



NaBH₄ Surface Modification on CeO₂ Nanorods Supported Transition-Metal Catalysts for Low Temperature CO Oxidation

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In this report, CeO₂ nanorods (CeO₂NR) were first chemically etched by different amounts (0.6, 3 and 6 wt %) of NaBH₄, which were employed to understand the etching effect on the support structure, surface defects, and reducibility of modified CeO₂NR supports. The 6 wt % NaBH₄ etched CeO₂NR was further used as support materials to load transition-metals (TM: Cu, Co, Ni, Fe and Mn) catalysts, in order to investigate the support etching effect on the reducibility and catalytic performance of CeO₂NR

supported TM catalysts. In comparison with the catalytic performance of CeO₂NR supported TM catalysts in literature, the 6 wt % NaBH₄ etched CeO₂NR supported catalysts show clearly enhanced CO oxidation performance at lower temperature, which is mainly attributed to the created surface defects by boron doped CeO₂ surface during NaBH₄ chemical etching and strong metal-support interaction.

1. Introduction

The surface structure (i.e., crystal/defect/electronic structures) of catalyst supports plays a critical role in metal catalyst dispersion, stabilization, and even reactive gases adsorption and migration for heterogeneous catalysis.^[1,2] Various oxides (SiO₂, Al₂O₃, ZrO₂, MgO, TiO₂ and CeO₂) have been widely used as catalyst support materials and/or promoters in heterogeneous catalysis, due to their excellent thermal stability, variable oxygen stoichiometry, redox property, acid-base character, and tunable crystal and electronic structures.^[3–12] Along with other oxides, CeO₂, as a reducible/active oxide support in supported catalysts,^[13] is well-known for its promoting role in CO oxidation reaction. The excellent performance of CeO₂ can be attributed to its high oxygen storage capacity with reversible Ce³⁺/Ce⁴⁺ redox pair, mobile surface oxygen species and rich surface oxygen vacancies.^[14,15] Furthermore, CeO₂ nanocrystals with different morphologies, such as nanocubes (NC), nanospheres (NS), nanooctahedra (NO) and nanorods (NR) have been intensely investigated on the support morphology and exposed crystal plane effects on the catalytic activity of CeO₂ supported catalysts.^[16,17] According to others' and our previous work,^[13,18,19] CeO₂NR supported metals (i.e. Au and Cu) show superior activity in water-gas shift reaction and CO oxidation compared to CeO₂ NC and NO supported counterparts. In addition, Lykaki et al.^[11] reported that CeO₂NR shows the highest activity when employed as supporting carrier of the Cu phase for CO oxidation when compared to irregular-shaped CeO₂ nanoparticles. Thus, in this study, CeO₂NR powder was selected as

the catalyst support to study the surface modification effect on CO oxidation reaction.

To further optimize the promoting and/or synergistic effects of oxide supports, several strategies can be utilized to modify or transform the surface structure/composition of supports, including thermal treatment, chemical etching, and ion implantation etc. For example, Yang et al.^[20] used low temperature plasma treatment to modify the surface structure of CeO₂ nanoflakes and found that the Ce³⁺/Ce⁴⁺ ratio, surface oxygen vacancy concentration and O₂²⁻ anions content (in peroxide) increased under reducing plasma atmosphere. Konsolakis et al.^[21] recently reviewed the surface structure modification of CeO₂ by employing advanced preparation methods and modification routes. Among various methods, chemical etching treatment can dissolve part of the surface or modify the surface structure/composition of supports at low temperature, which shows great potential for generating favorable catalyst trapping sites and active sites for gas-gas or gas-solid reactions.

Sodium borohydride (NaBH₄) is commonly used as a strong reducing agent in industrial and laboratory applications. The main working mechanism of its high reducibility is that it can react with water to form sodium metaborate and hydrogen ($\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$ (1)). In supported metal catalysts, NaBH₄ was reported to be relatively effective in reducing the precursors of TMs and noble metals from ionic to metallic states on the support surface.^[22–25] On the other hand, there are a few studies on NaBH₄ employed as a chemical etching agent. For instance, Hua et al.^[26] reported that the addition of NaBH₄ can change magnetite microcrystals structure from microoctahedra to magnetite (111) single crystal microplates (shape change) by forming Fe–B amorphous alloy at first and then self-assembling into single crystal structure. For the application of support oxides, Zhang et al. used NaBH₄ as an etchant to control the surface roughness of silica shells.^[27]

In this work, NaBH₄ was used to chemically etch CeO₂NR powders and modify the surface structure, and we demonstrate

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that this treatment can promote the low temperature oxygen storage capacity and catalytic activity of CeO₂NR.

2. Experimental Section

2.1. Preparation of pristine CeO₂NR support

CeO₂NR powder was synthesized by a hydrothermal method as reported previously.^[13] 88 mL 0.1 M cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) and 8 mL 6.0 M sodium hydroxide (NaOH) in deionized water (DI water) were mixed and stirred for 30 seconds. After stirring, the mixtures were added into a Teflon liner with stainless-steel autoclave. The autoclave was heated to 90 °C and kept for 48 h. Finally, the sample was filtered and dried at 60 °C overnight to get dry CeO₂NR powder.

2.2. NaBH₄ chemical etching of CeO₂NR powder

The obtained CeO₂NR powder was treated with NaBH₄ in the following steps. First, CeO₂NR powders were added into DI water in three 250 mL beakers. 0.6, 3 and 6 wt% of NaBH₄ (weight percent = NaBH₄/(NaBH₄ + CeO₂) × 100%) were added into the CeO₂/water suspension mixture and stirred for 12 h on a hotplate magnetic stirrer. Then the samples were filtered and dried at 60 °C for 12 h. After that, the powders were calcined at 300 °C for 5 h in air. This temperature was chosen to make sure that boron species can strongly interact with CeO₂NR but not high enough to lead to agglomeration of CeO₂NR and surface defect reduction during high temperature calcination. Finally, the samples after calcination were labeled as x wt% NaBH₄-CeO₂NR (x = 0.6, 3 and 6). Typically, 6 wt% NaBH₄-CeO₂NR was also denoted as mCeO₂NR ("m" refers to "modified").

2.3. Deposition of TM catalysts on modified CeO₂NR

The modified CeO₂NR supported TM catalysts were fabricated by a precipitation-deposition method. Typically, the as-prepared 6 wt% NaBH₄-CeO₂NR (mCeO₂NR) powders (0.5 g) were first suspended in 100 mL of DI water with moderate magnetic stirring. Then, 10 wt% of precursors (weight percent = MO_x/(MO_x + CeO₂) × 100%) (Cu(NO₃)₂·2.5 H₂O, 98%, Acros Organics; NiCl₂, 98%, Acros Organics; Co(NO₃)₂·6 H₂O, 98.0~102.0%, Alfa Aesar; Fe(NO₃)₃·9 H₂O, 99+, Acros Organics; and Mn(CH₃COO)₂, 98+, Alfa Aesar), were added (dissolved) in the suspensions above. During the stirring, pH was kept ~9 by adding aqueous ammonia (NH₃·H₂O) into the suspensions. Then the samples were aging at 80 °C for 4 h. After that, the precipitates were filtered and dried at 80 °C overnight. Finally, the catalyst powders were calcined at 400 °C for 5 h in air. This calcination temperature (400 °C) was a little higher than that (300 °C) for CeO₂NR, which ensures a complete decomposition of transition-metal precursors. The powders after calcination were denoted as 10MO_x-mCeO₂NR (M = Cu, Ni, Co, Fe and Mn).

2.4. Catalyst characterizations

All samples before characterization and catalytic activity test were calcined. The support materials (CeO₂NR, 0.6/3/6 wt% NaBH₄-CeO₂NR) were calcined at 300 °C for 5 h and the supported catalysts (10MO_x-mCeO₂NR; M = Cu, Ni, Co, Fe and Mn) were calcined at 400 °C for 5 h. The heating rate was 10 °C/min.

The powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert MPD diffractometer using Cu K α radiation (λ =

1.5418 Å) in the Bragg's angle range from 5° to 90°. The operating voltage and current for XRD during scanning were 45 kV and 40 mA, respectively. The scanning rate was 0.01° per second. The XRD Rietveld refinement analysis was performed on the GSAS-II to obtain the lattice parameters and cell volume of the samples. The Raman spectra of the catalysts were collected on a Horiba Labram HR 800 Raman Spectrometer (with 100 long-working-distance objective, NA = 0.60) using a 532 nm laser module scanned in the range of 200–1500 cm⁻¹. The instrument was calibrated by standard silicon wafer (520.7 cm⁻¹) every time before measurement.

