DRIFTS study of photo-assisted catalytic CO + NO redox reaction over CuO/CeO₂-TiO₂

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Abstract

CuO/CeO₂-TiO₂ catalysts have been widely studied for the thermocatalytic NO reduction with CO. Here, we examine to what extent this reaction can be photocatalytically enhanced beyond the mere thermocatalytic activity by irradiating the catalyst with UV light under reaction conditions while observing the reaction progress via DRIFTS (Diffuse reflectance infrared Fourier transform spectroscopy). The reaction was studied in a batch reactor at four temperatures (35, 65, 100, and 200 °C). The most pronounced effect of photocatalytic enhancement was observed at 65 °C where an enhanced CO conversion of 64.4% was achieved, compared with 11.5% CO conversion without UV irradiation. The photocatalytic enhancement of the CO conversion diminished as the temperature increased to 200 °C, where the CO conversion process became entirely dominated by thermal catalysis. The promoting effect of ceria on the CO+NO reaction has been revealed and rationalized on the basis of physical and chemical characterizations results. XPS and TPR results suggest that the electronic state interaction between Ce and the other two components (Ti and Cu) in the catalysts might lead to a higher oxygen vacancy concentration that facilitates oxygen transport from ceria to copper species resulting in the high catalytic activity for NO reduction by CO.

Key words: Photocatalysis; CO; NO; DRIFTS; Copper; Ceria; Titania

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1. Introduction

The rapidly growing number of automobiles and industrial activities has lead to significantly increased NO_x [1] and CO emissions. To deal with this situation, catalytic reduction of NO_x with CO has been widely studied as an effective and economical technique for simultaneous removal of both NO_x and CO with major focus on noble metal catalysts, such as Pt, Rh, Pd, and Au [2,3,4,5]. Recently, much attention has been paid to developing highly efficient non-precious metal catalyst for automobile exhaust purification, especially base metal or metal oxide catalyst. Among them, copper (or copper oxide) catalysts were found to have activities for the NO_x reduction with CO comparable to those exhibited by precious metal catalysts. It has been proposed that the active sites are related to Cu^+ species where the activation of NO molecules occurs [6, 7]. The copper oxide active sites exhibit facile redox interplay with both reducing and oxidizing reactants [8, 9, 10]. Cu-CeO₂ catalysts have high activity for the deNO_x reaction, as the redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$ imparts high oxygen storage capacity [11]. It has been proposed that in Cu/CeO₂ catalysts two types of NO dissociation sites exist, namely metallic copper and oxygen vacancies in ceria [12, 13].

There have also been some attempts to photocatalytically remove NO using TiO₂[14, 15]. In Japan surfaces and the walls of buildings and tunnels have been coated with photocatalytically active TiO₂ to remove NO from ambient air [16]. One of the earliest studies of copper-based photocatalytic decomposition of NO was conducted over silica supported copper oxides [17] and Cu/ZSM-5 [18]. The key to this photocatalytic activity appears to be the reduction of Cu^{2+} ions into Cu^+ ions, which lead to the formation of nitrosyl adducts in presence of CO at room temperature. Upon irradiation with UV light, electron transfer is believed to take place from excited Cu^+ ions into the π -antibonding orbitals of the adsorbed NO species with back-donation to vacant orbitals of Cu^+ ions. The resulting charge separation weakens the NO bonds and

facilitates the decomposition of the NO molecules. Most photocatalytic studies reported in the literature have been carried out at near ambient temperature conditions, where the NO conversion is low. In general, the rates of photocatalytic reactions tend to be much lower than the rates of corresponding thermocatalytic reactions. There have only been a few photocatalytic studies at elevated temperatures. For example Wu et al. studied the photocatalytic oxidation of NO adsorbed on TiO₂ and on Cu/TiO₂ catalysts under UV irradiation in the temperature range from ambient to 500 °C [19]. They observed that pure TiO₂ was more effective for photocatalytic oxidation than Cu/TiO₂. Nitrites adsorbed on TiO₂ were converted very quickly to nitrates. On Cu/TiO₂, however, adsorption of NO led to the formation of surface nitrites on TiO₂ sites, but also of nitrosyls on Cu²⁺ sites. Upon UV irradiation, photogenerated superoxo species preferentially oxidized these nitrosyl species rather than the nitrites. Only recently has the question been raised to what extent thermocatalytic gas phase reactions can be photocatalytically enhanced at elevated temperatures as Westrich et al. showed that the oxidation of ethylene over TiO₂ could be photocatalytically enhanced in the temperature range up to 200 °C [20]. Increasing the temperature beyond 200 °C diminished the enhancement effect due to increased nonradiative, multiphonon recombination of charge carriers, and at about 350 °C the thermal oxidation rate became dominant. Here, we are exploring if it is possible to photocatalytically enhance the thermal catalytic reaction between NO and CO in the temperature range of 35 °C to 200 °C, by comparing the in-situ DRIFTS spectra obtained under thermal catalytic reaction conditions with the DRIFTS spectra obtained in presence of UV irradiation.

