



Kinetic study of CO oxidation over CuO/MO₂ (M = Si, Ti and Ce) catalysts

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ABSTRACT

A series of supported CuO/MO₂ catalysts (M = Si, Ti and Ce) were prepared using a chemisorption-hydrolysis method and tested for CO oxidation. Kinetic study was carried out to investigate reaction pathways on these catalysts. The power-rate law reaction expressions over CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂ were $r = 1.78 \times 10^{-7} P_{\text{CO}}^{0.85} P_{\text{O}_2}^{0.22}$, $r = 1.62 \times 10^{-7} P_{\text{CO}}^{0.65} P_{\text{O}_2}^{0.19}$ and $r = 1.5 \times 10^{-7} P_{\text{CO}}^{0.7} P_{\text{O}_2}^0$, respectively. Activation energies were calculated to be 74.8, 53.4 and 46.3 kJ mol⁻¹ for the CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂ catalysts respectively. Elementary steps of CO oxidation were also proposed. For the CuO/SiO₂ catalysts, a Langmuir–Hinshelwood (L–H) model involving chemisorption of CO and O₂ on surface Cu atoms was proposed; for the CuO/TiO₂ catalysts, a L–H model involving chemisorption of CO on Cu atoms and chemisorption of O₂ on TiO₂ was proposed, which resulted in an interfacial reaction between the two species. For the CuO/CeO₂ catalysts, a Mars van–Krevelen model involving chemisorbed CO on Cu atoms reacting with lattice oxygen in CeO₂ was proposed. Effect of CuO particle size was also evaluated. It was found that the active site on the periphery of the CuO–TiO₂ and CuO–CeO₂ interface was more active on large CuO crystallite than that on small one. The enhanced activity could be interpreted by the higher concentration of chemisorbed CO on the active site on the larger CuO crystallite.

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1. Introduction

Catalytic CO oxidation has been extensively investigated due to its practical applications in indoor air cleaning, automotive exhaust treatment and fuel cells [1,2]. Besides, CO oxidation has been taken as a model reaction to study the reaction mechanism and catalyst structure – reactivity correlation. The catalyst systems for CO oxidation usually contain either noble metals such as Au [3,4], Pd [5,6] and Pt [7–9], or transition metals such as Mn [10] and Cu [11–14]. Also, supports play very important roles in CO oxidation, when the metals are loaded on reducible oxides such as MnO₂ [15,16], SnO_x [17,18], Fe₂O₃ [3,19], TiO₂ [20] and CeO₂ [21,22], they exhibit high activities.

It is worth noting that CuO catalysts are attractive for CO oxidation, due to the fact that they are very active for this reaction [12,23] and the lower cost compared to other noble metal catalysts. The high activities of Cu catalysts are usually attributed to the synergy between the Cu species and the support. For example, in our recent work, the enhanced activity for CO oxidation over CuO/CeO₂ catalyst was due to the synergy of surface CuO species and the CeO₂ support, as the former provided sites for CO

chemisorption and the latter was responsible for oxygen activation [24]. Moreover, the reaction pathway of CO oxidation may also change, depending on the different natures of the Cu catalysts. For example, both Langmuir–Hinshelwood (L–H) mechanism [25] and Mars van–Krevelen model [26] were proposed for CuO/CeO₂ catalysts. In this sense, detailed kinetic study is very useful in order to understand the reaction pathways.

Another important issue in CO oxidation is structure sensitivity. Extensive investigations on CO oxidation over supported CuO catalysts showed that it is a structure sensitive reaction. Our previous works confirmed that the finely dispersed CuO particles were much more active than the large ones [12,13]. However, one must concern the fact that CO oxidation over supported metal catalysts takes place at the metal–support interface (particularly for the reducible oxides such as TiO₂ and CeO₂), which could be applied for both noble metals such as Au [27] and transition metal such as Cu [28]. Then, it seems that only the interfacial sites are directly involved in the reaction, and the calculation of intrinsic activity should be based on the modified reaction model which contains “real” active sites.

Therefore, to probe the reaction pathways over supported CuO catalysts, three oxides with different properties were selected (SiO₂, TiO₂ and CeO₂). Detailed kinetic studies were conducted in order to illustrate CO oxidation pathways over these catalysts. Moreover, catalysts with different CuO particle sizes were tested,

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and particle size effect was analyzed based on different reaction models.

2. Experimental

2.1. Catalyst preparation

Support CeO_2 was prepared using a sol-gel method. Certain amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water and heated at 90°C , then citric acid with twice molar of Ce salts was added. The solution was continuously stirred at 90°C until a viscous gel was obtained. The solid was dried at 120°C overnight and calcined at 500°C for 4 h. The final CeO_2 support had a surface area of $9.5\text{ m}^2\text{ g}^{-1}$. Other two supports SiO_2 and TiO_2 (P25) were commercially purchased, which had surface areas of 295 and $54\text{ m}^2\text{ g}^{-1}$, respectively.

Supported Cu catalysts were prepared using a chemisorption-hydrolysis method. In a typical synthesis, certain amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in deionized water, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ was drop wise added to this solution with the pH being controlled at about 9.0. Then 5 g of support (SiO_2 , TiO_2 or CeO_2) was added and the suspension was stirred for 20 min. The mixture was diluted to a volume of 2000 ml with deionized water at 0°C . After filtration and thorough washing, the solid was dried at 120°C overnight and finally calcined at 450°C for 4.5 h to obtain the final catalyst. The catalysts were designated as $x\text{CuO}/\text{MO}_2$ ($M = \text{Si}$, Ti and Ce), where x refers to the weight percentage of CuO in the catalyst.

2.2. Characterizations

The Cu contents in the catalysts were determined by inductively coupled plasma (ICP) analysis (Thermal Fisher, IRIS Intrepid II). Surface areas of the catalysts were determined by N_2 adsorption at 77 K on a Quantachrome Autosorb-1 apparatus.

X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractometer with $\text{Cu K}\alpha$ radiation operating at 40 kV and 40 mA. The patterns were collected in a 2θ range from 10 to 90° , with a scanning step of 0.15° s^{-1} .

High-resolution transmission electron microscopy (HRTEM) was performed on a JEM-2100F microscopy with a field emissive gun, operated at 200 kV and with a point resolution of 0.24 nm.

The reduction properties of the samples were measured by hydrogen temperature-programmed reduction (H_2 -TPR) experiments. The supported CuO catalyst was placed in a quartz reactor, and then heated from room temperature to 800°C at a rate of $10^\circ\text{C min}^{-1}$ in a H_2 - N_2 gas (5 vol.% H_2 , 30 ml min^{-1}). The hydrogen consumption during the reduction was determined by a gas chromatograph with a thermal conductivity detector (TCD). The water produced in TPR was trapped on a $5\text{ \AA}$ molecular sieve.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of CO chemisorption over the samples were recorded under reaction conditions using a NEXUS 670 Fourier transform infrared spectroscope equipped with a diffuse reflectance accessory (Harrick CHC-CHA-3), with a resolution of 4 cm^{-1} . An accumulation of 32 scans was used in collecting the spectra. About 20 mg of the catalyst was placed in the cell and pretreated at 300°C for 1 h in a flow of He (30 ml min^{-1}) in order to remove water and largely carbonates in the catalyst. Subsequently, the system was cooled down to 30°C , and the background spectrum was recorded. After the introduction of the gas mixture (1 vol.% CO in N_2 , 10 ml min^{-1}) for 10 min, the catalyst was purged with pure He for 20 min to remove the gaseous and physisorbed CO and then a spectrum was collected. The temperature was controlled with a thermocouple in direct contact with the sample, and circulating water was used to cool the body of the cell.

CO temperature-programmed desorption (CO-TPD) was conducted on a homemade apparatus connected with a mass spectrometer (MS, Qic-20 Benchtop, HidenAnalytical). Before the experiment, the sample was heated in a O_2/He flow (10% O_2 , 30 ml min^{-1}) at 300°C for 1 h to remove H_2O and largely carbonates. After that, the sample was cooled down to 30°C . Then a CO flow (30 ml min^{-1}) was introduced to the sample for 30 min, followed by purging with He (30 ml min^{-1}) for 30 min. Then the sample was heated from 30 to 400°C with a ramp of $10^\circ\text{C min}^{-1}$, and outlet gas was monitored by the MS with $m/e = 28$ (for CO) and 44 (for CO_2).