X-ray photoelectron spectroscopy (XPS) was employed by a Kratos Axis Ultra DLD spectrometer with monochromatic Al K α radiation (h ν = 1486.6 eV) under ultra-high vacuum (UHV) conditions with base pressure under 8 × 10⁻¹⁰ Torr. The samples were prepared by adding 2–3 droplets of the powder suspension with ethanol on a flat silicon wafer and waiting until a homogeneous thin film formed after ethanol evaporation in air. The carbonaceous C 1s line at 284.8 eV was used to calibrate the binding energies as an internal standard. CasaXPS software was used to analyze the XPS spectra.

Transmission electron microscope (TEM, FEI Tecnai F20) was operated to determine the morphologies and sizes of the powder samples at 200 kV. The TEM samples were prepared by suspending a small amount of powders in ethanol followed by ultrasonication for 15 seconds and then adding 2–3 droplets of suspension solution on ultrathin holey carbon film supported on copper grid (Ted Pella). Thermo Scientific Apreo scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS) detector was used to collect SEM images and EDS spectra of the powder samples at 20 kV. The samples of SEM were prepared by placing a small amount of the powders on conductive carbon tapes.

Single-point BET (Brunauer-Emmett-Teller) surface area of the powders was determined by measuring N₂ adsorption at liquid nitrogen temperature (~ -196 °C) using Micromeritics AutoChem II 2920 chemisorption analyzer, which was also used for hydrogen temperature programmed reduction (H₂-TPR). H₂-TPR was conducted to examine the reducibility (for both determining reduction temperature and hydrogen consumption) of the samples. The solid samples were placed in quartz U-tube and were heated from 30 °C to 900 °C at rate of 10 °C/min in a 10% H₂/Ar gas flow (50 mL/min). The response was detected using a thermal conductivity detector (TCD).

2.5. Catalytic activity test

The catalytic activity measurement for CO conversion was carried out with a fixed bed plug flow reactor system. Typically, 50 mg of catalyst was first mixed with quartz wool. The mixture was then loaded into the quartz tube reactor. The sample was heated from room temperature to 400 °C under a 1 vol% CO/20 vol% O₂/He gas flow (30 mL/min) corresponding to a weight hour space velocity (WHSV) value of 46000 mL h⁻¹ g_{cat}⁻¹. The reactants and products were analyzed by an online gas chromatograph (SRI multiple gas analyzer GC, 8610 C chassis) system. The conversion of CO (C_{CO}) was defined according to the following Equation [Eq. (1)]:

$$C_{CO}(\%) = ([CO]_{in} - [CO]_{out}) / [CO]_{in} \times 100 \quad (1)$$

Where [CO]_{in} is the influent CO concentration and [CO]_{out} is the effluent CO concentration.

3. Results and discussion

3.1. Morphological and structural characterizations

Figure 1(a) presents the XRD patterns of CeO₂NR supports before (pristine CeO₂NR) and after chemical etching treatment with 0.6, 3 and 6 wt% NaBH₄ addition. It can be seen that the diffraction peaks at *ca.* 28.5, 33.1, 47.5, 56.3, 59.1, 69.4, 76.7, 79.1 and 88.4° for all four CeO₂NR supports, correspond to face-centered cubic CeO₂ phase with fluorite structure (JCPDS #34-0394). After the chemical etching treatment by NaBH₄, based on the intensity and broadness of the XRD diffraction peaks, the crystallization degree of CeO₂NR appears to increase initially with 0.6 wt% addition of NaBH₄ but decrease with the increasing amount of NaBH₄ addition (3 and 6 wt%). The crystallite size sequence of CeO₂NR follows: 0.6 wt% NaBH₄-CeO₂NR (5.7 nm) > 3 wt% NaBH₄-CeO₂NR (5.5 nm) > 6 wt% NaBH₄-CeO₂NR (5.3 nm) > CeO₂NR (4.9 nm). A possible explanation for this order is that the heat release owing to the violent and exothermic reaction between NaBH₄ and water promotes the crystallization of CeO₂ when adding a small amount of NaBH₄, but the etching effect of NaBH₄ on the CeO₂ surface dominates when adding a large amount of NaBH₄. In addition, the lattice parameters of four CeO₂NR supports were examined by XRD Rietveld refinement analysis shown in Figure S1 and Table S1. The Rietveld refinement shows credible simulated XRD patterns that match well with the experimental data, and presents slight changes in the lattice parameters due to the B doping and generated defects.

According to Lykaki et al.,^[16] the lattice expansion of CeO₂ was observed with the formation of substantial amounts of Ce³⁺ in combination with oxygen vacancies. According to the contents of Ce³⁺ and oxygen vacancy (XPS analysis below) and reducibility (H₂-TPR analysis below) of three modified CeO₂NR supports, 6 wt% NaBH₄-CeO₂NR presents superior low-temperature reducibility with significant amounts of surface defects. Thus, 6 wt% NaBH₄-CeO₂NR was chosen as the support material for the following study on preparing CeO₂NR supported TM catalysts.

In Figure 1(b), the XRD patterns of modified CeO₂NR and five CeO₂NR supported TM catalysts (Cu, Co, Ni, Fe and Mn) are shown. Along with CeO₂ phase, among the five TM catalysts, only very weak diffraction peaks for CuO (JCPDS#45-0937) and NiO (JCPDS#44-1159) can be observed in 10CuO_x-mCeO₂NR and 10NiO_x-mCeO₂NR. It is evident that no oxides phases for Co, Fe, and Mn are visible. Compared to others' previous work,^[28,29] the modified CeO₂NR supported catalysts clearly show a better dispersion of TM oxide nanoclusters, indicating that NaBH₄ etching can promote the dispersion and/or diffusion of catalyst clusters on the surface of etched CeO₂NR. According to Chen's work,^[30] the modification or surface engineering on CeO₂ can generate abundant surface defects (i.e., Ce³⁺ and oxygen vacancies) which can act as active sites for Pt atom anchoring and stabilization. In this work, it is hypothesized that the strong reducing agent NaBH₄ reacts with surface species on CeO₂NR leading to the formation of surface defects such as oxygen vacancy or local nonstoichiometric CeO_{2-x} spots on the surface. These surface defects can act as anchor or trap sites for TM oxide nanoclusters resulting in better dispersion or promoted TM oxide diffusion into CeO₂NR lattice.

Figure 2(a) shows the Raman spectra of CeO₂NR supports before and after chemical etching treatments with 0.6, 3 and 6 wt% NaBH₄ addition. The strongest peak near 458 cm⁻¹ for all CeO₂NR samples attributes to triply degenerate F_{2g} mode of fluorite structure.^[31] The band at 255 cm⁻¹ was previously assigned to double degenerate TO mode (2TA) of CeO₂.^[31] Another main band near 600 cm⁻¹ can be assigned to the defect-induced band (D band),^[32] which can be used to estimate the oxygen defects concentration.^[33] According to Schilling and Wu et al.,^[34,35] the peak around 831 cm⁻¹ is attributed to peroxide species (O₂²⁻) in CeO₂ based on their experimental and DFT modeling results. It can be observed that the normalized intensity of I_D decreases after the 0.6 wt% NaBH₄ etching, but increases slightly with an increasing amount of NaBH₄ addition (3 and 6 wt%), indicating that there are higher concentration of oxygen vacancy defects in 3 and 6 wt% NaBH₄-CeO₂NR, which is consistent with the change in crystallinity from the XRD results (Figure 1(a)). On the other

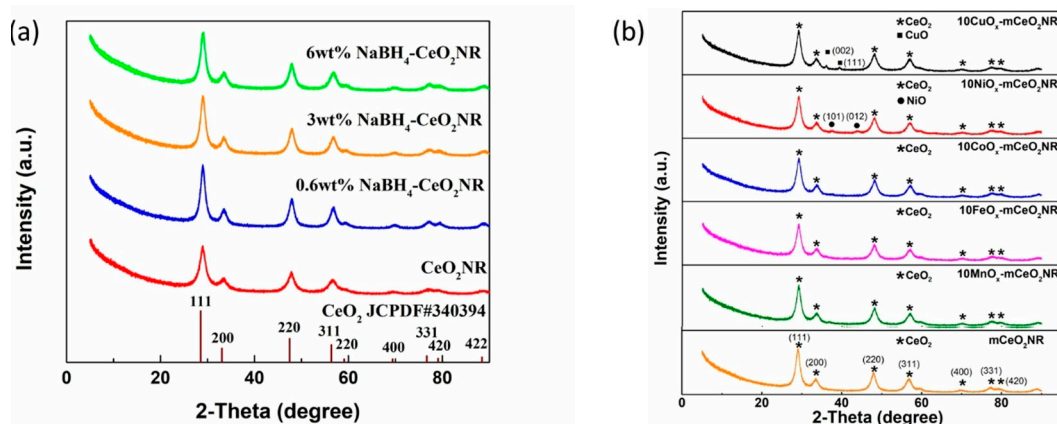


Figure 1. XRD patterns of (a) CeO₂NR supports with different amounts (0.6, 3, 6 wt%) of NaBH₄ addition and (b) modified CeO₂NR supported transition-metal catalysts with 6 wt% NaBH₄ addition.