2. Material and methods

2.1. Preparation of catalysts

CuO/CeO₂-TiO₂ catalyst, designated as CuCeTi, was prepared by the consecutive incipient wetness impregnation method. Ce(NO₃)₂·6H₂O (Sigma-Aldrich) and Cu(NO₃)₂·3H₂O (Sigma-Aldrich) were used as the precursors of copper and ceria, respectively. The CeO₂-TiO₂(CeTi) support was prepared by incipient wetness impregnation of TiO₂ (Degussa P25) with an appropriate amount of Ce(NO₃)₂ aqueous solution followed by drying at 80 °C for 12 h and then calcination at 450 °C for 6 h. Then an appropriate amount of Cu(NO₃)₂·3H₂O (Sigma-Aldrich) solution was added to CeO₂-TiO₂ by incipient wetness impregnation, to achieve the loadings of Cu/(Cu+Ce)=0.05 (atomic ratio) and (CuO+CeO₂)/TiO₂=50:50 (wt %). CuO/TiO₂ catalyst, designated CuTi, was prepared for comparison by incipient wetness impregnation of P25 with an appropriate amount of Cu(NO₃)₂·3H₂O solution to achieve the loading of Cu/(Cu+Ti)=0.05 (atomic ratio). The as-prepared catalysts underwent a drying step at 80 °C for 12 h and subsequent calcination in air at 450 °C for 6 h with a heating rate of 2 °C/min.

2.2. Characterization of catalysts

To determine the identity of crystalline phases in the catalysts, X-ray diffraction (XRD) patterns were obtained on a Rigaku rotating anode X-ray diffractometer equipped with a Cu K α radiation source (40 kV and 100 mA) and graphite diffracted beam monochromator at a scan rate (2 θ) of 4°/min (λ =1.5418). The BET surface area and the pore volume were determined from nitrogen adsorption at -196 °C using a Micrometrics ASAP 2020 adsorption apparatus. All the samples were degassed under vacuum at 350 °C for 8 h prior to the measurement. To analyze the surface status, X-ray Photoelectron Spectroscopy (XPS) analysis was conducted on a Kratos Axis Ultra XPS instrument with monochromatic Al source (14 kV and 8 mA). The binding energies and relative surface concentrations of Ti, Cu, O, and C in the samples were

analyzed from core scans with pass energy of 20 eV and an experimental error of the binding energy of ± 0.2 eV. The C1s peak ($E_b = 284.5$ eV) of adventitious carbon was used as a standard for binding energy calibration. Diffusive reflectance UV-visible spectra (DRS) were measured by a Thermo Evolution 300 UV-Vis spectrophotometer in the 220 -1100 nm range. A Philips XL30 FEG SEM coupled with EDAX system was used to analyze the surface compositions of Ti, Cu, and Ce by means of energy-dispersive x-ray spectroscopy (EDS). In addition, the catalyst samples were characterized by TEM, using a JEOL 3100R05 Double C_s-corrected analytical electron microscope.

Adsorption spectra of CO or NO on the catalysts were collected by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Bruker Tensor spectrometer equipped with a MCT detector cooled by liquid nitrogen. The catalyst samples were loaded into a Harrick Praying Mantis IR cell with two ZnSe windows and a quartz window located in the dome of the cell. To remove any organic contaminants, each catalyst sample was first heated at 400 °C for 1 h in air flow and then switched to a pure N₂ flow prior to cooling down to 35 °C in N₂ flow. Prior to admission of either CO or NO, background spectra were collected. Then the flow was switched to 2000 ppm of either CO or NO (both balance in N₂) for 30 min, a time sufficient to establish adsorption equilibrium. Then, the flow was switched back to pure N₂ flow, and spectra were recorded under flowing N₂ at temperatures of 35, 100, 200, and 300 °C, respectively. At each temperature, a 30 min equilibration time was allowed prior to recording of the spectra.