2.3. Catalytic testing

Catalytic CO oxidation was performed on a tubular quartz micro reactor (6 mm i.d.) using different amounts of catalyst (0.12–0.15 mm in size). Different weight of the catalyst was employed in order to control the CO conversion at low levels (typically below 20% at low reaction temperatures ($<100^\circ\text{C}$) to ensure a differential reaction mode). The catalyst was diluted with quartz sand in the same mesh size to 0.25 ml. A feed gas consists of 1% CO and 1% O_2 in N_2 with a total flow rate of $40\text{ ml (NTP) min}^{-1}$, corresponding to a space velocity (S.V.) of $9600\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$. The catalyst was directly exposed to reaction gas without any pretreatment. The reaction temperature was monitored by a thermocouple placed in the middle of the catalyst bed. The CO concentration in the reactor effluent was analyzed using an Agilent 6850 gas chromatograph equipped with a TCD detector attached to an HP PLOT column ($30\text{ m} \times 0.32\text{ mm} \times 12\text{ }\mu\text{m}$).

Concerning the intrinsic activity, three types of turnover frequencies (TOFs) were calculated based on the following definitions:

$$\text{TOF}_a (\text{s}^{-1}) = X_{\text{CO}} F_{\text{CO}} \frac{5M_{\text{Cu}}}{4m_{\text{Cat}}X_{\text{CuO}}D_{\text{CuO}}}$$

where X_{CO} is the CO conversion at certain temperature; F_{CO} is the flow rate of CO in unit of mol s^{-1} ; m_{Cat} is the amount of catalyst; X_{CuO} is the CuO loading in the catalyst; D_{CuO} is the dispersion of CuO; M_{Cu} is the molar weight of Cu (63.546 g mol^{-1}). The definition of TOF_a reflects the conventional calculation of turnover frequency based on the metal dispersion.

$$\text{TOF}_b (\text{s}^{-1}) = X_{\text{CO}} F_{\text{CO}} N_{\text{AV}} \frac{m_{\text{CuO,c}}}{m_{\text{Cat}}X_{\text{CuO}}}$$

where X_{CO} is the CO conversion at certain temperature; F_{CO} is the flow rate of CO in unit of mol s^{-1} ; N_{AV} is the Avogadro's constant; m_{Cat} is the amount of catalyst; X_{CuO} is the CuO loading in the catalyst; $m_{\text{CuO,c}}$ means the weight of a single CuO crystallite depending on its size, which could be derived from its volume obtained under the assumption of its semi-spherical shape and density of CuO (6.45 g cm^{-3}). The term $(m_{\text{Cat}}X_{\text{CuO}})/m_{\text{CuO,c}}$ indicates the number of CuO semi-spherical particles (with a specific diameter) in the catalyst, thus the definition of TOF_b reflects the turnover frequency of all the Cu atoms located on the $\text{CuO}-\text{MO}_2$ ($M = \text{Si}$, Ti , Ce) interface, corresponding to overall activity of the Cu atoms on the CuO-support periphery.

$$\text{TOF}_c (\text{s}^{-1}) = \frac{\text{TOF}_b}{8\pi d} = X_{\text{CO}} F_{\text{CO}} N_{\text{AV}} \frac{m_{\text{CuO,c}}}{(m_{\text{Cat}}X_{\text{CuO}}) 8\pi d}$$

where X_{CO} is the CO conversion at certain temperature; F_{CO} is the flow rate of CO in unit of mol s^{-1} ; N_{AV} is the Avogadro's constant; m_{Cat} is the amount of catalyst; X_{CuO} is the CuO loading in the catalyst; $m_{\text{CuO,c}}$ means the weight of a single CuO crystallite depending on its size, which could be derived from its volume obtained under the assumption of its semi-spherical shape and density of CuO (6.45 g cm^{-3}); d is the crystallite size of CuO; 8

Table 1

Actual loading, crystallite size, theoretical and actual hydrogen consumption of CuO catalysts.

Catalyst	CuO content/wt.%	CuO crystallite size/nm	H ₂ consumption/(mmol g _{cat} ⁻¹)	
			Nominal	Actual
1.0CuO/SiO ₂	0.62	1.3	7.75	7.61
2.0CuO/SiO ₂	1.46	1.7	18.3	18.2
5.0CuO/SiO ₂	4.24	2.8	53.0	51.7
10CuO/SiO ₂	9.62	5.0	120.2	121.3
20CuO/SiO ₂	15.5	10.7	193.8	194.3
1.0CuO/TiO ₂	0.68	1.7	8.50	8.32
2.0CuO/TiO ₂	1.51	2.1	18.9	18.5
5.0CuO/TiO ₂	4.16	2.5	52.0	52.4
10CuO/TiO ₂	7.85	5.4	98.1	98.3
20CuO/TiO ₂	19.8	9.0	247.5	245.6
1.0CuO/CeO ₂	0.58	1.8	7.25	14.4
2.0CuO/CeO ₂	1.18	2.6	14.8	25.2
5.0CuO/CeO ₂	3.82	3.9	47.8	69.1
10CuO/CeO ₂	7.57	6.9	94.6	123.6
20CuO/CeO ₂	15.6	9.5	195.0	211.5

is the average site density of Cu atom on the periphery, calculated by $\pi/2d_{\text{Cu-O}}$, where $d_{\text{Cu-O}}$ is the distance of Cu–O bond (0.195 nm). Since the TOF_b refers to overall activity of the Cu atoms on the CuO–support periphery, the term TOF_b/8πd (TOF_c) reflects the turnover frequency of each Cu atom located on the CuO–MO₂ (M = Si, Ti, Ce) interface.

2.4. Reaction kinetics

The kinetic study was performed on the same fixed bed reactor of the catalytic CO oxidation as mentioned above. The feed gases were measured with mass flow controllers and mixed prior to the reactor inlet. For kinetic measurements, the reactor was operated in a differential mode with CO conversion less than 15%. The catalyst used for kinetic study was 100 mg (100–120 mesh), which was diluted with quartz sand to a volume of 0.1 ml. The diluted catalyst was embedded with glass wool on both sides. A thermocouple was inserted into the middle of the catalyst bed to monitor the reaction temperature. Also, the absence of mass transport resistances was also checked by Weisz–Prater criterion for internal diffusion and Mears' criterion for external diffusion and the absence of heat transfer was checked by Mears' criterion [29]. For example, on the 5.0CuO/TiO₂ catalyst, the calculated values under kinetic conditions are 2.87×10^{-3} for the Weisz–Prater criterion for internal diffusion, 5.64×10^{-3} for the Mears' criterion for external diffusion

and 0.09 for the Mears' criterion for heat transfer. Those results ensure plug-flow and isothermal conditions within the catalyst bed. Partial pressure dependencies of the reaction rates were measured by adjusting the flow rate of 10% CO/Ar or 10% O₂/Ar, while keeping the total flow rate at 120 ml min⁻¹ by adjusting the flow rate of pure Ar. In this kinetic experiment, the concentration of CO or O₂ in the feed was varied between 0.1 and 3%. Each measurement was taken after stable rate was achieved, which took about 1 h. CO₂ concentration in the outlet gas stream was also analyzed by the same Agilent 6850 gas chromatograph mentioned above. Conversion of CO was calculated as follows:

$$X_{\text{CO}} = \frac{[\text{CO}]_{\text{in}} \text{vol.}\% - [\text{CO}]_{\text{out}} \text{vol.}\%}{[\text{CO}]_{\text{in}} \text{vol.}\%} \quad (1)$$

where $[\text{CO}]_{\text{in}}$ and $[\text{CO}]_{\text{out}}$ were the CO concentrations in the inlet and outlet gas (vol.%) respectively. And the X_{CO} was used to calculate the reaction rate as follows:

$$r_{\text{CO}} = \frac{N_{\text{CO}} \cdot X_{\text{CO}}}{W_{\text{cat}}} \quad (2)$$

where N_{CO} is the CO molar gas flow rate in mol s⁻¹, W_{cat} is the catalyst weight in grams, r_{CO} is the reaction rate in mol_{CO} g_{cat}⁻¹ s⁻¹.