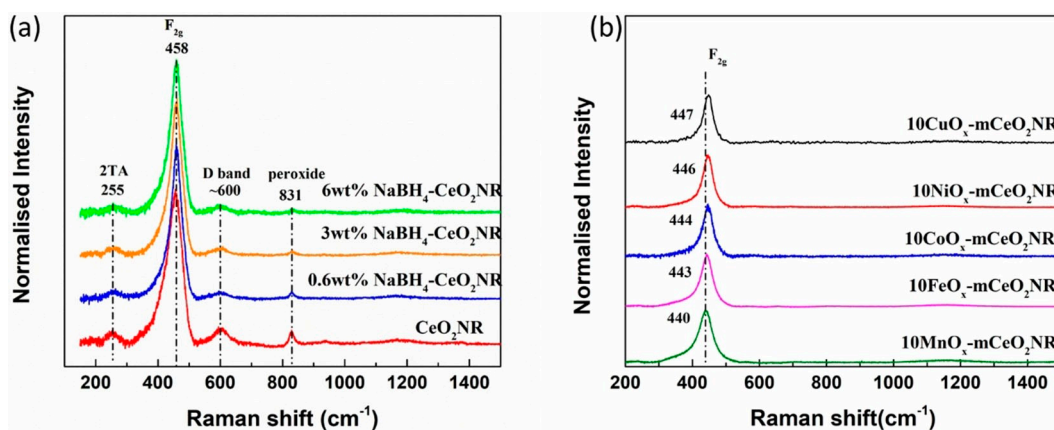


Figure 2. Raman spectra of (a) CeO₂NR supports with different amounts (0.6, 3, 6 wt%) of NaBH₄ addition, and (b) modified CeO₂NR supported TM catalysts with 6 wt% NaBH₄ addition.

hand, the normalized intensity of I_{peroxide} at 831 cm⁻¹ keeps decreasing with increasing amount of NaBH₄ addition, indicating O₂²⁻ is consumed during NaBH₄ etching.

According to Lohrenscheit and Christian,^[36] the peroxide species at ~832 cm⁻¹ appeared not to be catalytically active for CO oxidation on Au/CeO₂ catalyst. Furthermore, Zhao et al.^[23] used DFT simulation to investigate the reaction between peroxide and CO on partially reduced CeO₂ surface, and found that peroxide reacts with CO to form carbonate (not CO₂), which has a high desorption barrier to produce CO₂. Therefore, the formation of peroxide species on CeO₂ surface seems not to be beneficial to CO oxidation at low temperature. In this work, the NaBH₄ etching treatment cuts down the concentration of the peroxide species (Figure 2(a)) on the surface of CeO₂NR, which bypasses the formation of carbonate and could benefit the low-temperature CO oxidation to CO₂.

The Raman spectra of the modified CeO₂NR supported TM catalysts are presented in Figure 2(b). The F_{2g} peak shifts continuously from 458 cm⁻¹ (for mCeO₂NR) to lower wave-numbers at 447, 446, 444, 443 and 440 cm⁻¹ for 10CuO_x-mCeO₂NR, 10NiO_x-mCeO₂NR, 10CoO_x-mCeO₂NR, 10FeO_x-mCeO₂NR and 10MnO_x-mCeO₂NR, respectively, which suggests that the deposited TM oxides lower the symmetry of Ce–O bond or cause lattice distortion due to the formation of the TM–O–Ce bonds (solid solutions).

Interestingly, the order of the shifting values (Cu: 11 cm⁻¹ < Ni: 12 cm⁻¹ < Co: 14 cm⁻¹ < Fe: 15 cm⁻¹ < Mn: 18 cm⁻¹) of F_{2g} peak is consistent with the ionic radius sequence of the loaded TM (ionic radius: Cu²⁺: 87 pm > Ni²⁺: 83 pm > Co³⁺/Co²⁺: 68.5/79 pm ~ Fe³⁺/Fe²⁺: 69/75 pm ~ Mn³⁺/Mn²⁺: 72/81 pm).^[37] This implies that the substitution of TM ions with smaller ionic sizes cause less lattice stretch or distortion of Ce–O bonds in the CeO₂NR supported TM catalysts. The smaller F_{2g} shifting values for 10CuO_x-mCeO₂NR (11 cm⁻¹) and 10NiO_x-mCeO₂NR (12 cm⁻¹) also agree with the lower degree of solid solution formation shown in Figure 1 (b).

Figure 3 exhibits typical TEM images of mCeO₂NR support and mCeO₂NR supported TM catalysts. Shown in Figure 3(f), the

modified CeO₂NR support is 50–100 nm long and 4–10 nm in diameter. After the 10 wt% TM catalysts loading, no significantly visible size or shape change is observed for all catalyst samples. Figure 3(a–e) reveals the TEM images of 10CuO_x/NiO/CoO_x/FeO_x/MnO_x-CeO₂NR catalysts. In these supported catalyst samples, the apparent absence of large TM oxide clusters formed or found on modified CeO₂NR support is consistent with the XRD (Figure 1) and Raman (Figure 2) analysis, indicating good dispersion of TM oxides on the CeO₂NR surface or diffusion of TM oxides into CeO₂NR lattice. Shown in Figure 4, HRTEM images further reveal the good dispersion and strong anchoring of catalyst nanoparticles on CeO₂NR, which is owing to the abundant defective sites on CeO₂NR surface after the etching process.

3.2. Chemical and catalytic properties

The Ce 3d XPS spectra of the uncalcined and calcined CeO₂NR powders were collected in Figure S2, which shows little difference before and after calcination. After the NaBH₄ etching treatments, the surface composition and chemical states of CeO₂NR supports and supported TM catalysts were examined by XPS. By analyzing the Ce 3d spectra, the chemical states of Ce on the surface CeO₂NR supports were determined and shown in Figure 5a. Corresponding to the 3d_{3/2} and 3d_{5/2} spin-orbit coupling, the spectra of Ce 3d can be divided into 10 peaks, where the peaks v₀, v', u₀ and u' ascribe to the Ce³⁺ state, while the peaks v, v'', v''', u, u'', u''' attribute to the Ce⁴⁺ state. The concentration fraction of Ce³⁺ to the total Ce species was calculated by the integrated peak areas of Ce³⁺ and Ce⁴⁺ from the Ce 3d spectra. As shown in Figure 5a, the concentration fraction of Ce³⁺ is 11.5% for 0.6 wt% NaBH₄-CeO₂NR, 12.6% for 3 wt% NaBH₄-CeO₂NR and 13.5% for 6 wt% NaBH₄-CeO₂NR. The O 1s spectra for CeO₂NR supports are displayed in Figure 5b. In literature, the observed O 1s peaks around 530 eV in CeO_{2-x} are typically ascribed to three oxygen species: lattice oxygen; oxygen vacancy; and surface-chem-

