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Article

Carbon monoxide oxidation on copper manganese oxides prepared by selective etching with ammonia

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ABSTRACT

A series of copper manganese oxides were prepared using a selective etching technique with various amounts of ammonia added during the co-precipitation process. The effect of the ammonia etching on the structure and catalytic properties of the copper manganese oxides was investigated using elemental analysis, nitrogen physisorption, X-ray powder diffraction, scanning and transmission electron microscopy, X-ray photoelectron spectroscopy, H_2 temperature-programmed reduction, and O_2 temperature-programmed desorption combined with catalytic oxidation of CO. It was found that ammonia can selectively remove copper species from the copper manganese oxides, which correspondingly generates more defects in these oxides. An oxygen spillover from the manganese to the copper species was observed by H_2 temperature-programmed desorption, indicating that ammonia etching enhanced the mobility of lattice oxygen species in these oxides. The O_2 temperature-programmed desorption measurements further revealed that ammonia etching improved the ability of these oxides to release lattice oxygen. The improvement in redox properties of the copper manganese oxides following ammonia etching was associated with enhanced catalytic performance for CO oxidation.

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1. Introduction

Low-temperature carbon monoxide (CO) oxidation has attracted considerable attention in both academic and industrial fields [1–4]. Supported noble metal catalysts remain the most promising candidates for this reaction because of their distinguished activity and good stability [5–7]; however, the scarcity and high cost of precious metals are driving the search for more economic catalysts [8–13]. Copper manganese oxide (CMO), the major ingredient of hopcalite catalyst, is of great interest because of its low cost and relatively high catalytic activity for CO oxidation [14–17]. In general, the activity of copper manganese mixed oxides originates from the formation

of an amorphous $CuMnO_x$ hybrid, which is produced from the reaction between copper and manganese oxides [18–20].

Many synthesis methods have been developed to improve the efficiency of CMO, including co-precipitation [14], impregnation [21], sol-gel techniques [22], supercritical anti-solvent precipitation [23], and reduction methods [17]. Of these, co-precipitation is considered a convenient way of preparing catalysts with high activity. The preparation conditions have an important influence on the CMO activity. Hutchings and co-workers [14,24] discovered that selection of the correct aging time and use of a low calcination temperature are beneficial for preparing catalysts with high surface area and amorphous structure, which give high CO oxidation reactivity. The

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Cu/Mn ratio is also a crucial parameter which determines the phase composition in the final catalysts. It has been reported that CMO with a Cu/Mn ratio of 0.5 shows the best catalytic activity [24–28].

To date, it has been proved that the catalytic activity can be optimized by adjusting the composition, morphology, or structure of the CMO; however, investigations of their redox properties are rarely reported. In this work, a series of CMO catalysts were synthesized using a selective etching technique. With the aid of ammonia, Cu species can be selectively redissolved during the precipitation process because of the large difference in the stability constants of $[\text{Cu}(\text{NH}_3)_x]^{2+}$ ($\log\beta = 13.1$) [29] and $[\text{Mn}(\text{NH}_3)_x]^{2+}$ ($\log\beta = 1.57$) [30]. The composition and morphology of the final catalysts can therefore be manipulated. This facile pretreatment not only modifies the structure but also enhances the CO oxidation reactivity over CMO catalysts with a Cu/Mn ratio of ~ 0.3 , which is far below the reported optimized ratio of 0.5 [24–28]. Combining the results of various characterization methods, we determined the structural and redox property changes of selectively etched CMO catalysts. The effect of the preparation method on the CO oxidation reactivity is discussed based on these characterization results.

