one of the most feasible ways to solve the problem, since CO is always a byproduct accompanying the generation of NO in vehicle engine, as well as many stationary applications such as steel and coking factories.^[6]

Noble metals such as Au,^[7] Rh,^[8] Pt ^[9] and Pd ^[10] are frequently employed to prepare noble metal catalysts for NO + CO reaction. However, high cost, low abundance and poor thermal stability inhibit their large-scale application. Hence, many studies have been focusing on searching for the alternatives of noble metal. Under such backgrounds, transition metal oxides, particularly iron, cobalt, nickel and copper oxides, have received increasing attention, because they are cost-effective and easily available.

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Iron catalysts have been reported to present a remarkable catalytic performance in NO + CO reaction on account of the tremendous redox capacity.^[11] Robert et al. found that the redox active $Fe^{3+} \leftrightarrow Fe^{2+}$ centers took responsibility for the steady-state activity.^[12] Dong et al. reported the polymeric Fe³⁺ clusters were easier to be reduced into Fe^{2+} than isolated Fe^{3+} ions under CO atmosphere, leading to high activity of NO abatement.^[13] Nevertheless, mono iron catalyst always displays poor catalytic performance for NO elimination at low temperatures. [11,14,15] Nickel catalysts also exhibit an excellent activity in NO + CO reaction, especially for Ni-Ce catalysts, which can eliminate NO completely below 200 °C. For instance, Wang et al. prepared nickel catalysts by using different supports and the catalytic activity decreased in order of NiO/CeO₂ > NiO/γ-Al₂O₃ > NiO/TiO₂.^[16] Tang et al. synthesized NiO-CeO2 using a novel solid state method, which displayed an entire NO elimination capacity at 175 °C.[17] Tang et al studied the effect of exposed facets of CeO2 in NiO/CeO2 catalysts and found that the strong interaction between NiO and CeO₂ surface and the Ni²⁺ in the Ni-Ce-O structure are the crucial factors for the low-temperature catalytic activity.^[18] However, for these literature, the lifetime of catalysts and the effect of water were seldom reported since the nickel catalysts always show poor stability and H₂O resistance.

In this work, we prepared Fe-Ni mixed oxide catalysts via a sol-gel method. The effects of Fe/Ni molar ratio and calcination temperature on catalytic performance for NO + CO reaction were examined. The 250 °C calcined Fe0.5Ni0.5Ox-250 catalyst (Fe/Ni molar ratio is 5/5) displayed a superb NO elimination performance, the complete NO conversion temperature was as low as 130 °C, and the 100% NO conversion could be maintained over 40 h. To the best of our knowledge, this is the first study to report the Fe-Ni mixed oxide catalysts for NO reduction by CO at such low temperature. The influence of weight hour space velocity (WHSV), CO concentration and water on catalytic performance over Fe0.5Ni0.5Ox-250 were further examined. In comparison of previous studies, the catalytic performance of Fe_{0.5}N_{0.5}O_x-250 is higher than that of most reported non-precious metal catalysts, even comparable to precious metal catalysts. Based on the experiment results, the correlation between physiochemical properties and catalytic performance were discussed and a possible mechanism was proposed.

Results and Discussion

Catalytic activity

Figure 1a displays the NO conversion of NiO_x, FeO_x and Fe_aNi_bO_x-300 catalysts at the WHSV of 15000 ml•g⁻¹•h⁻¹. The NiO_x catalyst presents a negligible NO elimination efficiency below 150 °C, the complete NO conversion temperature (T_{100NO}) is higher than 300 °C. The FeO_x sample exhibits better catalytic performance than that of NiO_x, and the T_{100NO} is 200 °C. Compared to the Fe-only and Ni-only catalysts, all the Fe-Ni

mixed oxide catalysts show higher catalytic activities. In detail, the complete NO conversion temperature of Fe0.7Ni0.3Ox-300 is 160 °C. With the decrease of Fe/Ni molar ratio, the T_{100NO} exhibits a volcano-type tendency, the T_{100NO} of Fe_{0.5}Ni_{0.5}O_x-300 and Fe_{0.3}Ni_{0.7}O_x-300 are 140 and 170 °C, respectively. Figures 1b and 1c show the N₂O selectivity and CO conversion of the catalysts mentioned above. Since N₂ yield (%)= NO conversion × (1- N₂O selectivity) ×100%, when the NO conversion is 100% and N_2O selectivity is 0%, the N2 yield is 100%. Table 1 shows the temperatures of 100% N_2 yield $(T_{100N_3}),$ complete NO conversion (T_{100NO}) and CO conversion (T_{50CO}) of each sample. As a result, Fe_{0.5}Ni_{0.5}O_x-300 possesses the highest catalytic performance, with the T_{100NO} at 140 °C, T_{100N_2} at 180 °C and T_{50CO} at 180 °C, which means that the NO can be eliminated completely at 140 °C and converted to N₂ entirely at 180 °C. On this basis, considering the significant effect of calcination temperature,^[19] we further examined the catalytic performance of Fe_{0.5}Ni_{0.5}O_x samples with varied calcination temperatures. The results are shown in Figure 2. As the calcination temperature rises from 200 °C to 350 °C, the T_{100NO} of Fe_{0.5}Ni_{0.5}O_x catalysts show a volcano-type tendency in the order of $Fe_{0.5}Ni_{0.5}O_x-200 > Fe_{0.5}Ni_{0.5}O_x-350 > Fe_{0.5}Ni_{0.5}O_x-300$ > $Fe_{0.5}Ni_{0.5}O_x$ -250. The $Fe_{0.5}Ni_{0.5}O_x$ -250 displays the optimal lowtemperature catalytic performance (T_{100NO} = 130 °C, T_{100No}= 160 °C). Either increasing (300 and 350 °C) or decreasing (200 °C) the calcination temperature will lead to decreased activity. In addition, since the Fe-Ni oxide catalysts were prepared from metal nitrates, the lowest activity, which belongs to Fe_{0.5}Ni_{0.5}O_x-200, should be ascribed to the incomplete decomposition of metal nitrates at such low temperature.