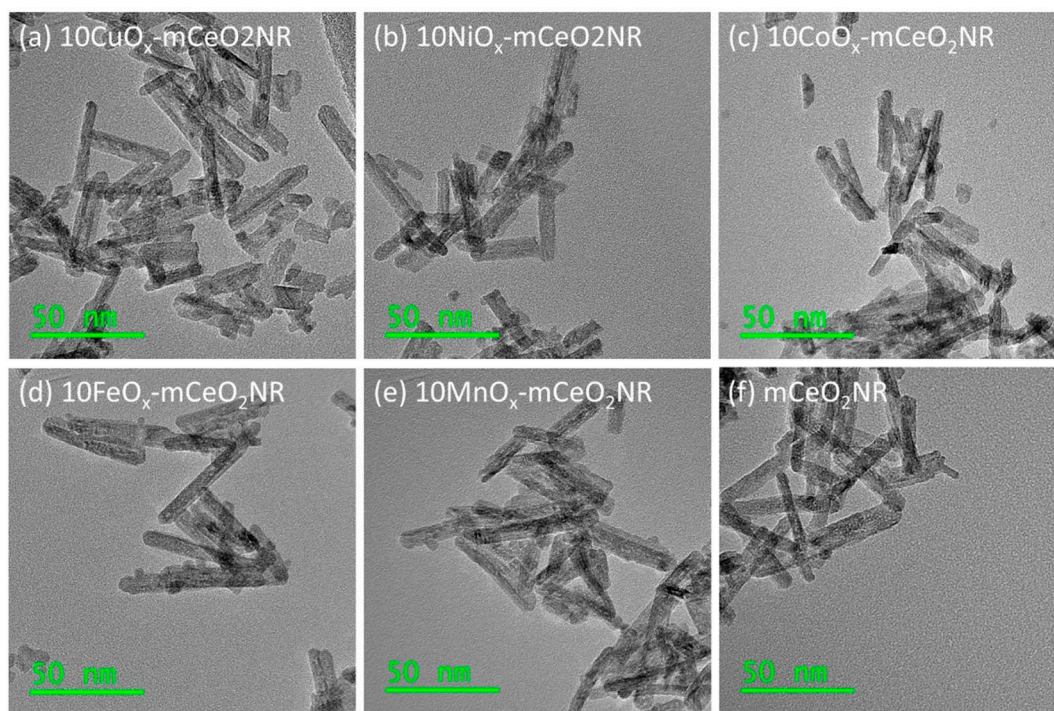


Figure 3. TEM images of (a) 10CuO_x-mCeO₂NR, (b) 10NiO_x-mCeO₂NR, (c) 10CoO_x-mCeO₂NR, (d) 10FeO_x-mCeO₂NR, (e) 10MnO_x-mCeO₂NR and (f) mCeO₂NR support.

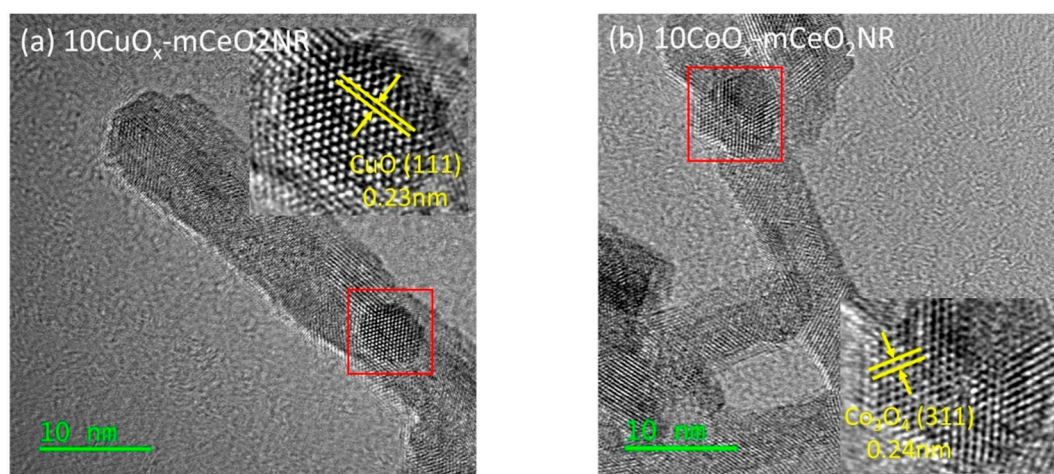


Figure 4. HRTEM images of (a) 10CuO_x-mCeO₂NR and (b) 10CoO_x-mCeO₂NR.

isorbed oxygen species or oxygen in hydroxyl groups.^[38,39] Due to the high concentration of surface oxygen vacancy,^[24] the peaks at 529.3 and 531.4 eV are assigned to lattice oxygen (O_L) and oxygen vacancy/defects (O_V) on the surface of CeO₂NR, respectively. The relative concentration of O_V is calculated by the integrated peak area ratio of O species ($O_V\% = \frac{O_V}{(O_V + O_L)} \times 100\%$). The calculated concentration fraction of O_V is 27.5% for 0.6 wt% NaBH₄-CeO₂NR, 46.5% for 3 wt% NaBH₄-CeO₂NR and 49.8% for 6 wt% NaBH₄-CeO₂NR. A combination of XPS and Raman spectroscopy results demonstrates that the NaBH₄ addition is favorable for the generation

of oxygen vacancy on CeO₂NR. Since oxygen vacancy can play a key role in the activation of gaseous oxygen to form active oxygen species, the extra oxygen vacancies created from NaBH₄ etching could accelerate oxygen activation and finally promote the catalytic CO oxidation performance compared to the untreated catalysts.^[40,41]

The B 1s spectra for the treated CeO₂NR supports are shown in Figure 5c. It is obvious that only the 3 and 6 wt% NaBH₄-CeO₂NR samples have detected B species on surface. Combined with Ce3d, O1s and B1s XPS spectra, it can be concluded that, with an increased amount of NaBH₄ addition,

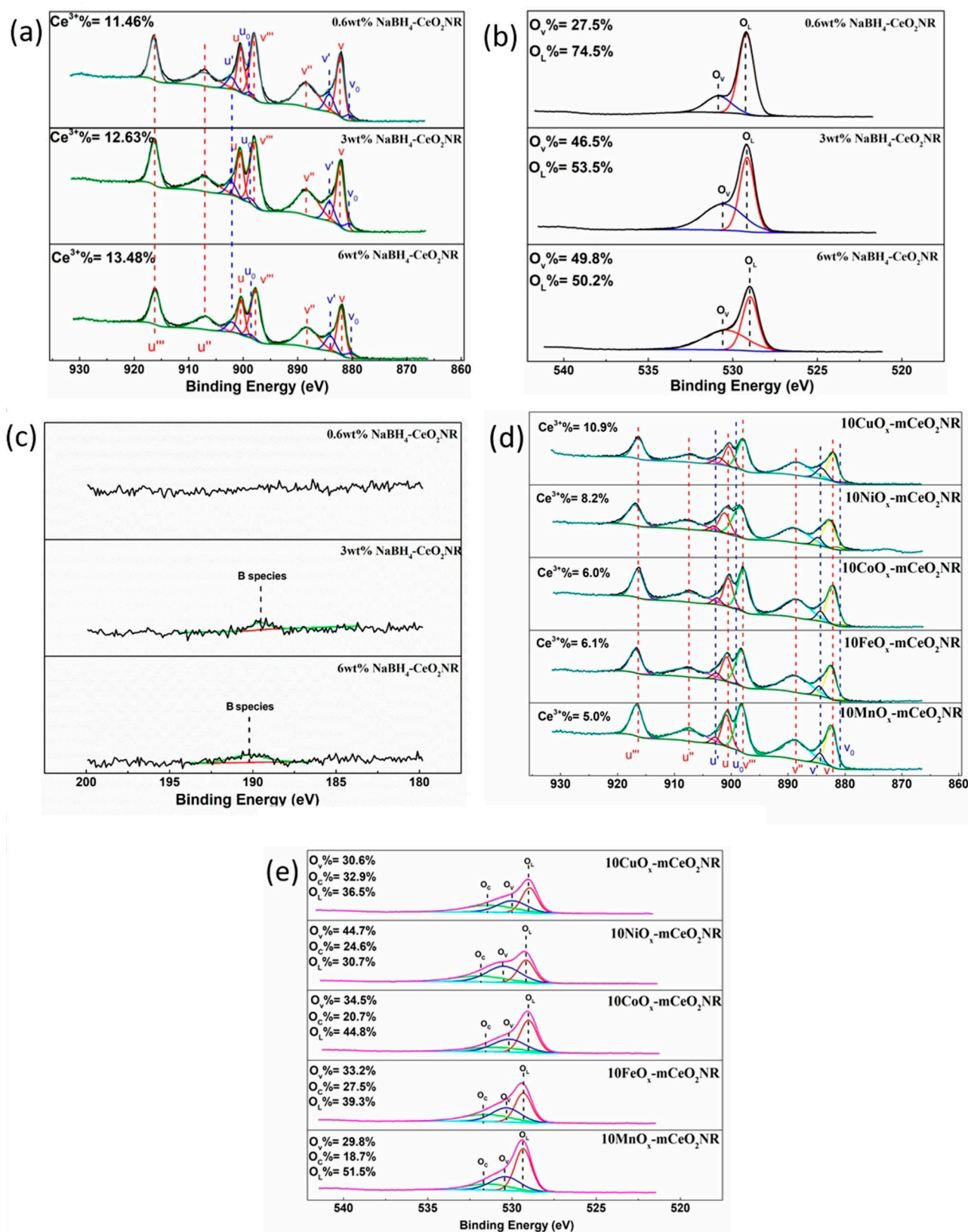
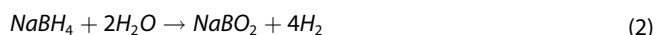