The power-rate law expressions were obtained by taking partial pressure of each reactant (kPa) and the reaction rate data and simultaneously fitting the entire data set by linear least squares regression analysis using the POLYMATH 5.1 program [30].

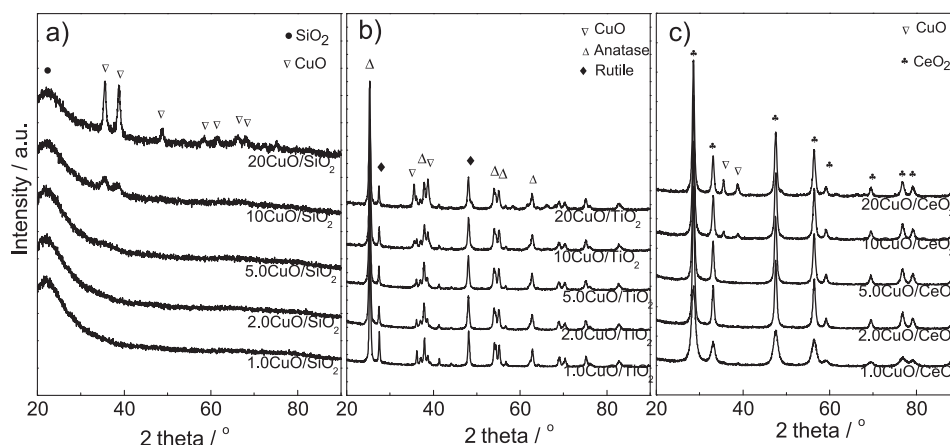


Fig. 1. XRD patterns of (a) CuO/SiO₂, (b) CuO/TiO₂ and (c) CuO/CeO₂ catalysts with different CuO loadings.

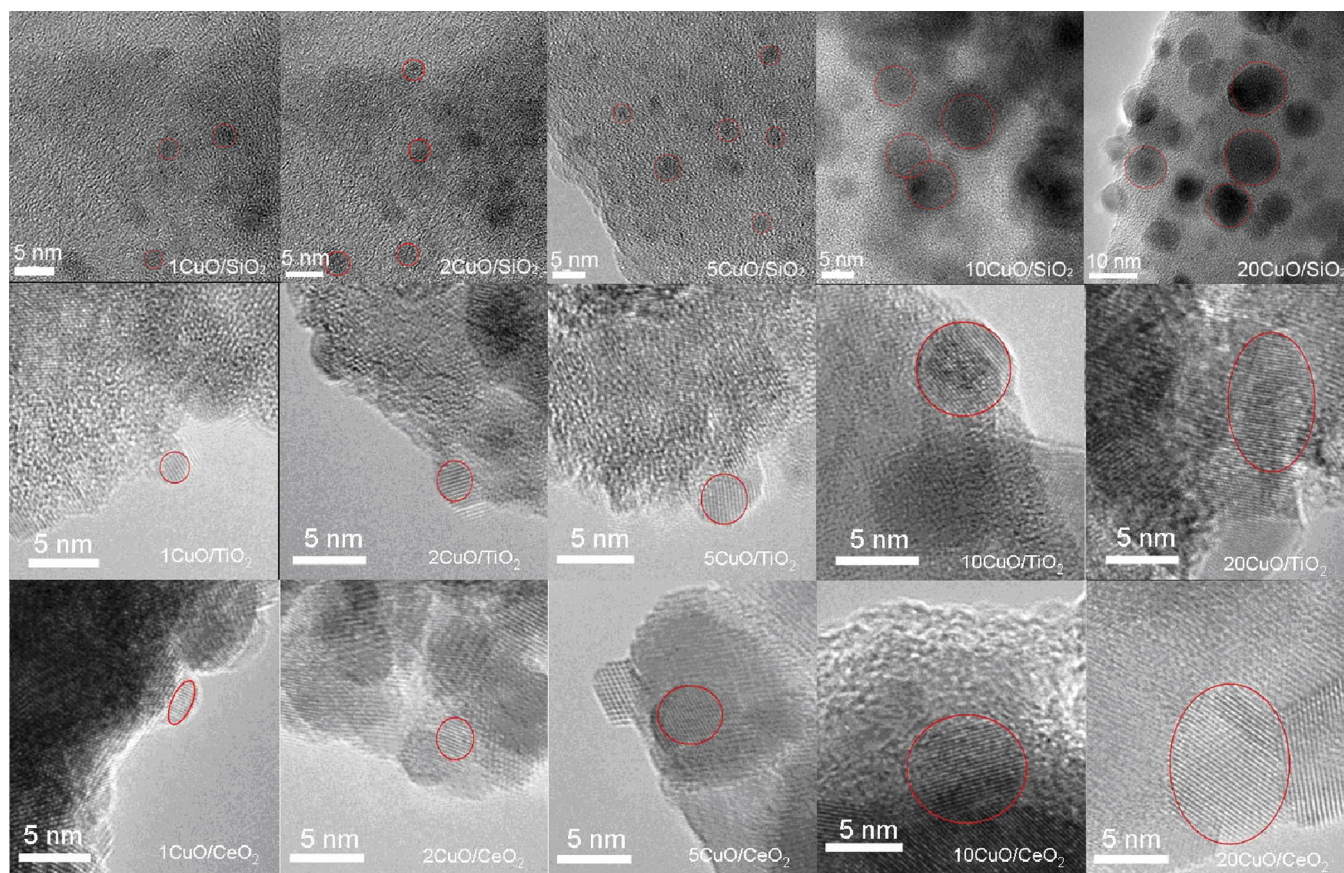


Fig. 2. HRTEM images of supported CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂ catalysts. The particles are marked by circles.

3. Results and discussion

3.1. Structural properties

The prepared CuO catalysts have surface areas of about 290, 54 and 9 m² g⁻¹, for the CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂ catalysts, respectively. And different CuO loadings do not change the surface area much. The actual CuO loadings of the samples are listed in Table 1. Fig. 1 presents typical XRD patterns of these samples. Fig. 1a clearly illustrates that the CuO/SiO₂ catalysts show amorphous SiO₂ characteristics at low CuO loadings (<5%), while crystalline CuO merges at high CuO loadings (>10%). For the CuO/TiO₂ catalysts, only mixed phases of rutile and anatase could be observed at low CuO loadings (<10%) because of the use of P25 as the support, but at high CuO loadings (>10%), CuO crystallites could also be detected. Same phenomenon was also observed on the CuO/CeO₂ samples, that is, at low CuO loadings only cubic CeO₂ phase is observed, while crystalline CuO is detected at high CuO loadings.

Morphologies and particle sizes of the CuO samples are estimated by TEM technique. It is clear that the low CuO-loading samples have small CuO particles while the high CuO-loading samples have large CuO particles. The calculated CuO particle sizes of the samples are listed in Table 1. For the CuO/SiO₂ samples, the CuO particle size ranges from 1.5 to 8.3 nm; for the CuO/TiO₂ samples, the CuO particle size ranges from 1.7 to 9.0 nm, while for the CuO/CeO₂ samples the values are 1.8 to 9.5 nm (Fig. 2).

3.2. Redox properties

Redox properties of the catalysts are analyzed by H₂-TPR technique, as shown in Fig. 3. For the CuO/SiO₂ catalysts (Fig. 3a), a

peak at about 270 °C is observed, which could be assigned to the reduction of CuO particles. With increasing CuO loadings, this peak becomes larger due to the higher amount of CuO content in the catalyst. Also, an additional weak peak at 230 °C appears, indicating different CuO particle size in the samples. For the CuO/TiO₂ catalysts (Fig. 3b), the low-loading samples (1.0CuO/TiO₂ and 2.0CuO/TiO₂) show two splitted reduction peaks at 180 and 190 °C, suggesting the different interactions between CuO and TiO₂. Moreover, this peak shifts to lower temperature with increasing CuO content in the catalyst, indicating the CuO in the high loading samples are more easily to be reduced. When the CuO is high (e.g. 5.0CuO/TiO₂), a reduction peak at about 250 °C is observed, which is probably due to the reduction of the free CuO species that are not interacting with TiO₂. The CuO/CeO₂ catalysts also show two reduction peaks (Fig. 3c). One peak at about 170 °C is assigned to the reduction of small CuO particles and the other peak at 200–270 °C is assigned to the reduction of large CuO particles [12]. Also, the calculated hydrogen consumption values are listed in Table 1. It is found that the CuO/SiO₂ and CuO/TiO₂ samples have very similar actual H₂ consumption values as the corresponding nominal values, indicating the reduction occurs only on CuO species. For the CuO/CeO₂ catalysts, the actual H₂ consumption values are larger than the corresponding nominal values, suggesting the simultaneous reduction of CeO₂ during the TPR process due to the typical spillover effect [24].