XRD

Figure 3a shows the XRD patterns of the NiO_x, FeO_x and Fe-Ni mixed metal oxide catalysts calcined at 300 °C. For the NiO_x sample, both metallic Ni (JCPDS-04-0850) and NiO phases (JCPDS-78-0423) can be observed, indicating the product should be a composite of metallic nickel and nickel oxide. The FeOx sample displays both hematite (α -Fe₂O₃, JCPDS-33-0664) and maghemite (γ -Fe₂O₃, JCPDS-39-1346). For the Fe_aNi_bO_x-300 samples, Fe_{0.7}Ni_{0.3}O_x-300, whose molar ratio of Fe/Ni is 7/3, presents the mixed phases of NiFe₂O₄ (2θ = 30.3°, 35.7° and 57.4°, JCPDS-10-0325) and NiO (20 = 43.3° and 62.9°, JCPDS-47-1049). As the Fe/Ni molar ratio decreases to 5/5, the NiFe₂O₄ diffraction peak becomes broad, which may cause by the strain.^[20] When the Fe/Ni molar ratio continues to decrease to 3/7, only NiO phase can be observed (2θ = 37.3°, 43.3° and 62.9°), implying the high dispersion of NiFe2O4 phase. Figure 3b displays the XRD patterns of Fe0.5Ni0.5Ox catalysts calcined at different temperatures. All the samples present diffraction peaks of NiFe₂O₄ and NiO phases.



a) 100

80

NO conversion (%) b 09

20

b)

N2O Selectivity (%)

100

80

60

40

20







Fig 2. Catalytic performance of Fe_{0.5}Ni_{0.5}O_x with different calcination temperatures. (Reaction conditions: [NO] =1000 ppm, [CO] =2000 ppm, [N₂] = balance; T = 100 - 300 °C; WHSV = 15000 ml·g⁻¹·h⁻¹)



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Fig 3. XRD patterns of (a) Fe_aNi_bO_x-300 with different Fe/Ni molar ratios; (b) Fe_{0.5}Ni_{0.5}O_x with different calcination temperatures.

Raman

Raman spectroscopy, an effective complement to acquire additional information that cannot be obtained by XRD, was employed to study the oxide phases of the as-prepared samples, and the results are shown in Figure 4. From the Raman spectra of FeO_x (Figure 4a), two bands appear at 216 and 283 cm⁻¹, the former one is associated with the A_{1a} vibrational modes of Fe_2O_3 , and the latter origins from the red-shift for the Eg modes of Fe₂O₃.^[21] For the NiO_x sample, since nickel metal shows no Raman signal, the band appears at 497 cm⁻¹ is ascribed the Ni-O vibration modes.^[22] As the Fe_aNi_bO_x-300 were synthesized, the Raman spectra are different. For the Fe_{0.7}Ni_{0.3}O_x-300 sample, the band at 497 cm⁻¹ is related to the NiO signal, and the two bands appear at 315 and 688 cm⁻¹ are associated with the generation of NiFe₂O₄. ^[23]With the continuing decrease of Fe/Ni molar, the band at 497 cm⁻¹ for the Fe_{0.7}Ni_{0.3}O_x-300 shifts to higher wavenumbers. For the Fe-Ni mixed oxide, the addition of iron can cause the redshift of Ni-O band, which has been reported on bulk Ni3Fe oxides.^[24] Thus, the bands at 558 and 571 cm⁻¹ for the Fe_{0.5}Ni_{0.5}O_x-300 and Fe_{0.3}Ni_{0.7}O_x-300 can be attributed to the Ni-O band. For the Fe0.5Ni0.5Ox samples calcined at different temperatures, the Raman spectra are similar (Figure 4b), all the

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 $Fe_{0.5}Ni_{0.5}O_x$ samples exhibit two main bands, NiO at 545-555 cm⁻¹ and NiFe₂O₄ at 685-690 cm⁻¹, indicating the mixed phases of NiO and NiFe₂O₄, which is in accordance with the XRD result.

Table 1. Catalytic performance and specific surface areas of catalysts.								
Sample	T _{100NO} (°C)	T _{100N2} (°C)	T _{50C0} (°C)	S _{BET} (m²/g) ^a				
FeO _x	200	> 200	250	95				
NiO _x	> 300	> 300	> 300	35				
Fe _{0.7} Ni _{0.3} O _x -300	150	200	200	142				
Fe _{0.5} Ni _{0.5} O _x -300	140	180	180	177				
Fe _{0.3} Ni _{0.7} O _x -300	170	200	200	152				
Fe _{0.5} Ni _{0.5} O _x -200	180	> 200	> 200	181				
Fe _{0.5} Ni _{0.5} O _x -250	130	160	160	209				
Fe _{0.5} Ni _{0.5} O _x -350	150	170	170	168				
[a] Determined by the BET method								



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Fig 4. Raman spectra of (a) Fe_sNi_bOx-300 with different Fe/Ni molar ratios; (b) Fe_{0.5}Ni_{0.5}O_x with different calcination temperatures.

N₂ adsorption-desorption

The N₂ adsorption-desorption isotherms of as-prepared catalysts are shown in Figure S1, all the samples display the distinct hysteresis loops in the P/P0 from 0.4 to 1.0, implying the existence of mesoporous structure. The specific surface areas (S_{BET}) are summarized in Table 1. The S_{BET} of FeO_x is 95 m²/g, while for NiO_x, it is only $35 \text{ m}^2/\text{g}$. In comparison with monometallic catalysts, the Fe-Ni mixed oxide catalysts have higher specific surface areas. The S_{BET} of $Fe_{0.7}Ni_{0.3}O_x\mathchar`-300,\ Fe_{0.5}Ni_{0.5}O_x\mathchar`-300$ and Fe_{0.3}Ni_{0.7}O_x-300 are 142, 177 and 152 m²/g, respectively. The specific surface areas of Fe0.5Ni0.5Ox samples with varied calcination temperatures are also displayed in Table 1. With the increase of calcination temperature, the specific surface area of $Fe_{0.5}Ni_{0.5}O_x$ first increases, then decreases, exhibiting that the sample calcined at 250 °C possesses the highest S_{BET} (209 m² /g). A large SBET is beneficial for the adsorption of NO and CO, which can elevate the catalytic performance.^[25] Thus, the highest SBET is a reason for the optimal NO elimination capacity of Fe_{0.5}Ni_{0.5}O_x-250.