2. Experimental

2.1. Catalyst preparation

All chemicals were of analytical grade and used without any further purification. The CMO was prepared by co-precipitation using sodium bicarbonate (NaHCO_3) as the precipitant and copper acetate $[\text{Cu}(\text{OC}_2\text{H}_3)_2]$ and manganese acetate $[\text{Mn}(\text{OC}_2\text{H}_3)_2]$ as the precursors. Typical synthesis procedures are as follows: (1) 18 mmol of NaHCO_3 was dissolved in 22.5 mL of deionized water with an initial pH value of ca. 8; (2) 7.5 mmol of $\text{Cu}(\text{OC}_2\text{H}_3)_2$ and 15.0 mmol of $\text{Mn}(\text{OC}_2\text{H}_3)_2$ were mixed with 22.5 mL of deionized water; (3) the mixed solution was added to the solution containing the precipitant at 25 °C under vigorous stirring; (4) fixed volumes (1 mL) of 0, 5, 10, and 15 mmol of ammonia were rapidly dropped into the above solutions; (5) the suspensions obtained were aged for 30 min under vigorous stirring at 25 °C; (6) the precipitates were finally filtered, washed, and dried in air at 50 °C overnight, followed by calcination at 300 °C for 2 h. The obtained copper manganese oxide catalysts were denoted as CMO- X ($X = 0, 5, 10$, and 15), where X corresponds to the amount of added ammonia (mmol).

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were measured using a Rigaku D/MAX-2400 diffractometer with a $\text{Cu } K_\alpha$ radiation source (40 kV, 100 mA, $\lambda = 0.154\,056\text{ nm}$). The morphologies of the catalysts were characterized using an FEI Quanta 450 scanning electron microscope (SEM) equipped with a cooled energy-dispersive X-ray (EDX) spectrometer from Oxford Instruments for point-resolved elemental analysis. Transmission electron microscope (TEM) images were obtained with an FEI F30 microscope with an accelerating voltage of 300 kV. The

Brunauer-Emmett-Teller (BET) surface area (A_{BET}) was measured by nitrogen sorption at -196 °C using a Micromeritics ASAP 2020 instrument. Before measurement, all samples were degassed under a pressure of 15 Pa at 200 °C for at least 4 h. Elemental analysis was performed by inductively coupled plasma (ICP) atomic emission spectroscopy using an Optima 2000DV instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo VG ESCALAB250 with $\text{Al } K_\alpha$ radiation at 15 kV and 10 mA. The binding energy (BE) of each element was calibrated using a C 1s photoelectron peak at 284.6 eV. Temperature-programmed reduction of hydrogen (H_2 -TPR) was performed on a Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD) by passing 8% H_2/Ar (flow rate of 50 mL/min) over 50 mg of sample (40–60 mesh) at a heating rate of 10 °C/min up to 900 °C. Before H_2 -TPR, the samples were pretreated at 200 °C for 1 h under a flow of He gas to ensure a clean catalyst surface. The system was then cooled to ambient temperature under He flow. The amount of hydrogen consumed by each catalyst was calculated from the peak area of the H_2 -TPR profile. Oxygen temperature-programmed desorption (O_2 -TPD) was performed on a Micromeritics AutoChem II 2920 apparatus. A 50-mg sample was pre-treated at 200 °C for 1 h with He, cooled to ambient temperature under He, and finally 5% O_2/He was contacted with the sample for 1 h. Desorption was carried out from ambient temperature to 900 °C at a heating rate of 10 °C/min under He flow (30 mL/min).

2.3. Catalytic tests

The oxidation of CO was tested in a tubular fixed-bed quartz reactor at atmospheric pressure using 200 mg of catalyst (40–60 mesh). The standard composition of the feed gas was 1% CO–20% O_2 –79% N_2 with a space velocity of 20 000 $\text{mL g}^{-1}\text{ h}^{-1}$. The temperature was ramped at a rate of 1 °C/min from 30 °C to the final temperature. The concentrations of CO were analyzed at the outlet of the reactor by a GC 7890T gas chromatograph (TECHCOMP Limited Company, China) equipped with a TCD.