3.3. CO DRIFTS

Representative DRIFT spectra of CO chemisorption on the CuO catalysts are demonstrated in Fig. 4. All the catalysts show a feature at about 2110 cm⁻¹, which is assigned to CO chemisorption on Cu⁺

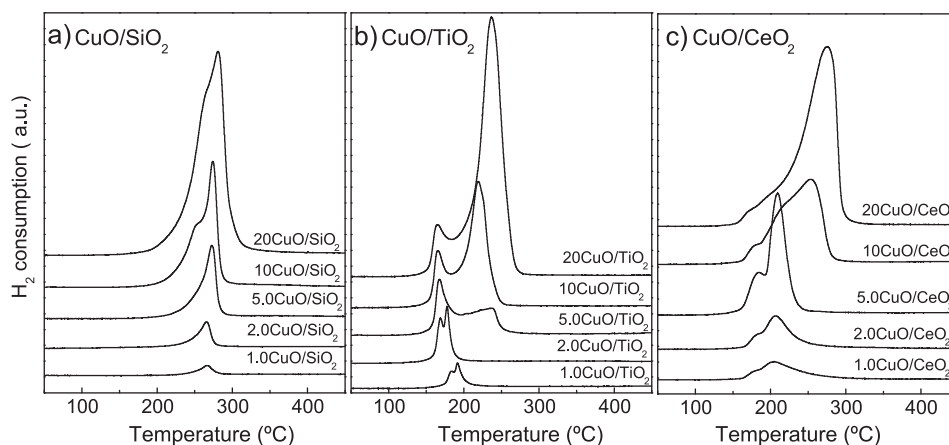


Fig. 3. H₂-TPR profiles of (a) CuO/SiO₂, (b) CuO/TiO₂ and (c) CuO/CeO₂ catalysts.

[31]. However, comparing these bands, it is found that the band intensity of the 5.0CuO/CeO₂ or 5.0CuO/TiO₂ is much stronger than that of the 5.0CuO/SiO₂, suggesting stronger CO chemisorption on the former catalysts. Moreover, characteristic band of carbonates at 1230–1566 cm⁻¹ is observed on the 5.0CuO/CeO₂ catalyst, implying that CO could easily react with lattice oxygen in the CeO₂ to form CO₂ molecules and deposit on the CeO₂ surface.

These DRIFT results clearly illustrate the different capabilities of CO chemisorption over these supported CuO catalysts. The CuO/SiO₂ catalyst contains mostly Cu²⁺ ions, which could hardly chemisorb CO. But for the CuO catalysts supported on reducible oxides such as TiO₂ and CeO₂, Cu⁺ ions could be present or stabilized on the catalyst, due to an interaction between the Cu species and the support oxide. For example, it was reported that stable Cu⁺ cations could be present in CuO/CeO₂ catalysts [32], and Cu²⁺ cations could be easily reduced to Cu⁺ during the reaction with CO molecules [33]. Furthermore, the formation of Cu⁺ species could be ascribed to its redox process of Ce⁴⁺/Ce³⁺ at the interfacial position of CuO and CeO₂ which could transfer electrons to Cu²⁺, resulting in the formation of Cu⁺ [34,35].

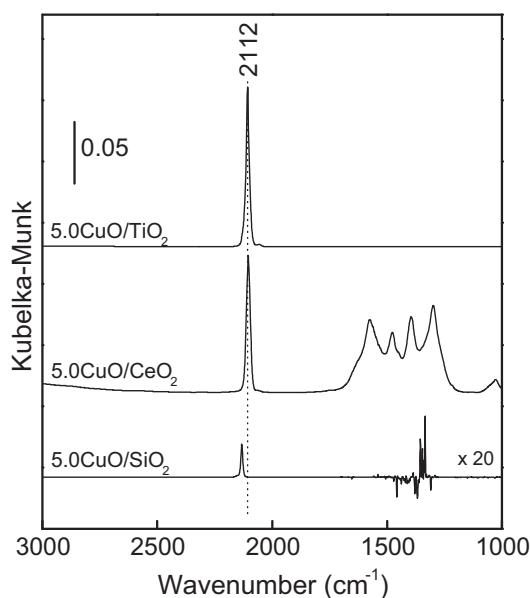


Fig. 4. DRIFT spectra of CO chemisorption over (a) 5.0CuO/SiO₂, (b) 5.0CuO/TiO₂ and (c) 5.0CuO/CeO₂ catalysts at 70 °C.

3.4. Kinetic study of CO oxidation over CuO catalysts

Kinetic investigation was carried out over three representative 5.0CuO/SiO₂, 5.0CuO/TiO₂ and 5.0CuO/CeO₂ catalysts. Note that the performances of these catalysts are different, various reaction temperatures were used to ensure the reaction was operated under differential mode. Reaction temperatures employed in this study were 240, 90 and 70 °C for the 5.0CuO/SiO₂, 5.0CuO/TiO₂ and 5.0CuO/CeO₂ catalysts, respectively. By changing partial pressures of CO and O₂, reaction rates based on CO conversions were calculated and the detailed results are listed in Table 2 and Figs. 5–7. It is clear that for the 5.0CuO/SiO₂ and 5.0CuO/TiO₂ catalysts, the reaction rate increases with both CO and O₂ partial pressure in the feedstock, indicating positive effect of CO and O₂ on the activity. However, for the 5.0CuO/CeO₂ catalyst, the reaction rate increases with increasing CO partial pressure, but it slightly decreases with increasing O₂ partial pressure in the feed gas. Based on the kinetic results, power rate law expression of the reaction rates of these catalysts were derived to be $r = 1.78 \times 10^{-7} P_{\text{CO}}^{0.85} P_{\text{O}_2}^{0.22}$ (5.0CuO/SiO₂), $r = 1.62 \times 10^{-7} P_{\text{CO}}^{0.65} P_{\text{O}_2}^{0.19}$ (5.0CuO/TiO₂, 90 °C) and $r = 1.5 \times P_{\text{CO}}^{0.7} P_{\text{O}_2}^{-0.08}$ (5.0CuO/CeO₂, 70 °C). These expressions imply that the CO oxidation may take different pathways these catalysts, especially note that the dependency of O₂ partial pressure over the 5.0CuO/SiO₂ (5.0CuO/TiO₂) and 5.0CuO/CeO₂ are very different. Also, Arrhenius plots (Fig. 8) of the three catalysts indicate that the apparent activation energies of CO oxidation over these catalysts are 74.8 kJ mol⁻¹ (5.0CuO/SiO₂), 56.4 kJ mol⁻¹ (5.0CuO/TiO₂) and 46.3 kJ mol⁻¹ (5.0CuO/CeO₂). These values reflect the fact that the reactivity follows the order of 5.0CuO/CeO₂ > 5.0CuO/TiO₂ > 5.0CuO/SiO₂. Moreover, Jernigan et al. [36] compared CO oxidation over Cu species with different oxidation states and found that the activation energies over the Cu⁰, Cu⁺ (Cu₂O) and Cu²⁺ (CuO) were 37.6, 58.5 and 71.1 kJ mol⁻¹, respectively. The similar activation energies of the CuO catalysts in the current work compared to those reported in literature also imply that the Cu species involved in CO oxidation are likely to be Cu⁺, which is evidenced in the DRIFTS results (Fig. 4).

Based on the reaction rate expressions, elementary steps of CO oxidation over CuO catalysts were derived.

For the 5.0CuO/SiO₂ catalyst, a classic Langmuir–Hinshelwood (L–H) reaction model involving competitive chemisorption of CO and O₂ on Cu surface atoms is proposed (Eqs. (1.1)–(1.5)).