Figure 5. XPS spectra of (a) Ce 3d, (b) O 1s, and (c) B 1s for the treated CeO_2NR supports, and (d) Ce 3d and (e) O 1s for the mCeO₂NR supported TM catalysts.

the concentration fraction of Ce^{3+} and O_v on the CeO_2NR surfaces increases, indicating that the NaBH_4 etching treatments result in more defect structures including oxygen vacancy and reduced surface. And the concentration of O_v increases remarkably with the appearance of B species on CeO_2NR surface, indicating that B species are associated to the oxygen vacancy defects. This result is consistent with the observation of the decreased peroxide species from Raman analysis (Figure 2a). Combined with the structural and chemical analysis results described above, we hypothesize the reason why the appearance of B on CeO_2NR surface can enhance the concentration of O_v might be related to NaBO_2 , the product of NaBH_4 hydrolysis as exhibited in Reaction 2. NaBO_2 reacts with the absorbed peroxide on CeO_2NR surface as shown in Reaction 3.



This reaction (Reaction 3) is similar to the synthesis reaction 4 of sodium perborate:



Reaction 3 between BO_2^- and O_2^{2-} not only consumes inactive peroxide species (O_2^{2-}) on CeO_2NR surface, also promotes the B incorporation or diffusion into CeO_2 lattice.

The chemical states of Ce on the surface of modified CeO_2NR supported TM catalysts were investigated and shown in Figure 5d. The concentration fraction of Ce^{3+} in each catalyst follows the order: $10\text{CuO}_x\text{-mCeO}_2\text{NR}$ (10.9%) > $10\text{NiO}_x\text{-mCeO}_2\text{NR}$ (8.2%) > $10\text{CoO}_x\text{-mCeO}_2\text{NR}$ (6.0%) ~ $10\text{FeO}_x\text{-mCeO}_2\text{NR}$ (6.1%) > $10\text{MnO}_x\text{-mCeO}_2\text{NR}$ (4.9%). The O 1s spectra for each catalyst are shown in Figure 5e. Compared to the XPS spectra of CeO_2NR supports (Figure 5b), a new type of oxygen species at ~531.8 eV is observed, which is assigned to the surface-chemisorbed oxygen species or oxygen in hydroxyl groups.^[42] The sequence of O_v concentration fraction for each catalyst except $10\text{CuO}_x\text{-mCeO}_2\text{NR}$ (30.6%) follows: $10\text{NiO}_x\text{-mCeO}_2\text{NR}$ (44.7%) > $10\text{CoO}_x\text{-mCeO}_2\text{NR}$ (34.5%) ~ $10\text{FeO}_x\text{-mCeO}_2\text{NR}$ (33.2%) > $10\text{MnO}_x\text{-mCeO}_2\text{NR}$ (29.8%), which agrees with the trend of Ce^{3+} concentration in these samples. A possible explanation for $10\text{CuO}_x\text{-mCeO}_2\text{NR}$ with high Ce^{3+} concentration is that the Cu^{1+} in Cu-based catalysts can react with Ce^{4+} to produce Cu^{2+} and Ce^{3+} , the reaction 5 is as follows:



The Cu 2p, Ni 2p, Co 2p, Fe 2p and Mn 2p spectra are shown in Figure 6a–e. According to Ren et al.,^[43] the main peaks in Cu 2p spectra at 933.5 and 953.4 eV are characteristic of Cu^{2+} species, while the peaks at 932.3 and 951.8 eV belong to Cu^+ species. The existence of Cu^+ was reported to facilitate the interplay between $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples, which can enhance the lattice oxygen mobility and create interfacial active sites of $\text{CuO}_x/\text{CeO}_2$.^[9,42]

The main peak centered at 854.9 eV is assigned to Ni^{2+} species in Ni 2p spectra, with a broad shake-up satellite peak at 861.0 eV.^[33] The Co 2p_{3/2} peaks can be divided into two main peaks: Co^{2+} at 779.4 eV and Co^{3+} at 781.0 eV.^[44] The concentration fractions of Co^{3+} and Co^{2+} are 41.2% and 58.8%, respectively, where the concentration fraction of Co^{2+} is lower than that in other's work. In addition, Figure S3 shows the Co LMM profile for $10\text{CoO}_x\text{-mCeO}_2\text{NR}$. The Co LMM signal at 767.6 eV can be ascribed to Co^{3+} , while the signal at 770.6 eV can be attributed to Co^{2+} . The concentration of Co^{2+} is 61.2% determined by Co LMM signal, which is consistent with the Co 2p analysis. According to Zhou et al.,^[45] Co^{2+} in tetrahedral sites is considered to be inactive for CO oxidation. As a result, lower Co^{2+} concentration on the surface of $10\text{CoO}_x\text{-mCeO}_2\text{NR}$ support catalysts favors the CO oxidation conversion at lower temperature.

Konsolakis et al.^[46] reported that the peaks around 709 ~ 711 eV and 711 ~ 713 eV are attributed to the Fe^{2+} and Fe^{3+} ions, respectively. The relative concentration of Fe^{2+} is 41.5%. Hillary et al.^[47] reported that the main three peaks for Mn 2p spectra are 640.8 eV, 641.9 eV and 644.1 eV, which correspond to Mn^{2+} , Mn^{3+} and Mn^{4+} , respectively. The concentration fractions of Mn^{2+} and Mn^{4+} are 33.7% and 28.4%, respectively, as shown in Figure 6e. Compared to Jampaiah et al.'s previous work,^[48] the concentration of Mn^{4+} is higher in our sample. According to Ma et al.,^[49] the higher valence state of Mn ions can create more oxygen vacancy on CeO_2 . In addition, to confirm the relative concentration of different Mn oxidation states,^[50,51] in Figure S4, the Mn 3s XPS spectrum for $10\text{MnO}_x\text{-mCeO}_2\text{NR}$ is shown. The intensity of Mn 3s region is relatively low. The XPS Mn 3s signal appeared at 84.4 eV can be ascribed to Mn^{4+} , while the signal at 83.8 eV can be noted as Mn^{3+} . The signal at 83.4 eV is assigned to Mn^{2+} . The concentration of Mn with different valence states is 26.1% for Mn^{4+} , 37.9% for Mn^{3+} and 36.0% for Mn^{2+} , which are consistent with the results from the Mn 2p analysis. Meanwhile, shown in Figure 7, the EDS composition analysis of $10\text{CuO}_x/\text{NiO}_x/\text{CoO}_x/\text{FeO}_x/\text{MnO}_x\text{-mCeO}_2\text{NR}$ clearly indicates the existence of TM oxides. The quantitative analysis presents that the supported TM catalysts have similar metal concentration (8.55 ~ 9.61 wt%), which are a little lower than the loading concentration (10 wt%) in the starting materials.