3. Results and discussion

3.1. Selective etching of copper manganese oxides

Fig. 1 presents the XRD patterns of the CMO- X catalysts. All samples show similar diffraction peaks at $2\theta = 31.4^\circ$, 32.3° , 37.1° , 42.1° , and 52.7° , suggesting that the major phases are mixtures of copper manganese hybrid oxides (CuMnO_x , JCPDS No. 41-0182) and manganese oxide (Mn_2O_3 , JCPDS No. 33-0900). The diffraction peak at $2\theta = 24.3^\circ$ indicates the presence of small amounts of manganese carbonate (MnCO_3 , JCPDS No. 44-1472). Because the catalysts were calcined at 300 °C, it is difficult to form complex oxides of CuMnO . The low resolution of the diffraction peaks indicates that the samples are poorly crystallized. These results are consistent with previous reports of amorphous CMOs prepared by co-precipitation [14,15,31–33]. The addition of ammonia hardly affected the

Fig. 1. XRD patterns of the CMO-X catalysts.

phase composition of the CMO-X catalysts.

SEM images of the CMO-0 and CMO-10 catalysts prepared with and without ammonia are presented in Fig. 2. The CMO-0 catalyst is composed of spherical particles with a size of ca. 1.5 μm . There is an obvious decrease of particle size in the CMO-10 catalyst. The particle morphology of the CMO-10 catalyst was also more irregular compared with that of the CMO-0 catalyst and the particle surface was rougher. TEM measurements were performed to characterize the local structure of a representative CMO-10 sample. Lack of crystalline order in the TEM (Fig. 2(e)) and high-resolution TEM images (Fig. 2(f)) reveals the amorphous nature of the CMO-10 sample, which is consistent with the poor crystallization confirmed by XRD measurements. Nitrogen physisorption measurements (Table 1) show that the BET surface area of the CMO-10 catalyst (139 m^2/g) is 1.6 times greater than that of the CMO-0 catalyst (85 m^2/g). The addition of ammonia evidently causes changes in size, morphology, roughness, and surface area of the CMO.

In the synthesis procedure, ammonia was added after the initial copper-manganese precipitates had formed. From the viewpoint of coordination chemistry, the stability constant of $[\text{Cu}(\text{NH}_3)_x]^{2+}$ is large, whereas the stability constant of $[\text{Mn}(\text{NH}_3)_x]^{2+}$ is only 1.57. The added ammonia will therefore be more inclined to etch the copper hydroxy carbonates (Eq.

Table 1

Physicochemical properties of the CMO-X catalysts.

Catalyst	Amount of ammonia ^a (mmol)	A_{BET}^b (m^2/g)	Cu/Mn molar ratio		
			ICP	EDX	XPS
CMO-0	0	85	0.61	0.55	0.43
CMO-5	5	121	0.66	—	0.37
CMO-10	10	139	0.33	0.40	0.29
CMO-15	15	144	0.26	—	0.17

^a In the preparation solution. ^b Measured by nitrogen physisorption.

(1)) generated in the precipitation process rather than the precipitate of the manganese species:

To verify whether such etching of ammonia occurred, the molar ratios of Cu/Mn in the CMOs were measured by ICP and EDX. The corresponding results are listed in Table 1. In line with expectation, the Cu/Mn ratio detected by ICP decreased from 0.61 to 0.26 with an increasing amount of ammonia. A similar trend is also shown by the EDX measurements. These results clearly indicate that ammonia selectively etches the copper species, which accounts for the fact that the addition of ammonia leads to changes of size, morphology, roughness, and surface area of the CMO.

3.2. Redox properties of copper manganese oxides

XPS can provide direct information on the chemical state of accessible metal oxide species on the surface, which generally determines the catalytic performance. Fig. 3 shows the Cu $2p_{3/2}$, Mn $2p_{1/2}$, and Mn $2p_{3/2}$ XPS spectra of the CMO-0, CMO-10, and CMO-15 catalysts etched with and without ammonia. The Cu $2p_{3/2}$ photoelectron peak is located at 934.4 ± 0.2 eV, and a characteristic satellite feature exists at a BE of 6 to 8 eV higher, indicating that the copper is present in the +2 oxidation state [12,23,34]. Similarly, the XPS peak of Mn $2p_{3/2}$ at 641.6 ± 0.3 eV confirms that Mn^{3+} species predominate in several samples [20,23,32,34–36]. The ammonia etching rarely changes the chemical state of the copper and manganese species on the surfaces of the CMO-X catalysts.