SET 1



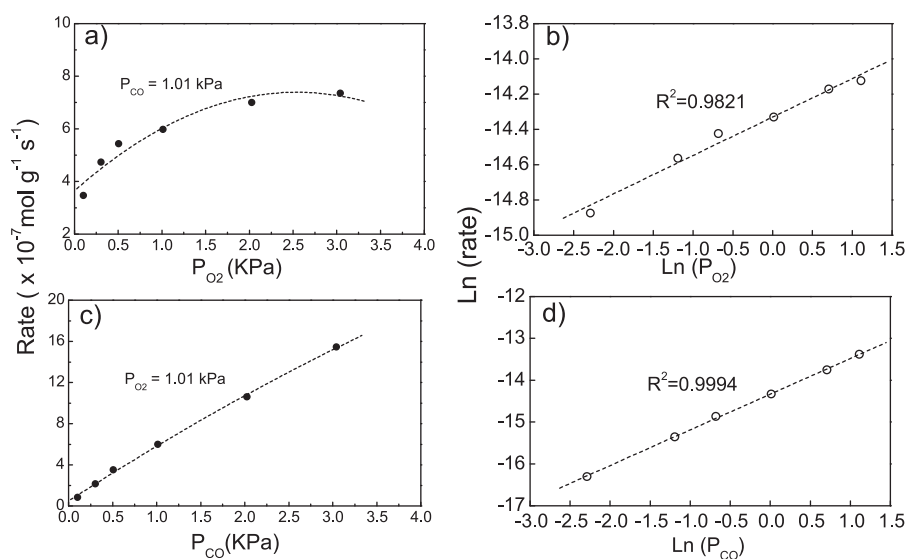


Fig. 5. Kinetic results of CO oxidation over 5.0CuO/SiO₂ at 240 °C.

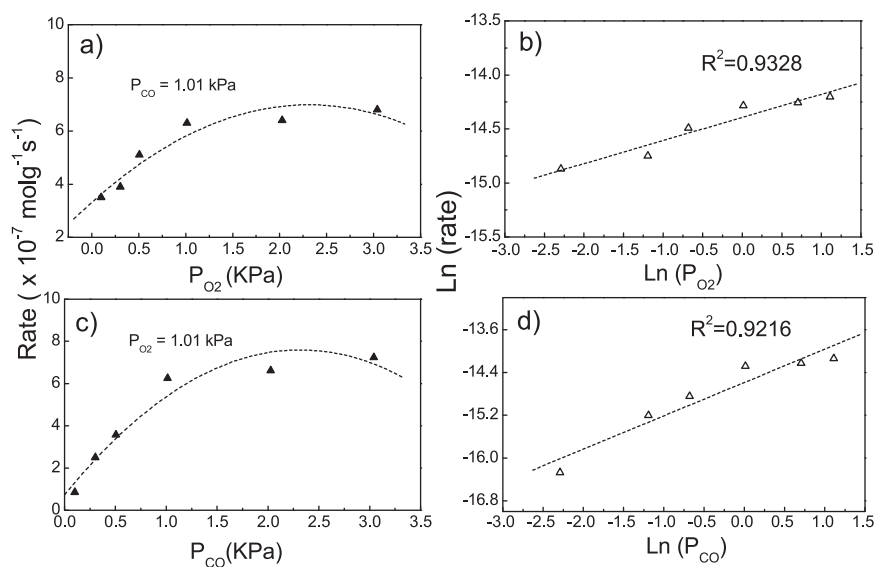


Fig. 6. Kinetic results of CO oxidation over 5.0CuO/TiO₂ at 90 °C.

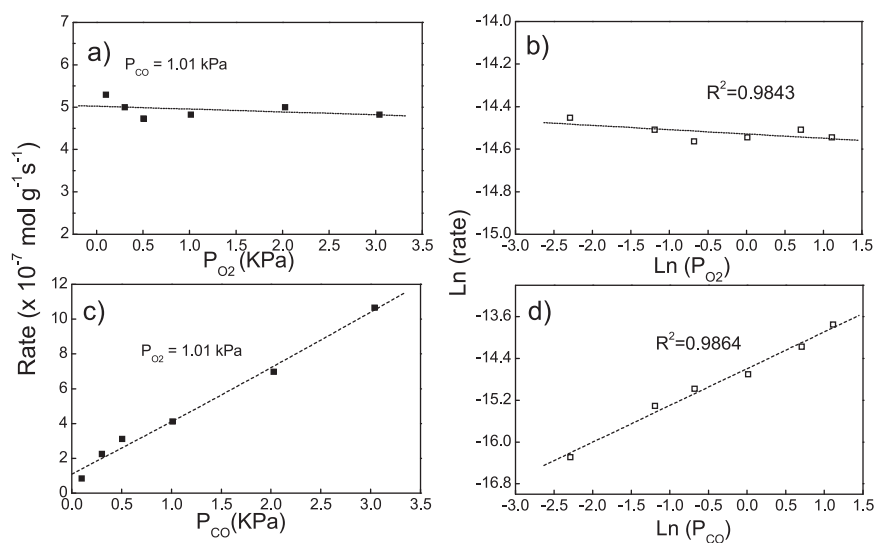


Fig. 7. Kinetic results of CO oxidation over 5.0CuO/CeO₂ at 70 °C.

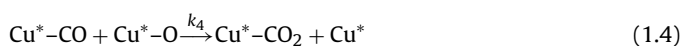
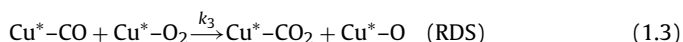
Table 2Summary of kinetic results of CO oxidation over 5.0CuO/SiO₂, 5.0CuO/TiO₂ and 5.0CuO/CeO₂ catalysts.

Partial pressure/kPa		CO conversion/%			Reaction rate ($\times 10^{-7}$ mol g ⁻¹ s ⁻¹)			Power rate expression
CO	O ₂	5CuO/SiO ₂	5CuO/TiO ₂	5CuO/CeO ₂	5CuO/SiO ₂	5CuO/TiO ₂	5CuO/CeO ₂	
1.0133	0.101	3.9	3.9	5.9	3.47	3.51	5.29	5CuO/SiO ₂ (240 °C) $r = 1.78 \times 10^{-7} P_{\text{CO}}^{0.85} P_{\text{O}_2}^{0.22}$
1.0133	0.304	4.7	4.4	5.6	4.73	3.90	5.00	
1.0133	0.5066	6.1	5.7	5.3	5.44	5.12	4.73	
1.0133	1.0133	6.7	7.0	5.4	5.98	6.25	4.82	
1.0133	2.0265	7.8	7.2	5.6	7	6.43	5.00	5CuO/TiO ₂ (90 °C) $r = 1.62 \times 10^{-7} P_{\text{CO}}^{0.65} P_{\text{O}_2}^{0.19}$
1.0133	3.0398	8.2	7.6	5.4	7.35	6.84	4.82	
0.101	1.0133	9.4	9.6	9.4	0.83	0.85	0.84	
0.304	1.0133	8.0	9.3	8.4	2.15	2.49	2.24	
0.5066	1.0133	7.9	8.0	7.0	3.51	3.57	3.11	5CuO/CeO ₂ (70 °C) $r = 1.5 \times 10^{-7} P_{\text{CO}}^{0.7} P_{\text{O}_2}^0$
2.0265	1.0133	5.9	3.7	3.9	10.61	6.61	6.98	
3.0398	1.0133	5.8	2.7	4.0	15.45	7.23	10.66	

Table 3

Crystallite size, CO conversion and TOFs values of CuO catalysts.

Catalyst	CuO crystallite size ^a /nm	CO conv./%	TOF _a ($\times 10^{-3}$ /s ⁻¹)	TOF _b /s ⁻¹	TOF _c ($\times 10^{-3}$ /s ⁻¹)
1.0CuO/SiO ₂	1.3	4.6 ^b	2.08	0.03	1.08
2.0CuO/SiO ₂	1.7	4.6 ^b	1.05	0.02	0.61
5.0CuO/SiO ₂	2.8	11.6 ^b	1.20	0.04	0.93
10CuO/SiO ₂	5.0	27.8 ^b	4.06	1.57	12.5
20CuO/SiO ₂	7.3	78.9 ^b	9.49	6.47	35.3
1.0CuO/TiO ₂	1.7	9.8 ^c	6.27	0.23	5.43
2.0CuO/TiO ₂	2.1	16.8 ^c	5.97	0.34	6.38
5.0CuO/TiO ₂	2.5	38.8 ^c	5.95	0.48	7.58
10CuO/TiO ₂	5.4	33.0 ^c	5.80	2.16	15.94
20CuO/TiO ₂	9.0	32.9 ^c	3.78	3.92	17.32
1.0CuO/CeO ₂	1.8	29.4 ^d	23.18	0.96	21.24
2.0CuO/CeO ₂	2.6	34.1 ^d	19.19	1.66	25.4
5.0CuO/CeO ₂	3.9	51.5 ^d	13.43	2.62	26.66
10CuO/CeO ₂	6.9	36.5 ^d	8.52	5.22	30.02
20CuO/CeO ₂	9.5	42.0 ^d	6.53	7.54	31.59

^a Based on TEM results.^b Reaction temperature was 260 °C.^c Reaction temperature was 120 °C.^d Reaction temperature was 100 °C.