To study the in-situ reaction of CO+NO inside the Harrick Praying Mantis IR cell, each catalyst sample was first heated in air at 400 °C for 1 h to remove organic contaminants, and cooled down to the desired reaction temperature in nitrogen flow. After collection of background spectra at the four reaction temperatures (35, 65, 100, and 200 °C) under flowing nitrogen, the

flow was switched to a mixture of 1000 ppm CO and 1000 ppm NO in N₂ at 200 ml/min (STP). After these reactant gases had been flowing through the reaction cell for 30 min, the valves on the inlet and outlet of the cell were closed, turning the DRIFT cell into a batch reactor. A series of infrared spectra with a resolution of 4 cm⁻¹ were recorded over a period of 8 hours to follow the course of the reaction. For “UV on” tests, a 100 W UV high-pressure mercury lamp (Blak-ray B-100) was turned on to irradiate the samples through the quartz window located on the dome of the IR cell. For the “UV off” tests, the same experimental protocol was followed, except now the catalysts were kept in the dark. To eliminate any influence of illumination on catalyst temperature, the UV light source was installed > 10 cm above the in-situ reaction cell, and the silica window blocked some of the illumination heat from reaching the surface of the catalyst. The reaction temperature was accurately measured by a k-type thermocouple and controlled by a temperature controller to compensate for any illumination heating. In addition, to protect the windows from overheating, flowing cooling water was used to cool down the upper dome. At all four temperatures we investigated, the illumination influence on the reaction temperature proved to be negligible.

In order to study the reducibility of CuO supported on different supports, the CuTi and CuCeTi catalysts were subjected to temperature-programmed reduction (TPR) in flowing H₂, using a Quantachrome ChemBET 3000 instrument with TCD detector.

3. Results and discussion

3.1. Characterization of catalysts

The EDS surface composition, BET surface areas, and pore volumes of CuCeTi and CuTi catalysts are provided in [Table 1](#). The EDS results showed a Cu/(Cu+Ce) atomic ratio of 0.057 on

CuCeTi, close to the nominal loading (0.05). However, the $(\text{CuO}+\text{CeO}_2)/\text{TiO}_2$ mass ratio of 1.76 obtained from EDS was much higher than the nominal $(\text{CuO}+\text{CeO}_2)$ content of 0.5 (50 wt.%). The change of surface area due to copper and copper-ceria modified TiO_2 was insignificant in this system, but a significant decrease of pore volume in the CuCeTi catalyst was observed. The results indicated that ceria enriches on the surface and some ceria could be inserted into the pores of titania in the CuCeTi catalyst. The much lower atomic ratio (0.015) of Cu on the surface of CuTi catalyst than the nominal Cu content of 0.05 indicated the insertion of Cu into the support.

The XRD patterns of samples P25, CeTi, CuTi and CuCeTi are shown in Fig. 1. The presence of the characteristic XRD peaks of both the anatase and rutile phases in the XRD patterns of P25 show that, as expected, these two phases co-exist in this support material. The peaks around $2\theta = 28.5, 33.1, 47.5, \text{ and } 56.3^\circ$ in the XRD patterns of CeTi and CuCeTi indicate the presence of the crystalline structure typical of CeO_2 . The absence of the characteristic peaks attributed to the CuO crystal phase for either CuTi or CuCeTi could be due to the low loading and high dispersion of CuO. The XRD intensity of TiO_2 was weakened due to the dilution by addition of ceria and copper oxide. Similar morphologies and uniform nano-scale particles (10-20 nm) were observed for both CeTi and CuCeTi catalyst samples (see Fig. S1 SEM and TEM images).

To further analyze the surface composition and the chemical bonding state, XPS analysis was conducted on CuTi and CuCeTi catalysts. The presence of the $\text{Cu}_{2p_{3/2}}$ peak at 933.2–934.2 eV and the shake-up satellite peak at 940.0–945.0 eV are characteristic of Cu^{2+} species, while the lower binding energy $\text{Cu}_{2p_{3/2}}$ peak at 932.4 eV is related to Cu^+ species (Fig. 2- $\text{Cu}_{2p_{3/2}}$). This indicates the co-existence of Cu^{2+} species and Cu^+ species in both catalysts. The larger content of Cu^+ species on the CuCeTi catalyst compared to the CuTi catalyst suggests that