Based on the XPS data, the Cu/Mn surface ratios of the CMO-X catalysts were also calculated (Table 1). The Cu/Mn ratio on the surface of the CMO-0 catalyst (0.43) is smaller than that in the bulk (0.61), which indicates surface enrichment in manganese even without the addition of ammonia [32,34–36]. With increasing addition of ammonia, the Cu/Mn surface ratio falls to 0.17. This further confirms that ammonia prefers to selectively etch copper rather than manganese species.

Investigation of the reducibility of the copper and manganese species was carried out using H_2 -TPR experiments. Fig. 4(a) presents the H_2 -TPR profiles of the CMO-X catalysts, which exhibit four peaks centered at 107 $^\circ\text{C}$ (α peak), 163 to 177 $^\circ\text{C}$ (β peak), 196 to 222 $^\circ\text{C}$ (γ peak), and 259 to 295 $^\circ\text{C}$ (δ peak), respectively. The peaks at high temperature (> 180 $^\circ\text{C}$) are due to the reduction of manganese species, while the lower temperature peaks (< 180 $^\circ\text{C}$) are associated with reduction of copper species [31,37]. Accordingly, the first two peaks were assigned to the reduction of copper species, whereas the last two peaks

Fig. 2. SEM images of the CMO-0 (a, b) and CMO-10 (c, d) catalysts; TEM image (e) and high-resolution TEM image (f) of the CMO-10 catalyst.

Fig. 3. Cu $2p_{3/2}$ and Mn $2p$ XPS spectra of the CMO- X catalysts.

Fig. 4. (a) H_2 -TPR and (b) CO-TPR profiles of the CMO- X catalysts.

can be attributed to the reduction of manganese species. It is evident that the β peak (due to copper species) and the γ peak (due to manganese species) predominate. Notably, both the β and γ peaks shift to higher temperature when accompanied by ammonia etching.

The consumptions of H_2 corresponding to the reductions of copper and manganese species were calculated. Table 2 shows the ratios of H_2 consumption in the two reduction stages. For the CMO-0 catalyst, the ratio of H_2 consumption for the reduction of copper species to that for manganese species is close to the theoretical value (1.02), as shown by the reduction of CuO to Cu and of Mn_2O_3 to $2MnO$. However, the H_2 consumption ratios for the catalysts etched by ammonia (such as CMO-10 and CMO-15) reached values of 2.08 and 2.34, respectively,

which are much larger than the theoretical value. This phenomenon is likely to be explained by a spillover model, as reported by Buciuman et al. [16], in which manganese oxide acts as an oxygen donor and copper oxide as an oxygen acceptor. We have confirmed by compositional analysis that the Cu/Mn ratio for the CMO-10 and CMO-15 catalysts decreases in comparison with that of the CMO-0 catalyst. However, in the H_2 -TPR results, the consumption of H_2 , which results from the reduction of copper species in the CMO-10 and CMO-15 catalysts, not only did not decrease, but actually increased relative to that of the CMO-0 catalyst. This implies that copper oxide may “extract” the oxygen from the manganese oxide lattice, i.e., selective etching of ammonia enhances the lattice oxygen mobility of the CMO.

Table 2

H_2 -TPR peak positions, the ratio of H_2 consumption by the copper species to that by manganese species, and the CO-TPR peak positions for the CMO- X catalysts.

Catalyst	H_2 -TPR peak position ($^{\circ}C$)				Ratio of H_2 consumption for CuO_x/MnO_x	CO-TPR peak position ($^{\circ}C$)				
	α	β	γ	δ		α	β	γ	δ	ϵ
CMO-0	106	163	196	293	1.02	174	210	244	281	325
CMO-5	109	167	196	295	1.02	173	214	243	287	315
CMO-10	106	175	220	262	2.08	168	187	230	269	332
CMO-15	107	177	222	259	2.34	167	186	239	265	347

To provide more reliable and straightforward evidence for this, CO-TPR measurements were conducted to detect the reactivity of lattice oxygen species. As seen in Fig. 4(b) and Table 2, several reduction peaks associated with copper (α , β , and γ) and manganese (δ) species shift to lower temperature with increasing amounts of ammonia, clearly indicating that the etching enhances the reactivity of lattice oxide species. Given that the copper species decrease with etching, such an obvious improvement in the reactivity of lattice oxide species with CO, especially associated with copper species, supports the conclusion that selective etching of ammonia enhances the lattice oxygen mobility in CMO.