This set of elementary steps results in a rate expression of:

$$r = \frac{k_3 K_1 K_2 [\text{CO}][\text{O}_2]}{(1 + K_1 [\text{CO}] + K_2 [\text{O}_2])}$$

The derivation of the elementary steps is verified based on the following facts:

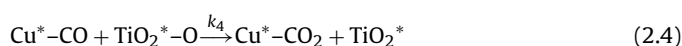
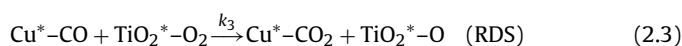
1. Mars van-Krevelen model and Eley Rideal model could be excluded because the former would result in a rate equation with a reaction order of 0 on O₂ partial pressure, and the latter would result in a rate equation with a reaction order of 1 on O₂ partial pressure, which are not consistent with the kinetic results in the present work.
2. The reaction between chemisorbed CO and O₂ is taken to be the rate determining step (RDS) and the chemisorption of either CO or O₂ is equilibrium. This is because if the CO or O₂ chemisorption is considered as the RDS, the reaction rate expression would contain reaction order of 1 on CO or O₂ partial pressure, which is not consistent with the obtained reaction orders of CO and O₂ in the power rate law equations between 0 and 1.
3. Chemisorption of CO on the CuO/SiO₂ was evidenced by DRIFTS result. Since the band intensity is very weak, it results in a high reaction order CO partial pressure (0.85).

4. Noncompetitive chemisorption of CO and O₂ may also occur, which could lead to a rate expression of $r = k_3 K_1 K_2^{1/2} [\text{CO}][\text{O}_2]^{1/2} / (1 + K_1 [\text{CO}] + K_2^{1/2} [\text{O}_2]^{1/2})$. This expression is also consistent with the kinetic results.

5. Dissociative chemisorption of O₂ on Cu surface atoms to form O adatom is also plausible. It could lead to a rate expression of $r = k_3 K_1 K_2^{1/2} [\text{CO}][\text{O}_2]^{1/2} / (1 + K_1 [\text{CO}] + K_2^{1/2} [\text{O}_2]^{1/2})$ (for competitive chemisorption of CO and O₂) or $r = k_3 K_1 K_2^{1/2} [\text{CO}][\text{O}_2]^{1/2} / (1 + K_1 [\text{CO}]) (1 + K_2^{1/2} [\text{O}_2]^{1/2})$ (for non-competitive chemisorption of CO and O₂). Both of these two expressions fit the kinetic results. A recent work by Liu et al. [37] reported that reaction between the chemisorbed CO and O adatom on Cu (311) plane was easier than that between CO and molecular O₂.

For the 5.0CuO/TiO₂ catalyst, a L-H reaction model involving chemisorption of CO on Cu surface atoms, chemisorption of O₂ on TiO₂ and two chemisorbed species reacting on CuO–TiO₂ interface is proposed. (Eqs. (2.1)–(2.5))

SET 2



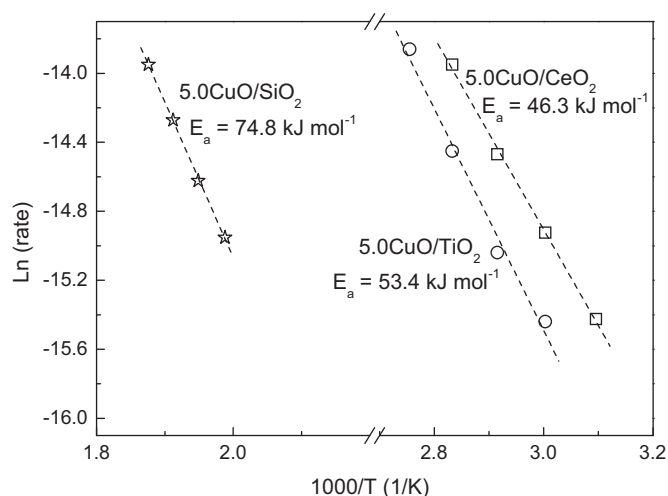


Fig. 8. Arrhenius plots for CO oxidation over 5.0CuO/CeO₂, 5.0CuO/TiO₂ and 5.0CuO/SiO₂ catalysts.



This set of elementary steps results in a rate expression of:

$$r = \frac{k_3 K_1 K_2 [\text{CO}][\text{O}_2]}{(1 + K_1 [\text{CO}])(1 + K_2 [\text{O}_2])}$$

The derivation of the elementary steps is verified based on the following facts:

1. Mars van-Krevelen model and Eley Rideal model could be excluded because the former would result in a rate equation with a reaction order of 0 on O₂ partial pressure, and the latter would result in a rate equation with a reaction order of 1 on O₂ partial pressure, which are not consistent with the kinetic results in the present work.
2. A L-H model involving chemisorption of CO and O₂ on Cu surface atoms (either competitive or noncompetitive) could lead to similar rate expressions as for the CuO/SiO₂ system, which are consistent with the kinetic results. But note that the CuO/SiO₂ become active at very high temperature (>200 °C, Fig. 6), it is not likely that it could catalyze the reaction at low temperature (e.g. 90 °C), thus the different behaviors of the 5.0CuO/SiO₂ and 5.0CuO/TiO₂ catalyst strongly suggests the role of TiO₂ in the reaction at low temperature, namely, it could participate in the reaction by chemisorbing O₂ molecules [9].
3. The reaction between chemisorbed CO and O₂ is taken to be the rate determining step (RDS) and the chemisorption of either CO or O₂ is equilibrium. This is because if the CO or O₂ chemisorption is considered as the RDS, the reaction rate expression would contain reaction order of 1 on CO or O₂ partial pressure, which is not consistent with the obtained reaction orders of CO and O₂ in the power rate law equations between 0 and 1.
4. Chemisorption of CO on the CuO/TiO₂ was evidenced by DRIFTS result. Since the band intensity is quite strong, it results in a relatively lower reaction order of O₂ partial pressure (0.65) compared to that of the CuO/SiO₂ (0.85).
5. Again, whether the chemisorption of O₂ on TiO₂ is dissociative or non-dissociative could not be distinguished. Dissociative chemisorption of O₂ on TiO₂ in the elementary steps will lead to a rate expression of $r = k_3 K_1 K_2^{1/2} [\text{CO}][\text{O}_2]^{1/2} / (1 + K_1 [\text{CO}])(1 + K_2^{1/2} [\text{O}_2]^{1/2})$ which also fits the kinetic results.