From the obtained results, Scheme 1 shows the conceivable mechanism of NaBH_4 etching on CeO_2NR . When NaBH_4 is added into the suspension of CeO_2NR , it starts to react with water and produce NaBO_2 and H_2 . At first, as a violent and exothermal reaction, the hydrolysis of NaBH_4 release a large amount of heat, which enhances the crystallization of CeO_2 (XRD result for 0.6 wt% $\text{NaBH}_4\text{-CeO}_2\text{NR}$, Figure 1(a)), decreases the amount of surface defects (Raman result for 0.6 wt% $\text{NaBH}_4\text{-CeO}_2\text{NR}$, Figure 2(a)). However, the produced H_2 can partially reduce the CeO_2 surface and create oxygen vacancy. And NaBO_2 from the product of the hydrolysis of NaBH_4 can react with the absorbed peroxide species O_2^{2-} . Due to the enriched surface defects on NaBH_4 treated CeO_2NR , defected CeO_2NR surface provides more sites to anchor/stabilize TM catalyst clusters with high dispersion.^[52]

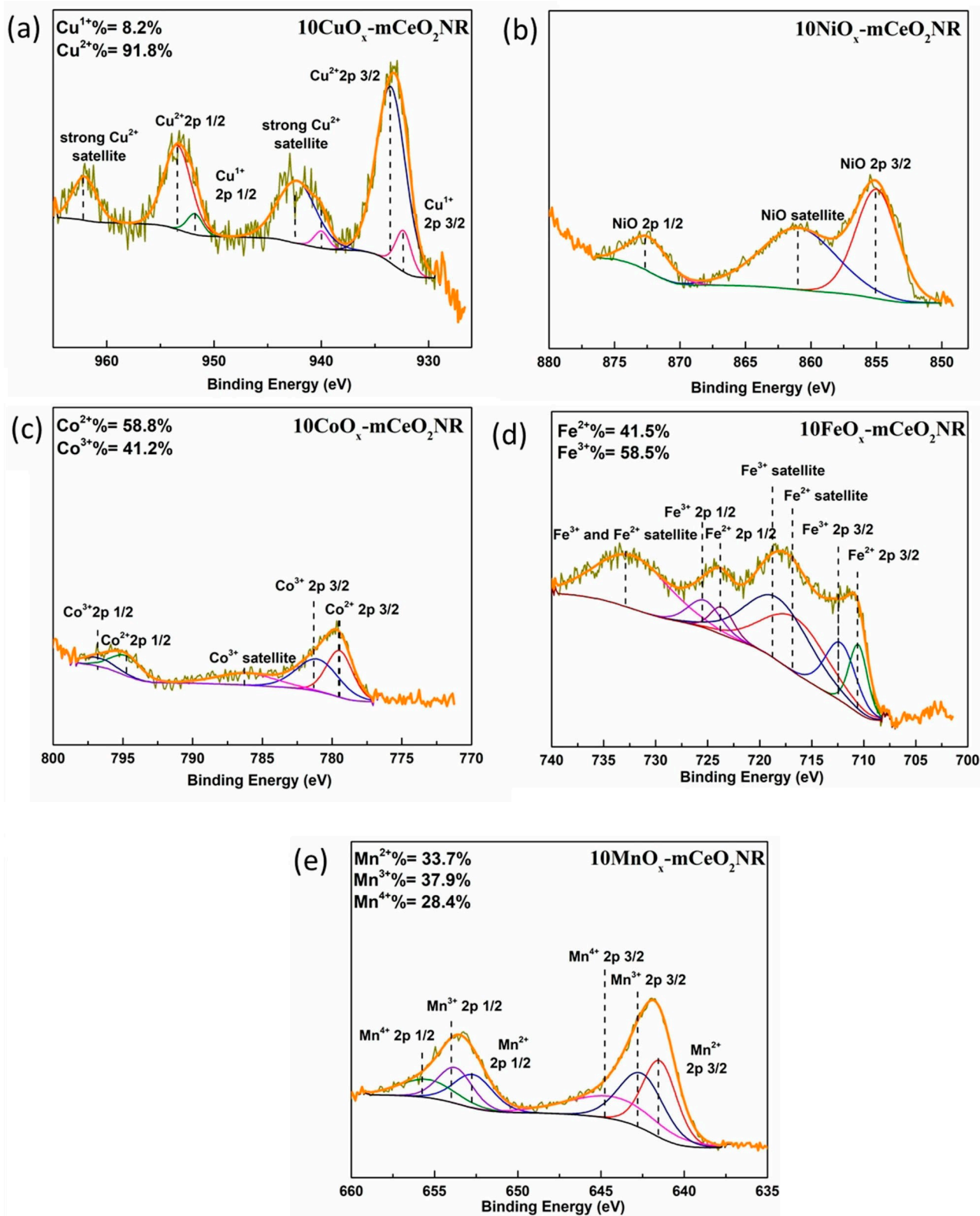


Figure 6. XPS spectra of (a) Cu 2p, (b) Ni 2p, (c) Co 2p, (d) Fe 2p, and (e) Mn 2p for the CeO₂NR supported TM catalysts.

Shown in Figure 8(a), for the pristine CeO₂NR, the H₂-TPR profile shows two major hydrogen consumption peaks at 480 °C and 746 °C, which correspond to the surface and bulk

reduction,^[53] respectively. For three NaBH₄ etched CeO₂NR supports, the onset temperature of the surface reduction peak of CeO₂NR clearly shifts towards lower temperature, especially

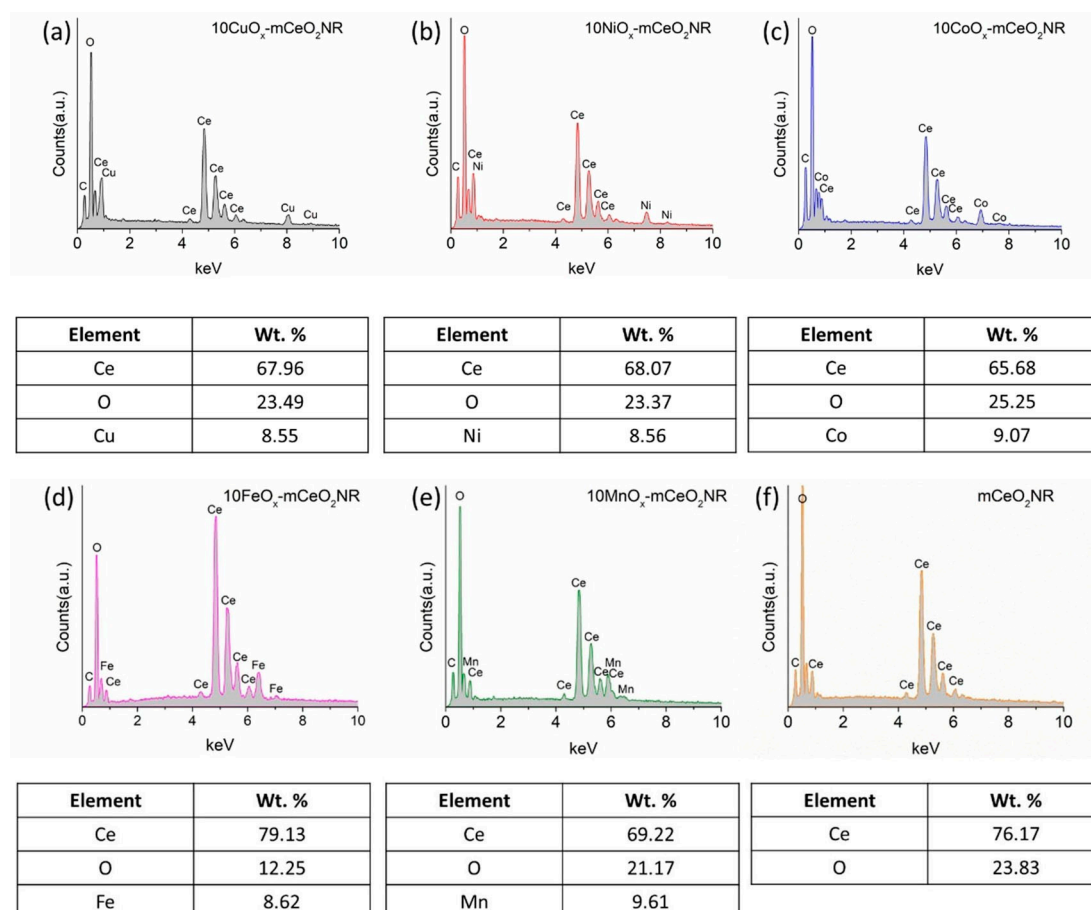
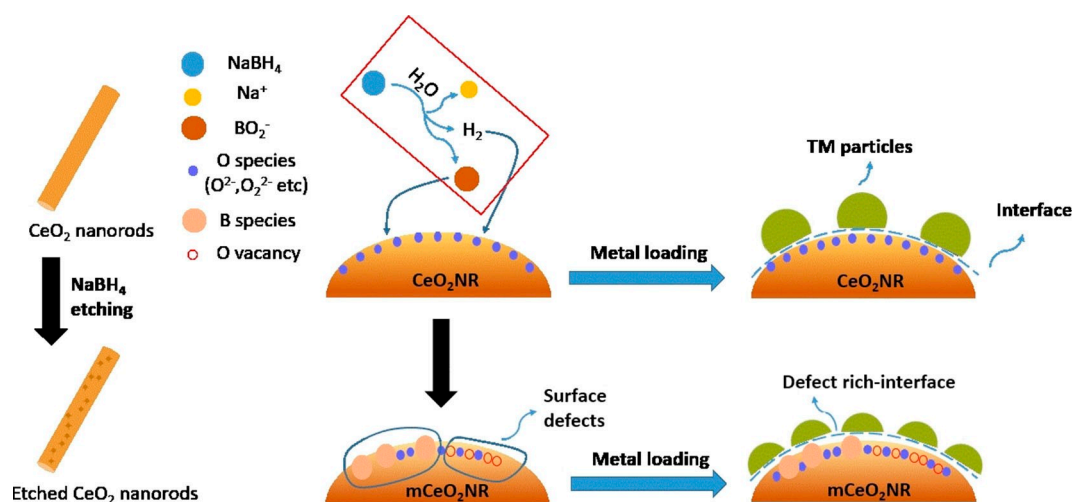


Figure 7. EDS spectra of (a) 10CuO_x-mCeO₂NR, (b) 10NiO_x-mCeO₂NR, (c) 10CoO_x-mCeO₂NR, (d) 10FeO_x-mCeO₂NR, (e) 10MnO_x-mCeO₂NR and (f) mCeO₂NR support.