O₂-TPD experiments were also carried out to investigate the properties of oxygen species in the CMO. Fig. 5 shows the O₂-TPD profiles of the CMO-X catalysts. A broad weak desorption peak is observed at low temperatures (< 200 °C), which can be attributed to chemisorbed oxygen on the CMO surfaces. Three desorption peaks occurring at high temperature (> 200 °C) suggest the presence of three kinds of lattice oxygen species. For bulk or supported manganese oxide, the O₂-TPD curve usually exhibits two peaks, at around 560 and 820 °C, which are due to oxygen desorption. Previous work [38,39] has assigned these two peaks to defective MnO_x species. These two desorption signals shift to lower temperature (approximately 100 °C) in our O₂-TPD curves. Considering the coexistence of copper components, this change could be ascribed to the interaction between copper and manganese species. In general, the peaks occurring between 200 and 400 °C in the O₂-TPD profiles are assigned to copper species. In the present case, the strong peaks at 352 to 394 °C represent desorption of lattice oxygen species bound to copper species. The positions of the desorption peaks related to copper species gradually shift to lower temperatures as the CMO are etched by increasing amounts of ammonia. This means that the selective etching process enhances the ability of lattice oxygen associated with the copper species to be released. These findings explicitly demonstrate that selective etching using ammonia improves the redox properties of CMO. However, it should be noted that excessive etching decreases the amount of desorbed oxygen species associated with copper, as exemplified by the O₂-TPD profile of the CMO-15 catalyst.

Fig. 5. O₂-TPD profiles of the CMO-X catalysts.

Fig. 6. Dependence of CO conversion on the reaction temperature for the CMO-X and CMO-ref catalysts. Reaction conditions: catalyst mass 200 mg; space velocity 20 000 mL g⁻¹ h⁻¹; feed gas 1% CO-20% O₂-79% N₂.

3.3. CO catalytic oxidation on copper manganese oxides

Fig. 6 shows the dependence of CO conversion on the reaction temperature for the CMO-X catalysts. CO conversion over all the catalysts increased with increasing reaction temperature. Using a 90% extent of CO conversion as a reference, the reaction temperatures for the CMO-0, CMO-5, CMO-10, and CMO-15 catalysts are 66, 50, 44, and 57 °C, respectively. The catalysts etched by ammonia appear to exhibit superior catalytic activity compared with those without ammonia etching. The CO conversions at 30 °C (C_{30} , Table 3) were also compared to gain more information on the catalytic behavior. The C_{30} increased from 32% to 62% as the ammonia content increased from 0 to 10 mmol, and then decreased to 44% at 15 mmol. The activity order from high to low is: CMO-10 > CMO-5 > CMO-15 > CMO-0. The specific rate (Table 3) of CO converted per gram of CMO per hour at 30 °C exhibits a similar trend. These results indicate that the etching treatment for the as-prepared copper-manganese precipitates using ammonia is favorable for CO oxidation. However, excess ammonia will inhibit the catalytic activity, as exemplified by the conversion decrease observed for the CMO-15 catalyst.

The N₂-sorption results show that ammonia etching of the copper-manganese precipitate leads to an increase in surface area, which is likely to enhance the exposure of active species and thereby improve the catalytic activity. However, there is no

Table 3
CO oxidation performances over the CMO-X and CMO-ref catalysts.

Catalyst	$T_{90\%}^a$ (°C)	C_{30}^b (%)	Specific rate c (mmol g ⁻¹ h ⁻¹)
CMO-0	66	32	9.6
CMO-5	50	56	18.5
CMO-10	44	62	25.8
CMO-15	57	44	27.6
CMO-ref	81	20	8.4

^a Reaction temperature of a 90% extent of CO conversion.

^b CO conversions at 30 °C.