H₂-TPR

H₂-TPR was then tested for the reducibility of the obtained catalysts. The results of pure FeO_x, NiO_x and Fe_aNi_bO_x calcined at 300 °C are shown in Figure 5a. The profile of FeO_x exhibits three reduction peaks at 270 °C, 328 °C and 625 °C, corresponding to the three steps of reduction procedure (Fe₂O₃→Fe₃O₄→FeO→Fe⁰),^[19,26] suggesting that the composition of FeO_x is pure Fe₂O₃, which is in line with the XRD and Raman results. For the NiO_x, two major reduction peaks emerge at 265 °C and 300 °C, the former one is related to the reduction of NiO to Ni^{δ+} and the latter is assigned to the reduction of Ni⁰. ^[27, 28]

When nickel was introduced into the Fe-only catalyst, the H2-TPR profiles are different from those of either FeO_x or NiO_x. For the Fe0.7Ni0.3Ox-300 sample, three reduction peaks can be observed at 300-600 °C. The low-temperature peak α is associated with the reduction of NiO (NiO \rightarrow Ni⁰), the peak β due to the reduction of Ni²⁺ to Ni⁰ and part of Fe³⁺ to Fe²⁺ in NiFe₂O₄ phase (NiFe₂O₄ \rightarrow Ni⁰+ Fe₃O₄), the peak γ at higher temperature is related to the reduction of Fe₃O₄ (Fe₃O₄ \rightarrow FeO \rightarrow Fe⁰).^[29,30] As the Fe/Ni molar ratio is 5/5, both the reduction peak α and β of Fe0.5Ni0.5Ox-300 shift to a lower temperature than that of Fe_{0.7}Ni_{0.3}O_x-300, appearing at 320 °C and 371 °C, respectively. Further reducing the Fe/Ni molar ratio to 3/7, the Fe_{0.3}Ni_{0.7}Ox-300 sample shows the reduction peak α at 330 °C and the peak β at 380 °C. Apparently, with the decrease of Fe/Ni molar ratio, the reduction peaks α and β firstly shift to low temperature, and then, shift to high temperature. The reducing capacity is a crucial factor to influence the catalytic performance in NO + CO reaction.^[31, 32] When metal oxide catalyst is exposed to the NO-CO mixture gas, the high-state metal species of catalyst can be reduced by the CO to form low-state metal species and surface oxygen vacancies (SOVs), which provide NO dissociation site and further facilitate

the NO conversion. Compared with Fe_{0.7}Ni_{0.3}O_x-300 and Fe_{0.3}Ni_{0.7}O_x-300 samples, Fe_{0.5}Ni_{0.5}O_x-300 shows a lower temperature of reduction peak α (320 °C) and γ (371 °C), indicating that the Fe-O-Ni structure is easier to be reduced to generate SOVs, lead to the higher efficiency of NO elimination.

The H₂-TPR profiles of Fe_{0.5}Ni_{0.5}O_x samples with varied calcination temperatures are shown in Figure 5b. All the profiles are similar, showing three reduction peaks between 250 °C and 550 °C. When calcination temperature is 200 °C, the peaks α and β on Fe_{0.5}Ni_{0.5}O_x-200 occur at 335 and 380 °C. As the calcination temperature increases, the position of the peaks exhibits a volcano-type tendency. For Fe_{0.5}Ni_{0.5}O_x-250, it shows the lowest temperature of the peaks α and β among all the Fe_{0.5}Ni_{0.5}O_x catalysts, signifying the easiest reducibility and more SOVs can be formed, resulting in the high catalytic activity at low temperature.

NO-TPD

It is well known that the NO adsorption/desorption ability is a crucial factor for the NO reduction by CO.^[33] Figure 6 displays the NO-TPD profiles of FeO_x, NiO_x, Fe_{0.5}Ni_{0.5}O_x-300 and Fe_{0.5}Ni_{0.5}O_x-250. Four peaks can be observed over the mentioned catalysts. The stripping peaks N1 below 200 °C are related to desorption of bridged nitrates.^[34] The N2 peaks at about 275 °C are assigned to desorption chelating nitrates and nitrites.[35] The N3 and N4 peaks above 300 °C are associated with the decomposition of surface nitrite and nitrate.^[36] For NiO_x catalyst, an obvious N2 peak can be observed at 275 °C, indicating the presence of chelating nitrates and nitrites on surface. The FeOx sample shows a strong N3 peak at 420 °C and a weak N1 peak below 200 °C, implying a small amount of bridged nitrates and a large number of nitrite and nitrate species on the surface. For the bi-metal samples, unlike the monometallic ones, only two apparent peaks can be seen below 300 °C, suggesting the NO adsorption species are mainly bridged nitrates, chelating nitrates and nitrites. Besides, although the NO-TPD profiles of Fe_{0.5}Ni_{0.5}O_x-250 and Fe_{0.5}Ni_{0.5}O_x-300 are similar, the N1 and N2 peaks for $Fe_{0.5}Ni_{0.5}O_x\mbox{-}250$ are more prominent than that for $Fe_{0.5}Ni_{0.5}O_x\mbox{-}300,$ revealing the stronger chemisorption of NO at low temperature. Based on the NO-TPD results, the intensity and area of N1 peak for these four catalysts is arranged in the following order: Fe_{0.5}Ni_{0.5}O_x-250 > $Fe_{0.5}Ni_{0.5}O_x$ -300 > FeO_x > NiO_x , in agreement with the NO elimination performance in Figure 1. Therefore, we consider the surface bridged nitrates plays an important role in the NO + CO reaction, the introduction of nickel species into the Fe catalyst can enhance the NO adsorption capacity at low temperature. Compared with other catalysts, more bridged nitrates species on the Fe_{0.5}Ni_{0.5}O_x-250 sample's surface can participate in the lowtemperature NO + CO reaction, resulting in enhanced catalytic performance.