the addition of ceria stabilized the reduced Cu^+ species. It has been reported that the active sites for the CO oxidation process are related to partially reduced copper oxide [10]. The binding energy of Cu^+ shifted by 1.0 eV from 933.2 eV in the CuTi catalyst to the higher position of 934.2 eV in the CuCeTi catalyst. There is also a small shift of 0.2 eV to lower binding energy in the binding energies of $\text{Ti}_{2p1/2}$ and $\text{Ti}_{2p3/2}$ in the presence of ceria (Fig. 2- Ti_{2p}). These shifts of binding energies of $\text{Cu}_{2p3/2}$ and Ti_{2p} might indicate an electronic state interaction between Ce and the other two components (Ti and Cu) in the catalysts [21]. The O 1s peak shown in Fig. 2- O_{1s} can be deconvoluted into two Gaussian sub-peaks with correlation coefficients better than 0.99. The sub-peak at lower binding energy can be attributed to lattice oxygen O^{2-} (denoted as O_β), and the sub-peak at higher binding energy is indicative of surface adsorbed oxygen (denoted as O_α), such as O_2^{2-} or O^- [22, 23, 24]. Compared to the CuTi catalyst, there is a shift of 0.5 eV to lower binding energy for both sub-peaks in the CuCeTi catalyst that might be indicative of a synergistic effect between Ce, Ti, and Cu species. The relative areas of the O_{1s} sub-peaks were used for a semi-quantitative estimation of the % O_α on the catalysts, calculated as $\text{O}_\alpha / (\text{O}_\alpha + \text{O}_\beta) * 100$. The O_α percentage on CuCeTi (25.02%) was much higher than that on CuTi (6.43%). This suggests that the addition of ceria might lead to more surface oxygen vacancies and higher oxygen mobility [25].

The diffuse reflectance ultraviolet-visible spectroscopy (DRS) was carried out on P25 (Ti), CuTi, and CuCeTi catalysts to further investigate the synergistic effect between Cu, Ce, and Ti species in the catalysts and to better understand the coordination environment of different sites. The DRS results are shown in Fig. 3. All three samples showed absorption bands in the 220-320 nm range, which could be assigned to ligand to metal $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ charge transfer transition and be related to electron excitation from the valence band to the conduction band of

TiO₂[26,27,28]. The CuTi and CuCeTi catalysts showed a slight increase in the absorption tail of UV-vis spectra at bands higher than 320 nm and a broad absorption at 800 nm. This can be related to electronic transitions involving copper ions [27]. The increased absorbance (CuCeTi > CuTi > Ti) corresponds to an increase in the formation rate of electron–hole pairs on the photocatalyst surface, and as a result a higher photocatalytic activity is gained. [29]. Additionally, a slight red shift can be observed on the CuCeTi catalyst, which indicates that the electrons in the valence band could more easily move into the conduction band and therefore generate electron-hole pairs, which might be beneficial to improving the redox properties of the catalysts.

To get insight into the effect of ceria on the improvement of catalyst properties, the difference spectra obtained by the subtraction between P25 and CuTi and between P25 and CuCeTi were obtained as shown in Fig. 3(Insert). A high intensity absorption peak at 376 nm was obtained for both CuTi and CuCeTi catalysts, which can be attributed to charge transfer from oxygen to copper $O^{-2} \rightarrow Cu^{+2}$, represented by isolated copper species[30]. Broader bands higher than 600 nm were also observed, which could be ascribed to the d-d transitions of Cu^{2+} in bulk CuO [31]. Furthermore, only for the CuCeTi catalyst an absorption band at 402 nm was observed. This additional adsorption peak can be assigned to the overlapped bands of charge transfers of TiO₂, CeO₂ and O-Cu-O complexes. It suggests the existence of electronic interactions among CuOx, CeO₂ and TiO₂. This is consistent with the notion that the addition of ceria facilitates the low temperature redox property of catalysts [31], in agreement with the XPS results.

3.2. NO and CO adsorption

Fig. 4 shows the adsorption spectra of CO and NO and their derivatives on the surface of the CuCeTi catalyst at 35 °C, and how these spectra changed with increasing temperature under flowing N₂.

For NO adsorption, the IR band at 1876 cm⁻¹ reflects the chemisorbed NO on strongly associated Cu²⁺ sites [19] and the band at 1185 cm⁻¹ can be attributed to bidentate nitrite adsorbed on TiO₂ sites [19,32]. A number of IR bands in the range of 1650-1200 cm⁻¹ can be generally attributed to N-O stretching vibrations of surface nitrate (NO₃⁻) and nitrite (NO₂⁻) species of different structures, but it is difficult to individually assign these IR bands since the N-O vibrations from different N-containing species (NO₃⁻ and NO₂⁻) overlap considerably in this region. One would need to understand the exact structure and geometry of the adsorption sites to come up with an accurate assignment of all the N-O stretching frequencies of surface NO [33, 34,35]. Nevertheless, on the basis of the assignments in the literature some of the IR bands could be assigned to surface bridging (1619 cm⁻¹) [6,36,37], bidentate (1605, 1458 cm⁻¹) [32,38], chelating nitrate (1566 cm⁻¹) [6], monodentate (1542 cm⁻¹) nitrates [38,39,40,41], and nitro or bidentate nitro species (1303 cm⁻¹) [33, 42].