^c Millimoles of CO converted per gram of copper per hour at 30 °C.

direct correlation between the specific rate of CO oxidation and increasing order of surface area, implying that the increase of surface area is not the dominating factor for the reactivity to CO oxidation over these catalysts. According to earlier studies, the catalytic activity for CO oxidation is optimal over CMO prepared using co-precipitation with an initial Cu/Mn ratio of 0.5 [24–28]. In the present study, however, the catalytic activity for CO oxidation was actually enhanced, although the Cu/Mn ratio on the CMO surface decreased after etching with ammonia.

Extensive studies have concluded that CO oxidation on CMO follows a Mars-van Krevelen mechanism. It appears that the redox behavior of copper and manganese species is most likely to affect the reactivity in CO oxidation. As described above, the CMO copper species are selectively etched by ammonia and correspondingly promote the formation of more defective sites. By means of H₂-TPR, we have confirmed that the ammonia etching process could enhance the mobility of lattice oxygen between the copper and manganese species. Direct evidence for this is further provided by the increase of the reactivity of the lattice oxygen species following ammonia etching, as proved by the shift of the oxygen desorption peak associated with the copper species to lower temperature in the O₂-TPD analysis.

It is usually accepted that the oxygen species associated with copper in the CMO are very reactive and may dominate the low-temperature catalytic activity for CO oxidation. In comparison, the CMO manganese species possess high oxygen adsorption capacity and are mainly involved in the activation of oxygen [10,11,21]. Our structural characterization points to an increase in the reactivity of lattice oxygen associated with the copper species as well as mobility of lattice oxygen from manganese towards copper following ammonia etching. It is apparent that the improved redox ability of the copper species following ammonia etching is associated with enhanced catalytic performance for CO oxidation.

To establish whether such improvement dominates the reactivity of CO oxidation, we further compared the catalytic performance of two catalysts with similar Cu/Mn ratios of ca. 0.33, one with ammonia etching, i.e., CMO-10, and the other without ammonia etching, named CMO-ref. It can be seen from Fig. 6 and Table 3 that the C₃₀ and specific rate of CO oxidation over the catalyst with ammonia etching are far higher than over the catalyst without ammonia etching. By excluding the effect of the Cu/Mn ratio, this result clearly confirms that improved redox ability of the copper species, which is enhanced by the ammonia etching, dominates the catalytic reactivity of CO oxidation in the present study. Paradoxically, however, in the case of the CMO-15 catalyst, both C₃₀ and specific rates of CO conversion actually decrease, although the lattice oxygen species bonded to copper are more easily removed and reintroduced in comparison with the CMO-10 catalyst. Other factors also apparently affect the catalytic activity and should be considered. Previous work [10,11,21] has shown that CO adsorption on the catalyst surface is an important factor influencing the CO oxidation. Some researchers have proved that the copper site on the CMO surface is an active site for the adsorption of CO. In our case, as the O₂-TPD analyses prove, the amount of desorbed

oxygen species bonding to copper on the CMO-15 catalyst decreases dramatically, indicating that excessive etching of copper occurs. Such a lack of copper species is bound to hinder the CO adsorption on the catalyst surface, and can also explain the low CO oxidation reactivity and high redox ability of the CMO-15 catalyst.

4. Conclusions

A selective etching technique using ammonia was applied to the co-precipitation synthesis of CMO. The structure and redox properties of the oxides were investigated using a variety of analytical techniques and their catalytic activity for CO oxidation subsequently evaluated. XRD and SEM results revealed that catalysts prepared with and without ammonia had a spherical morphology with poor crystallinity. After etching with ammonia, the particle size decreased from ca. 1.5 to ca. 1.0 μm, and the surface roughness of the spherical particles increased. Ammonia etching also substantially increased the BET surface area of the CMO. The compositional analysis obtained from ICP, EDX, and XPS confirmed a marked reduction in the Cu/Mn ratio in the bulk and on the CMO surfaces with the addition of ammonia, which indicated selective etching of the copper species by ammonia. For the ammonia-etched CMO, an oxygen spillover phenomenon from manganese to copper species, observed in H₂-TPR measurements, suggests that ammonia etching enhances the mobility of lattice oxygen species. The O₂-TPD results further revealed that ammonia etching increased the ability of the CMO to release lattice oxygen. This improved redox ability of CMO enhanced the catalytic oxidation of CO; an amount of 10 mmol ammonia resulted in the most efficient catalyst for CO oxidation.