Fig 6. NO-TPD profiles of FeO_x, NiO_x, Fe_{0.5}Ni_{0.5}O_x-250 and Fe_{0.5}Ni_{0.5}O_x-300.

XPS

XPS was utilized to investigate the surface elemental composition and chemical valence states of the as-prepared samples. Figure 7 shows the O 1s, Fe 2p and Ni 2p XPS spectra of FeO_x, NiO_x and Fe_aNi_bO_x catalysts calcined at 300 °C. The O 1s XPS spectra could be classified into two distinct peaks. The peak at 529.3-529.7 eV stems from lattice oxygen O^{2-} (O_L); the peak at around 530.9 eV is attributed to surface oxygen (O_S), including hydroxyl species and surface-adsorbed oxygen (O22-/ O⁻).^[37, 38] According to previous work,^[13, 39-41] surface oxygen species is a crucial factor for the NO reduction by CO, which can oxidize CO and promote the adsorption of NO. The proportion of each oxygen species is shown in Table 2. The O_S proportions of $Fe_{0.7}Ni_{0.3}O_x$ -300, $Fe_{0.5}Ni_{0.5}O_x$ -300 and $Fe_{0.3}Ni_{0.5}O_x$ -300 are 46.72%, 60.78% and 50.0%, obviously higher than that of FeO_x (27.17%). Particularly, the Fe_{0.5}Ni_{0.5}O_x-300 shows the highest O_S proportion among the three Fe-Ni mixed oxide catalysts, and it also shows the optimal NO elimination efficiency. On the other hand, the O_S proportions of NiO_x (47.53%) and Fe_{0.7}Ni_{0.3}O_x-300 (46.72%) are similar, but NiOx shows particularly poor NO removal capacity below 200 °C. That is because, in the Fe-Ni mixed oxide catalyst, the oxygen bonded by Fe and Ni ions, namely surface synergetic oxygen, is more active than the oxygen only boned by Ni ions in NiOx. [32] Figure 7b shows the Fe 2p XPS spectra. For FeOx, the peaks near 710 eV and 724 eV are ascribed to the Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The separation of the two peaks is 13.6 eV, implying that the main composition is Fe₂O₃,^[42] consistent with the XRD and Raman results. For the $Fe_aNi_bO_x$ -300 catalysts, the peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ appear at about 710 and 724 eV, respectively, and they are further deconvoluted into Fe2+ (710.3-710.6 eV, 723.6-724.0 eV) and Fe³⁺(712.2-712.7 eV, 726.0-726.3 eV).[43-45] The peaks at about 718 and 732 eV are related to the satellite peaks. Besides, in comparison with FeO_x, when nickel was added into Fe catalyst, all the Fe_aNi_bO_x-300 catalysts show a kind of peak at 705.2-705.6 eV, which is assigned to the "pre-peak", resulting from the generation of lattice defects on the catalyst surface.^[46] The Fe³⁺/Fe²⁺ ratios were shown in Table 2, the ratio decreases as following: $Fe_{0.5}Ni_{0.5}O_x-300 > Fe_{0.7}Ni_{0.3}O_x-300 > Fe_{0.3}Ni_{0.7}O_x-300$, exactly the same order as their catalytic activities (Figure 1a). Figure 7c shows the Ni 2p XPS spectra, where three peaks occur at 854-862 eV. The peaks at 854.4-854.6 eV and 856.0-856.1 eV present Ni²⁺ and Ni³⁺ respectively, and the peaks around 861.3 eV are attributed to the satellite peak.^[45, 47] As shown in Table 2, the Ni^{2+}/Ni^{3+} ratios of Fe_{0.7}Ni_{0.3}Ox-300, Fe_{0.5}Ni_{0.5}O_x-300 and $Fe_{0.3}Ni_{0.7}O_x$ -300 samples are 0.90, 1.11 and 0.78, visibly, $Fe_{0.5}Ni_{0.5}O_x$ -300 is the highest. It is worth noting that, compared with the NiO_x , the binding energy of Ni^{2+} , Ni^{3+} and satellite on Fe_aNi_bO_x-300 samples are higher, suggesting that the introduction of Fe can change the chemical environment of Ni.

Figure 8 displays the O 1s, Fe 2p and Ni 2p of Fe_{0.5}Ni_{0.5}O_x catalysts calcined at different temperatures. The Fe³⁺/Fe²⁺, Ni²⁺/Ni³⁺ ratios and oxygen species proportions are shown in Table 2. As a result, with the increase of calcination temperature, the O_S proportion increases at first and then decreases, Fe_{0.5}Ni_{0.5}O_x-250 exhibits the highest O_S percentage (69.85%). The ratios of Fe³⁺/Fe²⁺ and Ni²⁺/Ni³⁺ also present similar volcano-

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type tendency, the Fe³⁺/Fe²⁺ and Ni²⁺/Ni³⁺ ratios of Fe_{0.5}Ni_{0.5}O_x-250 are 1.35 and 1.22, higher than that of Fe_{0.5}Ni_{0.5}O_x -200, Fe_{0.5}Ni_{0.5}O_x -300 and Fe_{0.5}Ni_{0.5}O_x -350. From the XRD and Raman results, the Fe_aNi_bO_x samples present the mixed phases of NiFe₂O₄ and NiO. Since NiFe₂O₄ is an inverse spinel compound, NiFe₂O₄ shows the mixing valences of Fe and Ni.^[48] Therefore, Fe²⁺, Fe³⁺, Ni²⁺ and Ni³⁺ can be observed on the Fe_aNi_bO_x surface by XPS.