The band of chemisorbed NO at 1876 cm⁻¹ decreased with increasing temperature and disappeared completely at 200 °C. The bridging bidentate nitrates at 1619 cm⁻¹, 1605 cm⁻¹ and 1458 cm⁻¹, and bidentate nitrites at 1185 cm⁻¹, respectively, also decreased with increasing temperature accompanied by the formation of monodentate nitrates at 1542 cm⁻¹, 1566 cm⁻¹, and in the 1253 cm⁻¹ to 1241 cm⁻¹ interval. All of the species on the surface of catalyst desorbed once the temperature reached 400 °C. From the DRIFTS results of NO adsorption, it is deduced in agreement with the literature that monodentate and bidentate nitrites were further oxidized to nitrates by surface peroxo species or active oxygen atoms [19], and heating weakened the bond

between Cu ions and adsorbed species so that bridging bidentate nitrates transformed to monodentate and chelating bidentate nitrates [43, 44, 45].

For CO adsorption, an intensive IR band at 2115 cm^{-1} was detected, which arose from the overlapping bands of Cu(I)(CO)_2 and Ce(III)(CO) carbonyl species [46,47]. Cu(II) carbonyl species around 2200 cm^{-1} could not be observed in our case [48], since it is believed that the carbonyl of Cu(II) cations are unstable [49] and the electrophilicity of the Cu(II) cations is too weak to form carbonyls even at low temperatures [47]. A series of IR bands at $1700 - 1000\text{ cm}^{-1}$ could be attributed to carboxylate or carbonate species formed on the surface of catalysts [50], which might arise from the interaction of CO with Cu(I) sites to form Cu(I) and carboxylate or carbonate species [47,51]. When the temperature was raised above $200\text{ }^\circ\text{C}$, all IR bands disappeared, indicating that all of chemisorbed CO and carboxylate or carbonate species were desorbed and/or decomposed. For comparison, CO adsorption on CuTi catalyst was also determined, as shown in Fig. S2. It was observed the intensity of the IR band at 2115 cm^{-1} was much stronger but the intensities of a series of bands at $1700 - 1000\text{ cm}^{-1}$ were weaker than those over CuCeTi catalyst. It implies that it is more difficult for chemisorbed CO to transform into carbonate or carboxylate species on the surface of the CuTi catalyst.

3.3. In-situ NO and CO reaction

3.3.1 CuCeTi catalyst

Fig. 5 displays the IR spectra obtained when NO and CO reacted on CuCeTi catalyst under UV light on or off at different reaction temperatures in the closed batch reactor system. The IR bands around $2330 - 2360\text{ cm}^{-1}$ cannot be used to determine CO_2 generation since the intensities of these IR bands corresponding to CO_2 were too weak and could not be differentiated from

residual CO_2 in the atmosphere. As the reaction time went on, the growth of a series of bands at $1700 - 1000 \text{ cm}^{-1}$ (corresponding to nitrate, nitrite, carboxylate or carbonate species) was observed at the expense of the chemisorbed CO and NO bands at 2115 cm^{-1} and 1876 cm^{-1} at $35 - 100^\circ \text{C}$. At 200°C , desorption might be the cause for the obvious decrease of these bands. But by comparing the spectra under UV on and off at different temperatures, at 65°C and 100°C the relative apparent difference in CO consumption between spectra of UV on and off could readily be observed. However, at 200°C it proved difficult to distinguish the effect of UV irradiation on the CO consumption and the growth of reaction products.

The band at 2115 cm^{-1} is unique for chemisorbed CO. Its intensity reflects the coverage of CO adsorbed on the catalyst surface. Therefore, the intensity of the 2115 cm^{-1} peak is proportional to the amount of gaseous CO in the cell as long as the surface coverage is below saturation. In our case, the gas phase concentration of CO at the beginning of reaction is 1000 ppm, and under these conditions the surface is not completely saturated. To study the photocatalytic enhancement, the ratio of integrated area of the chemisorbed CO peak at 2115 cm^{-1} at each temperature, calculated by A_t/A_0 (the ratio of band area at time t (A_t) to the initial band area (A_0)), can be used to represent the relative concentration of gaseous CO in the isolated cell reactor. In other words, the A_t/A_0 ratio allows to quantify the extent of CO conversion in the closed cell reactor. Fig. 6 shows the conversion of adsorbed CO on the catalyst surface with reaction time under UV light on and off at each reaction temperature. At 35°C , only a small amount of CO was converted even under UV irradiation. Interestingly, a significant enhancement in the CO conversion under UV irradiation was achieved at 65°C , reaching about 64.4% compared with 11.5% with UV off. The difference between UV on and UV off narrowed with

increasing reaction temperature. It was found that at 200 °C the role of UV became negligible and thermal catalysis dominated the reaction.