For the 5.0CuO/CeO₂ catalyst, a Mars van-Krevelen model is proposed. This model involves chemisorption of CO on Cu surface

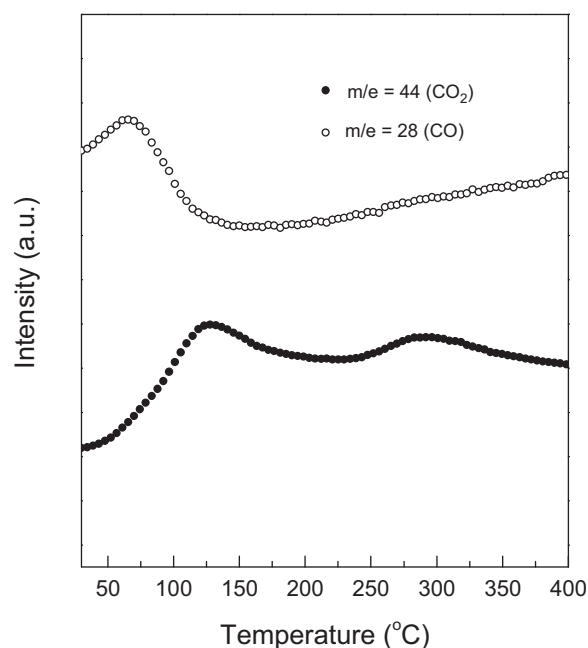
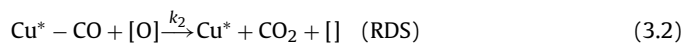


Fig. 9. CO-TPD profiles of 5.0CuO/CeO₂ catalyst.

atoms, which could further react with lattice oxygen in CeO₂. And then gas phase O₂ refill the oxygen vacancy to complete the reaction cycle. (Eq. 3.1–3.3)

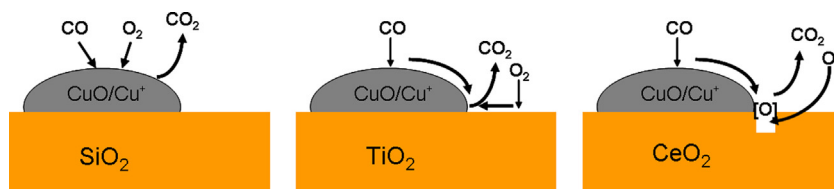
SET 3



This set of elementary steps results in a rate expression of: $r = k_2 K_1 [\text{O}] \frac{[\text{CO}]}{(1 + K_1 [\text{CO}])}$ where [O] refers to lattice oxygen, which is a constant under reaction conditions. [] refers to an oxygen vacancy.

The derivation of the elementary steps is verified based on the following facts:

1. Eley Rideal model could be excluded because it could result in a rate equation with a reaction order of 1 on O₂ partial pressure, which are not consistent with the kinetic results in the present work. The Mars van-Krevelen model is justified by the fact that the reaction order of 0 on O₂ partial pressure. Similar findings were also reported in our previous work [24].
2. A L-H model similar to that of the 5.0CuO/TiO₂ catalyst (Eqs. (2.1)–(2.5)) results in a rate expression of $r = k_3 K_1 K_2 [\text{CO}][\text{O}_2] / (1 + K_1 [\text{CO}])(1 + K_2 [\text{O}_2])$. If we assume that the chemisorption of O₂ on CeO₂ is near saturation on the surface ($K_2 [\text{O}_2] \gg 1$), the rate expression could be simplified to $r = k_3 K_1 [\text{CO}] / (1 + K_1 [\text{CO}])$. This rate expression has a reaction order of 0 on O₂ partial pressure, which is also consistent with the kinetic results. But Sedmak et al. [26] reported that in their CuO–CeO₂ catalyst, lattice oxygen would also participate the reaction and thus the reaction favored a Mars van-Krevelen model. To verify the involvement of lattice oxygen in the CO oxidation, CO-TPD was conducted and the results are shown in Fig. 9. It is found that desorption of CO occurs at about 60 °C; meanwhile, desorption of CO₂ is observed at about 130 and 290 °C, which could be assigned to the formed CO₂ molecules and decomposition of carbonates on the catalyst surface, respectively. These results confirms that the lattice



Scheme 1. Reaction models of CO oxidation over CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂ catalysts.

oxygen in CeO₂ could participate in the CO oxidation, which is also consistent with our DRIFT results, as the CuO/CeO₂ catalyst contains large amount of carbonates, which is likely formed by chemisorbed CO and lattice oxygen. Therefore, we also prefer a Mars van-Krevelen model instead of L–H model for the CO oxidation over CuO/CeO₂ catalyst.

These elementary steps of CO oxidation over the CuO/MO₂ catalysts reflects different pathways over the catalysts. For the CuO/SiO₂ catalyst, chemisorption and activation of both CO and O₂ take place on the surface Cu atoms, and the reaction of these two species follows a typical L–H reaction model. For the CuO/TiO₂ catalyst, CO and O₂ chemisorption takes place on the surface Cu atom and TiO₂, respectively, which results in a modified L–H reaction model (interface reaction). For the CuO/CeO₂ catalyst, the chemisorption of CO takes place on the surface Cu atom, while the lattice oxygen in CeO₂ also involves in the reaction, thus results in a Mars van-Krevelen model. A simplified scheme of CO oxidation over these supported CuO catalysts is demonstrated in Scheme 1.

3.5. CO oxidation over CuO catalysts

CO oxidation was performed on the CuO/MO₂ catalysts and the results are shown in Fig. 10. For the CuO/SiO₂ catalysts (Fig. 10a), the activity increases with CuO content in the catalyst, with the 20CuO/SiO₂ possessing the highest activity. For the CuO/TiO₂ and CuO/CeO₂ catalysts (Fig. 10b and c), the activity increases with CuO loading, reaching a maximum at the CuO content of 5.0 wt.%; however, further increase of CuO content in the catalyst results in a slight decline in the activity. As a whole, the activity follows an order of CuO/CeO₂ > CuO/TiO₂ > CuO/SiO₂. For example, the CuO/SiO₂ catalysts become active at reaction temperature of about 200 °C, while the CuO/TiO₂ and CuO/CeO₂ could completely convert CO to CO₂ at 200 and 150 °C, respectively. The different activities are closely related to the chemical natures of the catalysts. It has been reported that for the supported CuO catalysts, the activity usually correlates to the synergy of Cu species and the support, especially

for those reducible supports such as CeO₂ [31,38]. Such a synergy results from the chemisorption of CO on the surface Cu atoms and oxygen activation on the reducible support, as these two facts are crucial for the CO oxidation. The DRIFT results (Fig. 4) reveal that the CuO/SiO₂ catalyst can hardly chemisorb CO molecules, while the CuO/TiO₂ and CuO/CeO₂ catalysts can remarkably chemisorb CO molecules. The enhanced capability of CO chemisorption on the CuO/TiO₂ and CuO/CeO₂ could be one reason for the promoted activity obtained on these two catalysts. Comparing the CuO/TiO₂ and CuO/CeO₂ catalysts, it is found that the CuO/CeO₂ is slightly more active than the CuO/TiO₂, probably due to the unique properties of CeO₂. The presence of oxygen vacancies in the CeO₂ has been recognized to be very important for CO oxidation, as they could activate O₂ molecules to the generation of O₂[−] anion radical [39,40], which is believed to readily react with CO molecules to form CO₂.

3.6. Effects of CuO particle size on the reactivity

Based on the results in Fig. 10, various TOF values were calculated and listed in Table 3. For better understanding, these values were plotted as CuO particle size versus TOFs and the results are shown in Fig. 11.

For the TOFa (Fig. 11a), it is found that these values decline with CuO particle size for the CuO/TiO₂ and CuO/CeO₂ catalysts, which has often observed. However, the values increase with CuO particle size for the CuO/SiO₂, and the reason remains unclear. In addition, since the CO oxidation takes place at the metal-support interface for the CuO/TiO₂ and CuO/CeO₂ as confirmed by kinetic investigation, activity based on the atoms located on the periphery of CuO–TiO₂ and CuO–CeO₂ (TOF_b) was also calculated as shown in Fig. 11b. It is found that TOF_b values increase with increasing CuO particles in the catalysts, which is understandable because a large CuO particle contains more Cu atoms on the periphery compared to a small CuO particle. Moreover, if we consider the activity of each Cu atom on the periphery as defined as TOF_c, it is found that the value increases with CuO particle size (Fig. 11c), which is consistent with our previous report [28] and could be explained based on

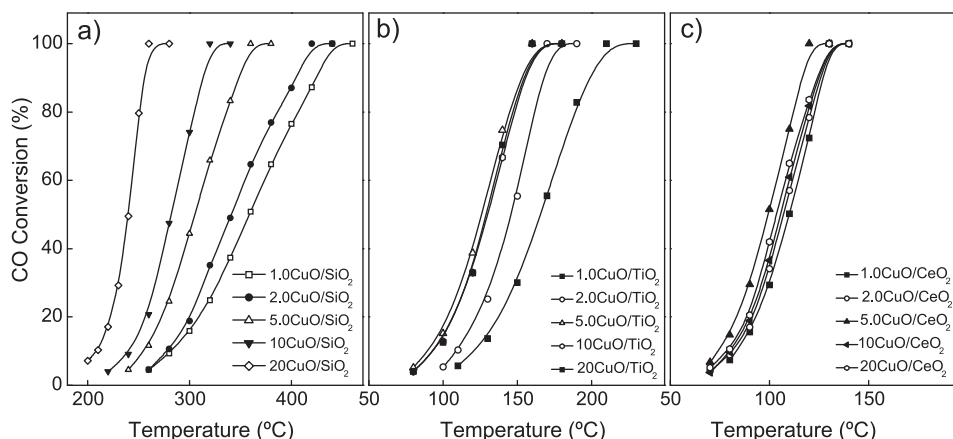


Fig. 10. CO oxidation over (a) CuO/SiO₂, (b) CuO/TiO₂ and (c) CuO/CeO₂ catalysts.