According to the result mentioned above, the Fe-Ni mixed oxides with varied Fe/Ni molar ratios and calcination temperatures display different surface chemical valence states. Interestingly, the highest Fe³⁺, Ni²⁺ and O_S proportions belong to Fe_{0.5}Ni_{0.5}O_x-250, which also shows the highest NO elimination capacity among all the as-prepared catalysts. Thus, we speculate that the catalytic performance is not only correlated with the abundant surface oxygen species but also related to the high percentage of Fe³⁺ and Ni²⁺ on the surface of the catalyst. It is reported that an interaction between different species in the metal mixed oxide catalysts, namely, redox cycle, plays an essential role for the NO reduction by CO. For instance, the redox cycle such as $Cu^{2+} + Mn^{3+} \leftrightarrow Cu^{+} + Mn^{4+}$ [31], $Ce^{3+} + Cu^{2+} \leftrightarrow Ce^{4+} +$ Cu^{+,[34, 49]} Ce³⁺+ Fe³⁺ \leftrightarrow Ce⁴⁺+ Fe^{2+,[50]} and Co³⁺+ Fe²⁺ \leftrightarrow Co²⁺+ Fe^{3+[51]} can promote the catalytic performance As we know, the electronegativity of Ni (1.91) is larger than that of Fe (1.83), and electrons may migrate from Fe2+ to Ni3+ to generate Fe3+ and Ni2+ in the catalysts. Hence, we propose a solid-state charge-transfer redox couple of $Fe^{2+} + Ni^{3+} \leftrightarrow Fe^{3+} + Ni^{2+}$ on Fe-Ni mixed oxides, and the redox cycle can shift to right through varying the Fe/Ni molar ratio and calcination temperature, which can enhance the catalytic activity for NO elimination.

Table 2. Surface compositions of as-prepared catalysts.								
Sample	Fe ³⁺ /Fe ²⁺	Ni ²⁺ /Ni ³⁺	O _S (%)	O _L (%)				
FeOx	-	-	27.17	72.83				
NiOx	-	0.49	47.53	52.47				
Fe _{0.7} Ni _{0.3} O _x -300	1.13	0.90	46.72	53.28				
Fe _{0.5} Ni _{0.5} O _x -300	1.21	1.11	60.78	39.18				
Fe _{0.3} Ni _{0.7} O _x -300	0.95	0.78	50.0	50.0				
Fe _{0.5} Ni _{0.5} O _x -200	0.95	0.81	63.50	36.50				
Fe _{0.5} Ni _{0.5} O _x -250	1.35	1.22	69.85	30.15				
Fe _{0.5} Ni _{0.5} O _x -350	1.10	0.98	37.50	62.50				

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Catalytic performance of Fe_{0.5}Ni_{0.5}O_x-250

Effect of WHSV

Since the optimal catalytic activity is possessed by Fe_{0.5}N_{0.5}O_x-250, we further investigated the effect of weight hour space velocity (WHSV), CO concentration and water due to their significant influence in actual applications. Figure S2 displays the NO conversion of Fe_{0.5}N_{0.5}O_x-250 with varied WHSVs. When the WHSV is 30000 ml•g⁻¹•h⁻¹, the 100% NO conversion temperature is 140 °C. When the WHSV decreases, the NO conversion of Fe_{0.5}N_{0.5}O_x-250 increase, because the residence time of reactant gas in the catalyst bed is inversely proportional to WHSV, indicating that suitably raising temperature is an effective way to enhance the NO conversion at a higher space velocity.

Effect of CO concentration

The effect of CO concentration on the NO conversion over Fe_{0.5}N_{0.5}O_x-250 sample was investigated. As a result in Figure S3, the T_{100NO} is proportional to CO concentration from 4000 to 1000 ppm. Using the reactant gas with CO concentration of 4000 ppm, T_{100NO} is 120 °C. When the CO concentration is reduced to 2000 and 1000 ppm, T_{100NO} increases to 130 and 140 °C, respectively. The results above clearly demonstrate the positive effect of relatively high CO concentration on NO conversion over the Fe_{0.5}N_{0.5}O_x-250 sample. For the catalytic reduction of NO by CO, CO can react with surface-capping O²⁻ of catalyst to form surface oxygen vacancies (SOVs), which promote the dissociation of NO molecules and enhance the NO conversion ^[31, 32]. We speculate that as the concentration of CO increases, more SOVs are generated on the catalyst surface, resulting in an enhanced NO elimination performance.

Stability and water resistance

Moreover, the lifetime property of Fe_{0.5}N_{0.5}O_x-250 was examined. Figure 9a shows the NO conversion in the time course at 130 °C. The catalytic stability test result reveals that the catalytic activity maintains a very high NO conversion of 100% and no obviously decrease can be observed over 40 h.

Although the Fe0.5N0.5Ox-250 sample exhibits high catalytic stability under the dry condition of CO-NO-N₂, two intractable problems: oxygen and moisture, should be considered. It is wildly reported that the O₂ in reactant gas can competitively consume CO and thus finally decrease the NO conversion.^[52, 53] Fortunately, recent years, a rotate reactor was invented to solve the problem by preventing the mixing of CO and O2 via a NOx adsorptionreduction process, which could avoid the adverse effect of oxygen.^[54, 55] However, moisture, the other inevitable negative factor, should be taken into consideration. Figure 8a also shows the effect of moisture on the catalytic stability of Fe0.5N0.5Ox-250 sample at 130 °C. In the nonappearance of H₂O, the NO can be converted entirely. When ~2.5 vol.% moisture is added, the NO conversion decreases from 100% to ~40% in 1 h. In addition, after reacting under the moist condition for 20 h, when moisture is removed, the NO conversion returns to 100% in 2 h and no obvious deactivation can be seen in the next 8 h. The results demonstrate that the deactivation of Fe_{0.5}N_{0.5}O_x-250 catalyst caused by ~2.5 vol.% moisture at 130 °C is reversible. To further