In order to confirm our hypothesis that NO provides oxygen to CO during the reaction rather than CO oxidation by the superficial oxygen on the catalyst, the reaction on the CuCeTi catalyst was performed at 65 °C in the presence of CO only under UV illumination. The integrated CO band intensity result showed that the amount of CO adsorbed on the surface of catalyst remained almost constant, confirming that CO_{ad} cannot be consumed in the absence of NO even under UV illumination for 8 h, as shown as inset in Fig. 6.

3.3.2. CuTi catalyst

To explore the role of ceria in the CO+NO reaction, the photocatalytic activity of the CuTi catalyst was compared with that of the CuCeTi catalyst at 65 °C. The reaction time dependence of the integrated area ratio of CO_{ad} is shown in Fig. 7. It is notable that the coverage of CO_{ad} on the surface of CuTi catalyst did increase instead of decrease with time. Furthermore, the increase in the amount of CO_{ad} was larger under UV illumination than when UV was off. It can be ruled out that this increase of the amount of CO_{ad} was caused by non-equilibrium of CO adsorption on the surface of the CuTi catalyst, since the integrated peak areas of CO, NO, and CO₂ in the first 30 min provided clear evidence that the adsorption of CO had reached equilibrium prior to turning the UV source on. A possible explanation is that a competitive adsorption of CO and NO exists on the surface of catalyst. Comparing the adsorption of individual NO and CO on CuTi catalyst (see Fig. S2), it was observed that the intensities of NO_{ad} bands were relatively weaker than those of CO_{ad} bands and the temperature of NO_{ad} desorption (100 °C) is also much lower than that of CO_{ad} desorption (200 °C), indicating a weaker interaction between NO and the

surface of the catalyst. When both NO_{ad} and CO_{ad} are present on the surface of the CuTi catalyst, they would be consumed simultaneously in the $\text{NO} + \text{CO}$ reaction. The remaining adsorption sites could then be preferentially occupied by CO in the gas phase. Thus, if the reaction rate was slower than the CO adsorption rate, it could result in an increase of the CO_{ad} coverage with reaction time. Furthermore, the increased NO consumption caused by UV illumination resulted in more CO adsorbed on the surface of catalyst. These results explain why the catalytic activity over the CuTi catalyst is much lower than that over the CuCeTi catalyst.

For comparison purposes, the reaction in the presence of CO only was also performed under UV illumination at 65°C over the CuTi catalyst. The integral result showed that CO_{ad} couldn't be converted in the absence of NO even under UV illumination (Fig. S3), which is consistent with the results observed over the CuCeTi catalyst.

The results confirm the promoting role of ceria in the CuCeTi catalyst on the $\text{CO} + \text{NO}$ redox reaction, and also confirm that NO acts as an oxidizer to provide oxygen for CO conversion. The oxidation of CO and the reduction of NO are in principle dependent on the transfer of oxygen, which is in turn a function of the catalyst reducibility[43]. It is known that ceria in the catalyst provides active sites, since the valence changes of ceria from $4+$ to $3+$ and vice versa involve oxygen transfer. The interaction of copper oxide and ceria may also play a role. Thus, it is interesting to characterize the redox behavior of CuCeTi and CuTi catalysts.

3.4. H_2 -TPR

In order to study the reducibility of CuTi and CuCeTi catalysts, H_2 -TPR experiments were performed with the results shown in Fig. 8. For the CuTi catalyst, two reduction peaks were observed below 300°C , implying the existence of at least two types of copper species. According

to the literature, a similar two-step reduction event has also been found on othersupported CuO catalysts[21,52,53]. The peak (δ) at lower temperature (183 °C) could be attributed to the reduction of highly dispersed copper oxidesthat are strongly associated with the TiO₂ support. The peak (θ) at higher temperature (258 °C) could be ascribed to the reduction of relatively larger copper oxide crystallites that are weakly interacted with TiO₂,althoughno copper oxide crystallites were detectable in the XRD patterns.