Scheme 1. The mechanism of NaBH₄ etching on CeO₂NR and TM-CeO₂NR support catalysts.

for the 3 and 6 wt% NaBH₄-CeO₂NR. Two new surface reduction peaks at 394 °C (18% lower than 480 °C) and 336 °C (30% lower than 480 °C) are evident for the 3 and 6 wt% NaBH₄-CeO₂NR, indicating that the addition of NaBH₄ signifi-

cantly transforms the surface structure and/or chemical composition of CeO₂NR. Combined with XPS analysis (Figure 5c), these low temperature reduction peaks may be associated with the appearance of boron species on CeO₂NR surface in 3 and 6 wt%

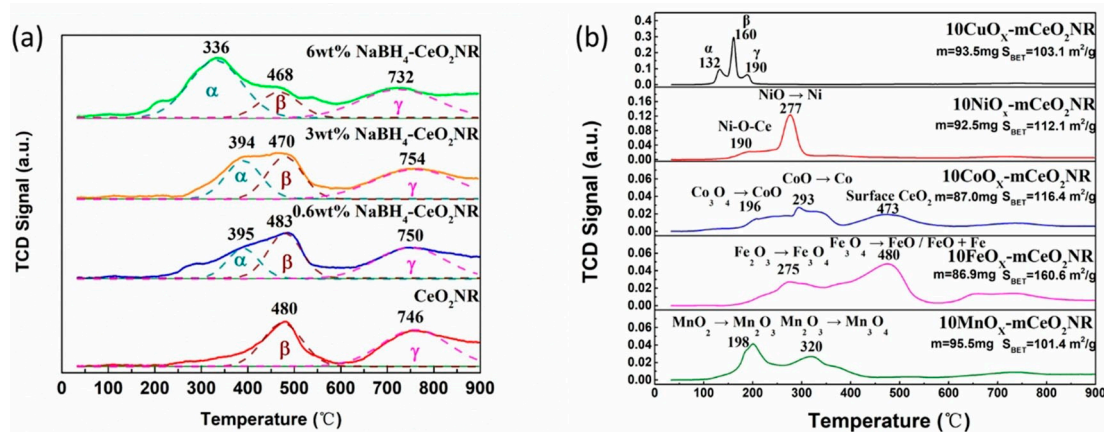


Figure 8. TPR profiles of (a) CeO_2NR supports with different amounts (0.6, 3, 6 wt %) of NaBH_4 addition and (b) modified CeO_2NR supported TM catalysts with 6 wt % NaBH_4 addition.

$\text{NaBH}_4\text{-CeO}_2\text{NR}$. A possible explanation is that these new peaks appearing under 400°C is owing to the boron species-related defects (doping structure and/or new oxygen vacancy) which boosts the surface reduction of CeO_2NR .

The BET surface area and H_2 consumption of the pristine and treated CeO_2NR supports are summarized in Table 1. With a roughly constant BET surface area for all four samples, the total H_2 consumption of CeO_2NR increases after NaBH_4 modification especially at low temperature region (30 to 600°C), which is consistent to the trend of peroxide/boron/oxygen vacancy concentration from the Raman and XPS analysis.

Figure 8(b) shows the H_2 -TPR profiles of modified CeO_2NR supported TM catalysts. For $10\text{CuO}_x\text{-mCeO}_2\text{NR}$ catalyst, there are three distinctive peaks at 132°C (peak α), 160°C (peak β) and 190°C (peak γ). Guo et al.^[54] reported that the peak α is ascribed to the reduction of the highly dispersed CuO_x species strongly interacting with CeO_2NR . Wang et al.^[55] sign the peak β as the reduction of CuO_x species weakly interacting with CeO_2NR . According to Luo et al.,^[42] the peak γ is corresponding to the reduction of bulk CuO .^[56] For $10\text{NiO}_x\text{-mCeO}_2\text{NR}$ catalyst, according to the literatures,^[33,57, 58] the peak at 190°C attributes to the surface active adsorbed oxygen species (i.e. in Ni-O-Ce) and the peak at 277°C is corresponding to the reduction from highly dispersed NiO species to Ni . For $10\text{CoO}_x\text{-mCeO}_2\text{NR}$ catalyst, the first intense reduction peak at 196°C is assigned to the reduction of Co_3O_4 phase to CoO and the second peak at 293°C is due to the reduction of CoO to metallic Co .^[59,60] The broad peak around 473°C is due to the surface reduction of

CeO_2NR support. Compared to CeO_2 supported CoO_x in the previous work,^[29] two cobalt related reduction peaks are at lower temperature, which could be due to the promotion effect of defective surface structure of CeO_2NR after NaBH_4 etching. The $10\text{FeO}_x\text{-mCeO}_2\text{NR}$ catalyst exhibits two peaks at 275°C and 480°C , which can be attributed to the reduction of iron species (Fe^{3+} and Fe^{2+}), i.e., $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ and $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ or $\text{FeO} + \text{Fe}$.^[61–63] When compared to the reported results,^[29] these two peaks also shift to lower temperatures, indicating the defects on CeO_2NR surface can also promote the reduction of FeO_x . For $10\text{MnO}_x\text{-mCeO}_2\text{NR}$, the peaks at 198°C and 320°C are assigned to the reduction of MnO_2 to Mn_2O_3 and Mn_2O_3 to Mn_3O_4 ,^[29,48] respectively. These reduction temperatures are much lower than the values from the hybrid oxides with different Mn/Ce contents, indicating to the formation of $\text{MnO}_x\text{-CeO}_x$ solid solution with $-\text{Mn-O-Ce}-$ bonds that can lower the oxygen vacancy formation energy and enhance the mobility of oxygen species.^[64]

The BET surface area and H_2 consumption of modified CeO_2NR supported TM catalysts are summarized in Table 2. Compared to the previous work without NaBH_4 etching,^[29] the H_2 consumption for $10\text{NiO}_x\text{-mCeO}_2\text{NR}$, $10\text{CoO}_x\text{-mCeO}_2\text{NR}$, $10\text{FeO}_x\text{-mCeO}_2\text{NR}$ and $10\text{MnO}_x\text{-mCeO}_2\text{NR}$ increases 45 %, 7 %, 90 % and 36 %, respectively.

From Table 2, the measured H_2 consumption is reasonably consistent with the theoretical H_2 consumption except for the $\text{MnO}_x\text{-CeO}_2$ sample, which is probably due to incomplete reduction for the actual sample.

Table 1. BET surface area and H_2 consumption of CeO_2NR supports.

Sample	Crystallite size of CeO_2 [nm]	BET surface area [m^2/g]	H_2 consumption (30 to 600°C) [$\mu\text{mol/g}$]	H_2 consumption (600 to 900°C) [$\mu\text{mol/g}$]	H_2 consumption (total) [$\mu\text{mol/g}$]
CeO_2NR	4.9	120	455.8	606.2	1062.0
0.6 wt % $\text{NaBH}_4\text{-CeO}_2\text{NR}$	5.7	124	741.2	558.2	1299.4
3 wt % $\text{NaBH}_4\text{-CeO}_2\text{NR}$	5.5	121	740.4	511.1	1251.5
6 wt % $\text{NaBH}_4\text{-CeO}_2\text{NR}$	5.3	120	1026.2	553.8	1580.0

Table 2. BET surface area, H₂ consumption of modified CeO₂ supported TM catalysts and unmodified CeO₂ supported TM catalysts.