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investigate the effect of moisture, transmission FTIR was carried out to inspect the used Fe0.5N0.5Ox-250 catalyst under different conditions. As shown in Figure 9b, the used Fe_{0.5}N_{0.5}O_x-250 catalyst at stage 1 (for 40 h under dry condition) displays a slight absorption peak at 1384 cm⁻¹, this is caused by the antisymmetric stretching vibration of nitro species.[56-58] The used Fe0.5N0.5Ox-250 at stage 2 (reacted for 10 h under dry condition + 20 h under moist condition) shows a sharper peak at 1384 cm⁻¹ than that of stage 1, suggesting the vibration of nitro species is more intensive. As the moisture is removed, the intensity of the absorption peak at 1384 cm⁻¹ for the used catalyst at stage 3 is back to stage 1. The experiments imply that the water vapor can aggravate the accumulation of nitro species on the catalyst surface, but the accumulation is reversible. According to the results, we consider the active sites on the catalyst surface are occupied by H₂O as the moisture added, leading to the less consumption of the nitro species on the active sites and inhibition of catalytic performance. When the moisture is removed, the H₂O molecules absorbed on the catalyst surface can be rapidly removed by the flowing reactant gas, thus releasing the active sites. After that, parts of the surface nitro species are decomposed, resulting in a decrease of the intensity of nitro species and recovery of the NO elimination efficiency.



Fig 9. (a) Stabilities of the Fe_{0.5}Ni_{0.5}Ox-250 catalyst under dry and moisture condition. (Reaction conditions: [NO] = 1000 ppm, [CO] = 2000 ppm, [H₂O] = 2.5 vol.%, [N₂] = balance; T = 130 °C; WHSV = 15000 ml•g⁻¹•h⁻¹); (b) FTIR spectra of the Fe_{0.5}Ni_{0.5}Ox-250 catalyst under different stages.

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Additionally, the catalytic activity and stability of Fe_{0.5}N_{0.5}O_x-250 under moist condition was examined, and the result is shown in Figure 10. Compared to under dry condition (Figure 1b), when ~2.5 vol.% moisture is introduced into the feed gas, T_{100NO} of Fe_{0.5}N_{0.5}O_x-250 increases from 130 °C to 180 °C, indicating the negative effect of moisture at low temperature. The lifetime study is also shown in Figure 10, Fe_{0.5}N_{0.5}O_x-250 displays that the stability of 100% NO conversion is more than 30 h at 180 °C. We also compare the NO elimination efficiency of Fe_{0.5}N_{0.5}O_x-250 with many reported catalysts, the results are summarized in Table S1. The catalytic performance of Fe_{0.5}N_{0.5}O_x-250 is higher than that of most reported non-precious metals, even comparable to precious metal catalysts.



Fig 10. Catalytic performance of the Fe_{0.5}Ni_{0.5}O_x-250 catalyst. (Reaction conditions: [NO] =1000 ppm, [CO] = 2000 ppm, [H₂O] = 2.5 vol.%, [N₂] = balance; T = 100 - 300 °C; WHSV = 15000 ml•g⁻¹•h⁻¹)

Catalytic mechanism discussion

For the NO + CO reaction, researchers have put forward many mechanisms to explain the reaction pathway over different catalysts. From many previous studies, [14, 32, 59, 60] a reaction cycle (cycle 1) can be summarized as the following pathways: 1. The catalyst surface was reacted with CO to generate surface oxygen vacancies. 2. The NO molecular was activated by the surface oxygen vacancies to produce N and O radicals. 3. The N radical combined with another NO molecule to generate N2O or combined together to form N2. 4. The O radical reacted with CO to produce CO2. In addition to cycle 1, some researchers proposed another reaction cycle (cycle 2). In cycle 2, pathways 1-3 are similar to that of cycle 1, however, after the NO was dissociated and surface oxygen vacancies was formed, the O radicals dissociated from the NO were more prone to fill in the oxygen vacancies to generate new surface oxygen species than react with CO to form CO₂, that is, the reduced catalyst surface could be re-oxidized by NO.[61, 62]





In order to explore the possible reaction mechanism over Fe-Ni mixed oxide catalysts, XPS analysis was used to investigate the variation of surface chemical valence states over Fe_{0.5}Ni_{0.5}O_x-250 sample treated by different reactant gases. Figure 11 shows the XPS spectra of fresh catalyst, CO-pretreated catalyst (purged by 2000 ppm CO at 250 °C for 200 min, WHSV=15000 mL.g⁻¹.h⁻

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¹) and NO-adsorbed catalyst (pretreated by 2000 ppm CO at 250 °C for 200 min, then switched to 1000 ppm NO at the same temperature for 200 min to adsorb NO, WHSV=15000 mL.g⁻¹.h⁻¹). Figure 11a shows the spectra of Fe2p. For the fresh catalyst, the peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ appear at 710.88 and 724.08 eV, respectively. After the treatment of CO, the peaks of Fe 2p_{3/2} and Fe 2p_{1/2} shift to low-valence state, appearing at 709.98 and 722.68 eV. The NO adsorption process does not return the spectrum of Fe back to the initial position. For the Ni 2p spectra, the Ni 2p_{3/2} and Ni 2p_{1/2} peaks shift to the low-valence state after the treatment of CO in comparison of a fresh one, besides, the valence state of Ni⁰ can be observed at 852.08 eV and 869.38 eV, after the adsorption of NO, the positions of Ni species exhibit almost no change. According to the XPS test, the high-valence ions (Fe³⁺, Ni³⁺ and Ni²⁺) on catalyst surface can be reduced to the lowvalence states (Fe²⁺, Ni²⁺ and Ni⁰) under CO atmosphere, but the low-valence species are difficult to be oxidized back to the initial valence state by the following treatment of NO. The result also can be proved by the O 1s spectra, the proportion of surface oxygen species changes from 69.85%→33.09%→34.60% after the CO and NO treatment. That is, the catalyst surface can be reduced by CO to form oxygen vacancies, but the oxygen vacancies are hard to be re-filled by the O stems from NO.