For the CuCeTi catalyst, the reduction peaks of surface ceria in the range from 300 to 600 °C[12, 54]were not observed in the present work. The peak (θ) at 258 °C, which was observed in the CuTi catalyst and assigned to the reduction of relatively larger copper oxide crystallites, was also absent. The latter could be attributed to the weight loading of CuO in the CuTi catalyst (0.05) being 4 times higher than that (0.012) in the CuCeTi catalyst. The peak (γ) at 195 °C was observed, which could be ascribed to the reduction of Ti species [21]. This peak was absent in the CuTi catalyst, implying the existence of an interaction between ceria and TiO₂ support. Two other peaks, which were located at lower temperatures of 128 °C (α) and 174 °C (β), could be assigned to the reduction of two types of copper species, respectively. The peak shift to lower temperatures for CuO reductionindicates that the addition of ceria facilitates the reduction of copper oxide catalyst and theinteraction with dispersed copper species. It has been reported that the electron conduction between two redox couples ($\text{Ce}^{4+}/\text{Ce}^{3+}$, $\text{Cu}^{2+}/\text{Cu}^{+}$) is related to oxygen self-diffusion [55], which occurs not only in the ceria lattice but also between ceria and supported metal [56]. The rate of oxygen diffusion was dependent on temperature and oxygen vacancy concentration [57]. In the copper-ceria system, the oxygen vacancies sandwiched between copper oxide crystallites and ceria crystallites acted as “bridge” for the migration of oxygen from ceria to copper particles during the reduction [12]. The increased oxygen vacancy

concentration was obtained through the introduction of ceria, in good agreement with the results of XPS. Therefore, the two copper species were reduced at relatively lower temperature. Additionally, via integrating and comparing the areas of the reduction peaks for the two catalysts, it was found that the H₂ consumption in the CuCeTi catalyst was 8.4 times larger than that in the CuTi catalyst, suggesting that the redox property of the CuCeTi catalyst is significantly enhanced by the presence of ceria. It has been reported that this improvement in reduction might result from the surface structural changes of catalyst stimulated by ceria species since these structure change could enhance the oxygen transport ability [12]. Thus, we can conclude that the copper-ceria-TiO₂ interaction leads to relative flexible oxygen transport from ceria to copper species and to high oxygen vacancy concentration. Hence, more oxygen in the metastable copper oxide species can be trapped by CO, resulting in high catalytic activity for the CO+NO reaction.

3.5. The photocatalytic enhancement mechanism

The observed positive effect of ceria on the photocatalytic activity of TiO₂ was also reported in the previous studies for photodegradation of organics [58,59,60]. For photocatalytic NO+CO reaction, a refined mechanism on Degussa P25 photocatalyst has been described in the literature as follows [61]: first, an electron donor (Ti³⁺)-hole (O⁻) pair is created on TiO₂ by the excitation of a UV photon:

On the conduction band of TiO₂, Ti³⁺ reacts with NO to yield NO⁻, and on the valence band O⁻ reacts with NO to yield NO²⁻ and produce N₂O and NO³⁻ subsequently:

This reaction sequence agrees with the existence of nitrites and nitrates species in our IR spectra. Under irradiation CO can interact with NO^- to form CO_2^- as follows, which is consistent with our observation of carboxylate or carbonate species formed on the surface of catalysts:

Based on the above mechanism on P25 TiO_2 in the literature, a possible mechanism responsible for the enhanced photocatalytic NO+CO reaction by the addition of ceria could be proposed.

TiO_2 and CeO_2 have different band structure. Ceria possesses a narrow band gap in the range of 3.2 [62] and 2.76 eV [63], compared with TiO_2 (3.19 eV). Their coupling might lead to the formation of new energy levels between the valence and conduction bands of TiO_2 [64,65]. In this case, the electron would be more easily excited via $\text{Ce}^{4+} + \text{O}^{2-} \xrightarrow{\text{hy}} \text{Ce}^{3+} + \text{O}^-$, thus, more electron donors could be produced to trap NO via reaction (2) and $\text{Ce}^{3+} + \text{NO} \leftrightarrow \text{Ce}^{4+} + \text{NO}^-$, and finally consume more CO via reaction (6). On the other hand, photo-generated holes (O^-) could more easily reach the Ce-doped energy level because the addition of ceria decreased the energy gap of the composite photocatalyst, which efficiently separated the electrons and holes. Therefore, ceria can not only act as an electron donor but also efficiently prevent the recombination of electrons and holes, accelerating photocatalytic NO+CO reaction.