Sample	BET surface area [m ² /g]	H ₂ consumption (30 to 500 °C) in this study [μmol/g]	Theoretical H ₂ consumption (30 to 500 °C) [μmol/g]	H ₂ consumption (30 to 500 °C) in others' work ^[29] [μmol/g]
10CuO _x -mCeO ₂ NR	103	2125.2	2254.4	2369.0
10NiO _x -mCeO ₂ NR	112	2225.9	2708.8	1533.0
10CoO _x -mCeO ₂ NR	116	1800.3	2426.7	1680.7
10FeO _x -mCeO ₂ NR	160	2718.2	2934.6	1427.0
10MnO _x -mCeO ₂ NR	101	1611.6	3226.3	1187.8

3.3. CO oxidation performance

Figure 9 shows the CO light-off profiles for the modified CeO₂NR supports (Figure 9a) and modified CeO₂NR supported TM catalysts (Figure 9b). It can be noted that the sequence of CO conversion at 400 °C: 6 wt%NaBH₄-CeO₂NR (92.7%) > 3 wt%NaBH₄-CeO₂NR (81.6%) > 0.6 wt%NaBH₄-CeO₂NR (70.1%), which is consistent with the H₂ consumption results from H₂-TPR. The CeO₂NR supported CuO_x catalyst presents the best catalytic performance, which is owing to the strong synergistic

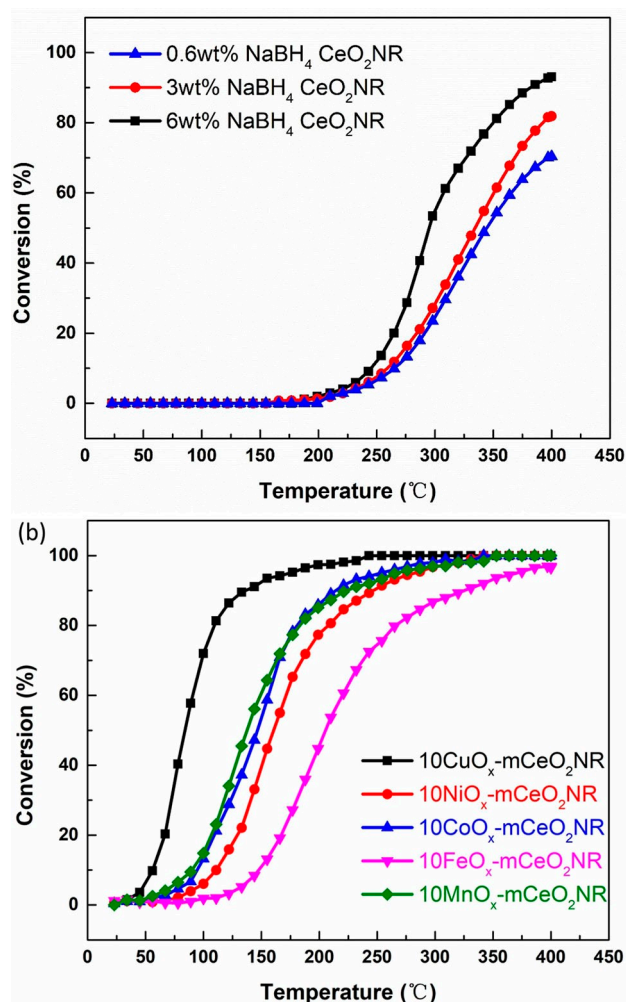


Figure 9. CO conversion of (a) 0.6/3/6 wt % NaBH₄ CeO₂NR supports and (b) modified CeO₂NR supported TM catalysts with 6 wt % NaBH₄ addition (WHSV = 46,000 mL h⁻¹ g_{cat}⁻¹).

interactions between CuO_x and CeO₂NR via redox couples of Cu²⁺/Cu⁺ and Ce⁴⁺/Ce³⁺ and favorable CO adsorption on Cu species.^[9,42] Meanwhile, the poor performance of CeO₂NR supported FeO_x catalysts is due to the weak interaction between FeO_x and CeO₂NR and poor activity of FeO_x.^[29] The apparent activation energies (*E_a*) for five modified CeO₂NR supported catalysts are shown in Figure 10 and their *E_a* values are compared with the results in the previous reports^[65–69] in Table 3. The values of the activation energies for 10CuO_x-mCeO₂NR, 10NiO_x-mCeO₂NR, 10CoO_x-mCeO₂NR, 10FeO_x-mCeO₂NR and 10MnO_x-mCeO₂NR are 40.1, 54.6, 48.1, 55.7 and 40.6 kJ/mol, respectively. It should be noted that these activation energies were calculated at similar low temperature (*ca.* < 100 °C)/low conversion (*ca.* 15 %) regions to minimize the effect of reactant concentration. Specially, the temperature region for the supported FeO_x catalysts was near 150 °C due to its very low conversion at low temperature. It is obvious that most of *E_a* values for the NaBH₄ treated catalysts are lower than those of un-etched catalysts, suggesting that the defects formed during NaBH₄ etching promote the low temperature CO oxidation. It can be observed that the catalytic performance results are consistent with the H₂-TPR results in the low temperature range. In addition, Figure S5 shows the TEM images of catalysts (10CuO_x-mCeO₂NR and 10CoO_x-mCeO₂NR) after the catalytic activity tests. It can be observed that CeO₂ keeps nanorod morphology and no apparent metal aggregation exists after test.

4. Conclusions

In summary, we report a simple approach to modify/transform the surface structure of CeO₂NR support through a chemical etching method with strong reducing agent NaBH₄. The “modified” CeO₂NR surface provides both B-doped CeO₂ sites and surface defect sites to disperse/stabilize small TM catalyst clusters. Among the three etched samples (0.6, 3 and 6 wt %

Table 3. T₅₀/T₁₀₀ and *E_a* of modified CeO₂ supported TM catalysts and unmodified CeO₂ supported TM catalysts in literature.

Sample	T ₁₀₀ [°C]	T ₅₀ [°C]	<i>E_a</i> [kJ/mol]	<i>E_a</i> in reference [kJ/mol]	Reference
10CuO _x -mCeO ₂ NR	243	84	40.1	56.0	[65]
10NiO _x -mCeO ₂ NR	342	159	54.6	54.9	[66]
10CoO _x -mCeO ₂ NR	342	138	48.1	54.0	[67]
10FeO _x -mCeO ₂ NR	~	205	55.7	53.5	[68]
10MnO _x -mCeO ₂ NR	353	136	40.6	63.0	[69]

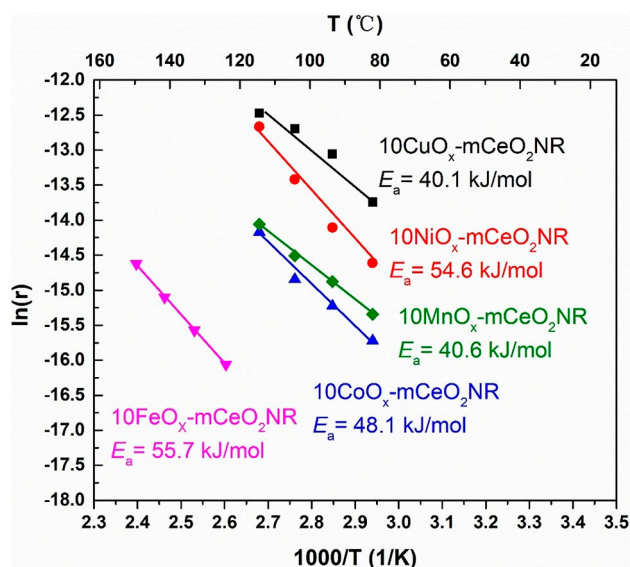


Figure 10. Arrhenius plots for CO oxidation over modified CeO₂NR supported TM catalysts with 6 wt% NaBH₄ addition.

NaBH₄ addition), the 6 wt% NaBH₄ etched CeO₂NR shows the best low temperature reducibility (surface reduction at 336 °C) with higher contents of surface Ce³⁺ and oxygen vacancy. In the five supported TM catalysts, due to stronger interface synergy effect, CeO₂ NR supported Cu catalysts presented better low temperature hydrogen consumption and higher CO oxidation. These results provide insights into the chemical etching effect of CeO₂NR support that NaBH₄ works both as reducing and etching agent to enhance the reducibility of support and offer a strategy to process surface engineering of oxide supported metal catalysts.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: CeO₂ nanorods · transition-metal oxide catalysts · chemical etching · oxygen storage capacity · CO oxidation

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