When the Fe_{0.5}Ni_{0.5}O_x-250 was used for 4 h at 150 °C and 250 °C, respectively, the composition of the used catalysts were characterized by XRD and XPS (see Figure S4). The XRD spectra of fresh and used catalysts are similar, both NiFe₂O₄ and NiO phases can be observed. However, the XPS spectra of the fresh and the used are different. For the used catalysts, comparing with the fresh one, we can see that: (1) The peaks of Fe 2p_{3/2} and Fe 2p_{1/2} shift to low-valence state after reaction. (2) The valence state of Ni⁰ can be observed after reaction. (3) As the reaction temperature increases, the O_S proportion decreases gradually. The results above clearly demonstrate that the catalyst surface was reduced during reaction.

In-situ DRIFTS of CO and NO co-adsorption was also utilized to explore the reaction process over Fe0.5Ni0.5Ox-250. As depicted in Figure 12, when the sample is exposed in the mixture gas at 50 °C, eight bands can be observed, which are attributed to bridging bidentate nitrates (1025 cm⁻¹),^[63] chelating bidentate nitrates (1205 cm⁻¹),^[14] linear nitrites (1276 cm⁻¹),^[14] monodentate nitrates (1501 cm⁻¹),^[64] vibrational modes of Fe-(NO)₂ (1760 cm⁻¹ $^{1}),^{[65]}$ NO adsorbed on Ni^{2+} (1833 $cm^{-1})^{[31]}$ and gaseous CO (2178 and 2120 cm⁻¹),^[66] respectively. When the temperature rises to 100 °C, a band can be observed at 1356 cm⁻¹, which belongs to the bidentate formate, resulting from the interaction between CO molecular and surface hydroxyls.^[64] Meanwhile, gaseous CO₂ can be seen in 2250-2400 cm⁻¹. When the temperature increases to 150 °C, the band of NO adsorbed on Ni²⁺ at 1833 cm⁻¹ is replaced by NO adsorbed on Ni⁺ at 1815 cm⁻¹, indicating that the Ni²⁺ is reduced to Ni⁺ in the reactant gas.^[67] In addition, two bands can be distinguished at 1217 cm⁻¹ and 1252 cm⁻¹, the former one can be deemed to the hydrogen carbonates with the $\delta(\text{C-O}...\text{H})$ vibration mode,^[68] and the latter is assigned to the bridged nitrates. ^[41] As the temperature gradually increases, the band of linear nitrites (1276 cm⁻¹) vanishes because of its poor stability at 200 °C.[68] Besides, the intensity of the band of NO adsorbed on

Ni⁺ becomes stronger at 200 °C and then decreases at 250 °C, implying that the Ni²⁺ is reduced to form Ni⁺ at first and then further reduced to Ni⁰, which is in line with the XPS results (Figure 11b). On the other hand, a new band derived from the coordinated CO_x with the low-state metal species appears at 1066 cm⁻¹ at 200 and 250 °C, also suggesting that the cations are reduced under NO + CO atmosphere.^[69]



Fig 12. in-situ DRIFTS of CO+NO co-adsorption over Fe0.5Ni0.5Ox-250.

Based on the XPS and in-situ DRIFTS results, the mechanism for NO reduction by CO over Fe_aNi_bO_x catalyst should follow the cycle 1. In detail, when the catalyst is exposed in the mixture gas, NO is adsorbed on the catalyst surface to form NO_x species. As the temperature increase, partial adsorbed NO_x species (bridging bidentate nitrates, chelating bidentate nitrates and linear nitrites) are desorbed/converted/dissociated. The surface oxygen is reacted with CO to form CO₂ and some generated CO₂ are absorbed on the surface to produce carbonate species. Meanwhile, the Fe-O-Ni structure is reduced to generate $Fe^{2+}\text{-}\text{-}Ni^{2+}$ and $Fe^{2+}\text{-}\text{-}Ni^0$ species (\square means surface synergetic oxygen vacancies, SSOVs). Previous literature have reported that SSOVs is a key factor to weaken the N-O band, which can dissociate NO to produce O and N radicals. $^{[32,\ 62,\ 70]}$ With the dissociation of NO, the O radicals are reacting with CO to form CO₂, while the N radicals can combine with another NO molecule to generate N₂O or combine together to generate N₂. The intermediate N₂O is further reduced to produce N₂ at higher temperature.

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Fig 13. Possible reaction mechanism of NO reduction by CO over $\mathsf{Fe}_a\mathsf{Ni}_b\mathsf{O}_x$ catalyst.

Conclusions

In this work, Fe-Ni mixed oxide catalysts were synthesized via a sol-gel method. Compared with the Fe-only and Ni-only catalysts, Fe_aNi_bO_x catalysts exhibit a tremendous enhancement of activity in NO + CO reaction. The Fe-Ni mixed oxide catalysts show higher specific surface area and NO adsorption capacity than monometallic ones. For the most active Fe0.5Ni0.5Ox-250 catalyst, NO can be entirely eliminated at 130 °C, and the 100% NO conversion is sustained for 40 h. The H₂-TPR and XPS analyses reveal that the easier reduction behavior, more surface oxygen species and stronger electron interaction between Fe and Ni (Fe²⁺ + Ni³⁺ \leftrightarrow Fe³⁺ + Ni²⁺) are the key factors to the NO elimination. The effect of CO concentration, WHSV and moisture (~2.5 vol.%) on the catalytic performance were explored. The addition of H₂O can decrease the NO conversion because of the nitrate deposits, but the deactivation is reversible. Fe0.5Ni0.5Ox-250 also exhibits an inspiring low-temperature catalytic performance under moist condition, NO can be converted completely at 180 °C and the lifetime is more than 30 h in the presence of ~2.5 vol.% water. The surface composition analyses (XPS and in-situ DRIFTS) during reaction indicate that the Fe-O-Ni structure can be reduced to form Fe²⁺-D-Ni²⁺ and Fe²⁺-D-Ni⁰, which promote the dissociation of NO. The dissociated O radicals are prone to react with CO to form CO₂ rather than re-fill into the oxygen vacancies on the catalyst surface. The N radicals react with NO molecules to generate N₂O or combine together to produce N₂. Overall, this study demonstrates that Fe-Ni mixed oxide catalysts possess high and steady NO removal performance in NO + CO reaction at low temperature. The catalytic process presents potential application value, and can be applied in locations such as stationary sources gas and automobile exhaust purification.