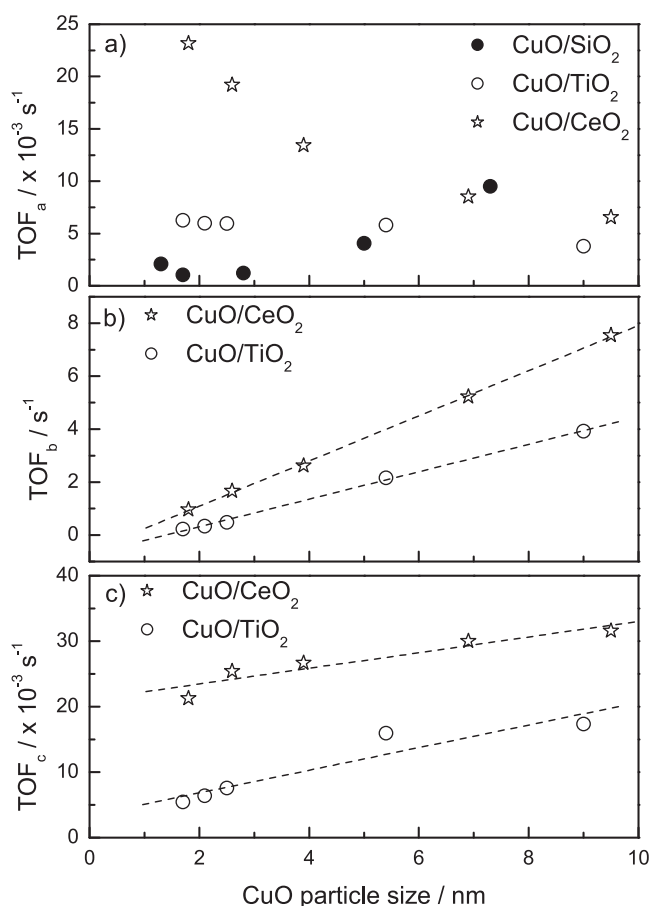


Fig. 11. Relationship between TOFs and CuO particle size of CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂ catalysts (for CuO/SiO₂ catalysts, the reaction temperature was 260 °C; For the CuO/TiO₂ catalysts, the reaction temperature was 120 °C; for the CuO/CeO₂ catalysts, the reaction temperature was 100 °C).

the reaction modeling over these two catalysts. For the CuO/TiO₂ catalyst, the reaction rate is $r = k_3[\text{Cu}^* - \text{CO}][\text{TiO}_2^* - \text{O}_2]$ (Eq. (2.3)); For the CuO/CeO₂ catalyst, the reaction rate is $r = k_2[\text{Cu}^* - \text{CO}][\text{O}]$ (Eq. (3.2)). These two expressions could be further simplified to $r = k[\text{Cu}^* - \text{CO}]$ for CuO/TiO₂ catalysts because $[\text{TiO}_2^* - \text{O}_2]$ is constant as the same TiO₂ support is used for the CuO/TiO₂ catalysts. For the CuO/CeO₂ catalyst, the rate expression could be simplified to $r = k'[\text{Cu}^* - \text{CO}]$ because the concentration of lattice oxygen [O] remains constant in the CuO/CeO₂ catalysts. Thus, the reaction rate is only dependant on the concentration of CO chemisorbed on the periphery Cu atom.

The concentration of chemisorbed CO on Cu atom could be derived as follows [28]:

$$V_{\text{ad},i} = \frac{V_{\text{ad}}}{8\pi d} \propto \frac{\alpha \cdot \rho \cdot 2\pi(d^2/2)}{8\pi d} \propto d$$

where $V_{\text{ad},i}$ is the concentration of the chemisorbed CO on the perimeter of a single CuO–TiO₂ or CuO–CeO₂ interface, V_{ad} is the total amount of CO chemisorbed on the surface of a single CuO semi-sphere, $8\pi d$ is the number of Cu sites on the perimeter, depending on the crystallite size, α is the sticking probability of CO molecules adsorbed on the surface of CuO crystallite, and ρ is the surface density of copper species.

It can be seen from the relationship It can be seen from the above relationship that the concentration of CO chemisorbed on the periphery of the CuO–TiO₂ or CuO–CeO₂ interface is proportional to the crystallite size of CuO. Therefore, such a relation could explain the higher reaction rate for the Cu atoms on a large CuO

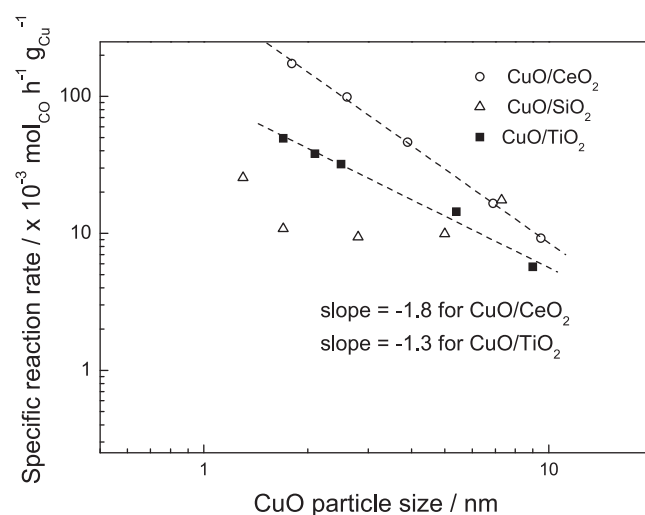


Fig. 12. Relationship between specific reaction rate (in $\text{mol}_{\text{CO}} \text{g}_{\text{Cu}}^{-1} \text{h}^{-1}$) and CuO particle size.

particle than that on a smaller one, due to the higher concentration of chemisorbed CO molecules.

Also, a relationship between CuO particle size and specific reaction rate based on metal content (in $\text{mol}_{\text{CO}} \text{g}_{\text{Cu}}^{-1} \text{h}^{-1}$) is established (Fig. 12). It is found that the reaction rates for the CuO/TiO₂ and CuO/CeO₂ are proportional to $d^{-1.3}$ and $d^{-1.8}$, respectively, while the dependence of d on the Cu/SiO₂ catalysts are random. The dependences particular that for the CuO/CeO₂ catalysts are consistent with the recent findings of Cargnello et al. [41], in which they found that the specific rates of CO oxidation over M/CeO₂ catalysts (M = Ni, Pd and Pt) had a metal particle size dependence of -2 , indicating the interfacial reaction over these catalysts.

4. Conclusions

In this work, kinetic studies were conducted on several supported CuO catalysts (CuO/SiO₂, CuO/TiO₂ and CuO/CeO₂) for CO oxidation. Different reaction models were derived, which depended strongly on the properties of the support oxides. For the CuO/SiO₂ catalysts, a L–H model involving chemisorption of CO and O₂ on surface Cu atoms was proposed; For the CuO/TiO₂ catalysts, a L–H model involving chemisorption of CO on Cu atoms and chemisorption of O₂ on TiO₂ was proposed, which resulted in a interfacial reaction between the two species. For the CuO/CeO₂ catalysts, a Mars van–Krevelen model involving chemisorbed CO on Cu atoms reacting with lattice oxygen in CeO₂ was proposed. Effect of CuO particle size was also evaluated. It was found that the active site on the periphery of the CuO–TiO₂ and CuO–CeO₂ interface was more active on the larger CuO crystallite than that on the smaller one. The enhanced activity could be interpreted by the higher concentration of chemisorbed CO on the active site on the larger CuO crystallite.

Acknowledgement

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