4. Conclusion

A CuCeTi catalyst has been examined at four temperatures with respect to its photocatalytic CO+NO redox reaction activity and compared to a CuTi catalyst. A promoting role of ceria on the activity has been revealed and rationalized on the basis of physical and chemical characterizations as well as in-situ DRIFTS results. A photocatalytic enhancement effect of UV illumination on the CO+NO reaction was most pronounced at 65 °C, but the enhancement faded away with increasing reaction temperature. Thermal catalysis became dominating at 200 °C. Results of reactions in the presence of CO only provided further insight into the mechanism involved in the CO+NO photocatalytic reaction over the CuCeTi catalyst, suggesting that NO rather than the superficial oxygen on the catalyst provides oxygen to CO. Further investigation has been performed by comparing the CuTi and CuCeTi catalysts for understanding the composition-structure property relationships. XPS and TPR results confirmed the existence of the electronic state interaction between Ce and the other two components (Ti and Cu) in the CuCeTi catalyst, showing that the copper-ceria-TiO₂ interaction leads to relative flexible oxygen transport from ceria to copper species and the high oxygen vacancy concentration. Hence, more reactive oxygen in the metastable copper oxide species is available for the oxidation of CO, resulting in the high catalytic activity for the CO+NO reaction.

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TEM images.

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Figure Captions:

Fig. 1. XRD profiles of CeTi, CuTi, CuCeTi, and P25 TiO₂.

Fig. 2. XPS spectra of Cu_{2p}3/2, Ti_{2p}, and O_{1s}.

Fig. 3. Diffuse reflectance UV–Vis spectra of P25, CuTi and CuCeTi catalysts. The inset represents the difference spectra (subtraction of P25 spectrum from CuTi and CuCeTi spectra, respectively).

Fig. 4. IR spectra of the variations of chemisorbed NO (a) and CO (b) and their derivatives on the surface of CuCeTi catalyst with increasing temperature.

Fig. 5. Dynamic changes of DRIFTS spectra of CO+NO reaction on CuCeTi catalyst under UV on and off in a closed system as a function of time: 35 °C (a), 65 °C (b), 100 °C (c), 200 °C (d).

Fig. 6. Time dependence of the integrated area ratio of CO_{ad} (2115 cm⁻¹) for the CO+NO reaction over CuCeTi catalyst under UV light on and off at different temperatures.

Fig. 7. Time dependence of the integrated area ratio of CO_{ad} (2115 cm⁻¹) for the CO+NO reaction over CuTi catalyst under UV light on and off at 65 °C.

Fig. 8. H₂-TPR patterns of CuTi and CuCeTi catalysts.

Table 1. Surface composition and physical properties of CuCeTi and CuTi catalysts.

Sample	Cu	Ti	Atomic ratio		Mass ratio (CuO+CeO ₂)/TiO ₂	BET surface area (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)
			Cu/(Cu+Ce)	Cu/(Cu+Ti)			
CuCeTi	2.59	54.31	0.057		1.76	46.7	0.183
CuTi	1.50	98.50		0.015		50.3	0.363

Table 2. Assignments of the FT-IR bands observed upon adsorption of NO and CO on catalyst.

Wavenumber /cm ⁻¹	Assignment	References
NO adsorption		
1876	NO adsorbed on strong associated Cu ²⁺ (Cu-O-Cu, or CuO-like structure), ν (NO)	[19]
1185	Bidentate nitrite, ν (NO ₂)	[19, 32]
1217	Nitrite adsorbed on Cu ²⁺ , possibly in the bidentate state, ν (NO ₂)	[33, 34, 35]
1619	Adsorbed, undissociated water, δ (H ₂ O) or bridged nitrate species on Cu ²⁺	[6, 36, 37]
1291-1288, 1540-1506	Monodentate nitrate, ν (NO ₃) on TiO ₂	[38,39,40]
1542	Monodentate nitrate (N=O stretch; intermediate of monodentate nitrate formation)	[41]
1253-1241, 1586-1576, 1605-1604	Bidentate nitrate, ν (NO ₃) on TiO ₂	[32, 37]
1458	Symmetric stretching mode of bidentate nitrate, ν (NO ₃) on TiO ₂	[38]
1566	Chelating nitrate species on Cu ²⁺	[6]
1320	Adsorbed nitro compounds, ν (-NO ₂)	[33, 42]
CO adsorption		
1220-1270, 1670-1530	Bidentate carbonate, ν_{as} (COO)	[50]
1420-1350, 1630-1560	Carboxylate, ν_{as} (COO ⁻) and ν_s (COO ⁻)	[50]
2115	Chemisorbed CO	[43, 46, 50]

Figure 1

Figure 2_Cu2p3/2

Figure 2_O1s

Figure 2_Ti2p

Figure 3

Figure 4

a

Figure 5b

b

Figure 5c

c

Figure 5d

d

Figure 6

Figure 7

Figure 8

Graphical Abstract