Experimental Section

Catalyst preparation

The Fe-Ni mixed oxide catalysts were prepared through a sol-gel method. Fe(NO₃)₃•9H₂O and Ni(NO₃)₂•6H₂O were utilized as the salt precursors. In detail, equal moles of metal nitrate (0.05 mol) and citric acid monohydrate (0.05 mol) were dissolved in deionized water to form a solution and stirred for 6 h at 25 °C. Then, the solution was evaporated in air at 70 °C for 8 h to form a sol. The obtained sol was dried at 80 °C overnight to form a dark red, foam-like solid. The solid samples were ground to powder and calcined at designed temperature for 4 h in air. The asprepared catalysts were denoted as Fe_aNi_bO_x-T, where a/b is the Fe/Ni molar ratio, T is the calcination temperature in degrees Celsius. For example, Fe_{0.5}Ni_{0.5}O_x-300 represents that 0.025 mol of Fe(NO₃)₃•9H₂O and 0.025 mol of Ni(NO₃)₂•6H₂O were employed, and the calcination temperature was 300 °C. Besides, Fe-only and Ni-only samples were synthesized by the same method with the calcination temperature of 300 °C, denoted as FeO_x and NiO_x.

Catalyst testing

NO reduction by CO was performed using a fixed bed reactor (6 mm I.D.). The blind experiment showed no activity from 100 °C to 300 °C. Before each measurement, 200 mg of sample (20-60 mesh) was pretreated in N₂ flow (20 ml/min) at 100 °C for 1 h to remove possible impurities. Then, a mixture gas consists of 1000 ppm NO, 2000 ppm CO, 2.5 vol.% H₂O (when used) and N₂ balance gas was introduced into the reactor. The total flow rate was 50 ml/min, corresponding to the weight hour space velocity (WHSV) of 15000 (ml·g⁻¹·h⁻¹). The concentrations of NO (m/z = 30), N₂O (m/z=44) and CO₂ (m/z=44) were analyzed using a mass spectrometry coupled to gas chromatography (GC-MS). The gas chromatograph was equipped with a Poropak Q column for separating N₂O and CO₂. After reaching steady state at each temperature, the gas concentrations were collected.

The NO conversion, CO conversion and N_2O selectivity are calculated by the following equations:

NO conversion (%) = (NO in - NO out) / NO in \times 100%

CO conversion (%) = CO_{2 out} / CO in \times 100%

 $N_2O_{selectivity}$ (%) = 2 × N_2O_{out} / (NO in – NO out) × 100% Where in and out indicate the inlet and outlet concentration of the corresponding gas.

Catalyst characterization

X-ray diffusion (XRD) spectra were performed using a RINT2000 vertical goniometer equipped with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Thermo Scientific ESCALAB 250Xi using a focused monochromatic Al K α source. In addition, the C1s peak at 284.6 eV was operated as the reference to calibrate all binding energies. Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 380 infrared spectrometer in the wavenumber ranging from 500 to 2000 cm⁻¹. Raman measurements were conducted using a DXR Raman Microscope scanning with a laser of 532 nm.

The N₂ adsorption-desorption isotherms were obtained on a Quantachrome NOVA touch LX³ instrument. The specific surface areas, S_{BET}, were calculated by using the Brumauer-Emmett-Teller (BET) method. Before testing, each catalyst was pretreated under vacuum at 200 °C for 3 h.

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H₂-TPR spectra of the as-prepared samples were obtained using a Micromeritics AutoChem2090 apparatus. Before each experiment, the catalyst (50 mg) was heated in N₂ (50mL/min) at 200 °C for 60 min, then, cooled to 50 °C. After that, the N₂ was switched to a 10% vol. H₂/N₂ mixture gas (50 mL min⁻¹) and heated up to 750 °C (heating rate = 10 °C/min).

NO-TPD analysis was operated in a continuous-flow apparatus with a TCD detector. Before each test, 50 mg of sample was purged in N₂ flow (50mL/min) at 200 °C for 1 h, then cooled to 50 °C. Then, the gas flow was switched to NO-He mixture gas (2 vol.% NO) and held for 30 min. After that, it was purged by He for 30 min for the removal of the physically adsorbed gas. At last, the catalyst was heated from 50 to 650 °C in helium (heating rate = 10 °C/min).

The *in situ* DRIFTS spectra were obtained on a Nicolet IZ10 FTIR spectrometer equipped with an MCT detector (Thermo Fisher, USA). The spectral resolution is 4 cm⁻¹ and the number of scans = 32. The sample (~10 mg) was mounted in quartz FTIR cell and purged for 60 min in Ar (250 °C, 50 mL/min). The background spectra at certain temperatures were recorded during the cooling process. After that, a stream of 2000 ppm CO -1000 ppm NO-Ar (50 mL/min) was introduced as the reactant gas, and the CO-NO co-adsorption spectrum was recorded by subtracting the corresponding background reference at each target temperature.

Conflicts of interest

There are no conflicts to declare

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FULL PAPER

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Fe-Ni mixed oxide catalysts show excellent catalytic performance for NO reduction by CO at low temperature. The correlation between physicochemical properties and catalytic performance were discussed. A possible mechanism was proposed.



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