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Graphical Abstract

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Carbon monoxide oxidation on copper manganese oxides prepared by selective etching with ammonia

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Selective etching of copper manganese oxides by ammonia improves the mobility and release of the lattice oxygen species, which substantially enhances the catalytic activity of these oxides for CO oxidation.

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选择性刻蚀制备铜锰复合氧化物及其CO催化氧化性能

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摘要: 由于在工业、环保和能源等诸多领域的潜在应用, 低温CO催化氧化催化剂的研发引起了广泛关注. 尽管贵金属表现出优越的CO氧化活性和稳定性, 但是其有限储量和高昂价格一直限制着它们的实际应用. 铜锰氧化物是著名的霍加拉特催化剂的主组分, 价格低廉, 催化氧化CO活性高, 可高效替代贵金属催化剂. 大量研究已证实, CO在铜锰氧化物上的氧化遵循氧化-还原机理, 因此调变铜锰氧化物催化剂的氧化-还原性能对于改善其CO氧化活性至关重要.

本文报道了一种简单的选择性刻蚀技术, 即在铜、锰前驱物共沉淀过程中引入氨水作为刻蚀剂, 利用氨水与铜离子的强络合作用选择性刻蚀铜组分, 调变铜锰氧化物的铜锰比, 有效改善了铜锰氧化物的氧化-还原特性, 从而提高了其CO氧化性能.

X射线粉末衍射(XRD)测试结果表明, 初始制备的样品结晶弱, 主要物相包含铜锰复合氧化物和氧化锰, 此外还存在少量碳酸锰. 不同浓度氨水刻蚀几乎未改变铜锰氧化物的物相组成. 透射电子显微(TEM)照片中几乎没有发现晶格相, 进一步证实这些铜锰氧化物的弱结晶本质. 扫描电子显微(SEM)照片显示初始制备的铜锰复合氧化物主要由1.5 μm左右的球形颗粒堆积而成, 氨水刻蚀后颗粒形状变得不规则, 表面更加粗糙, 样品比表面积也从刻蚀前的85 m²/g增加到139 m²/g. 理论上, 氨水与铜的络合作用更强, 样品主体和表面组成分析结果显示, 随着氨刻蚀量增加, 铜含量逐步降低, 这清晰证实了氨有效地选择性刻蚀了铜组分.

进一步运用X射线光电子能谱(XPS)、氢程序升温还原(H_2 -TPR)、CO程序升温还原(CO-TPR)和氧程序升温脱附(O_2 -TPD)等测试手段表征了铜锰氧化物的氧化和还原特性,特别是氨刻蚀后催化剂氧化-还原性能. XPS分析显示铜锰氧化物中铜和锰物种的氧化态分别为+2和+3,氨刻蚀并没有改变两物种的氧化态. H_2 -TPR和CO-TPR证实氨刻蚀有效促进了铜锰氧化物中晶格氧从锰到铜物种的迁移,氨刻蚀同时还增强了与铜和锰键合的晶格氧物种的反应活性. O_2 -TPD结果进一步表明,氨刻蚀显著改善了铜锰氧化物中与铜键合晶格氧的释放. 综合来看,氨刻蚀可有效促进铜锰氧化物的晶格氧迁移、释放和反应等氧化-还原特性.

CO氧化反应研究显示,氨刻蚀大幅度促进了铜锰氧化物的催化活性. 当反应温度在30 °C时,相比于初始制备的铜锰氧化物催化剂,氨水刻蚀的样品上CO转化率提高了30%,达到90%转化率时的温度降低了20 °C. 关联催化剂结构表征和CO氧化性能数据发现,以表面Cu量归一化的CO氧化反应速率与催化剂的氧化-还原性能正相关. 这一结果清晰证实氨刻蚀能显著改善铜锰氧化物的氧化-还原特性,进而有效促进其CO氧化活性.

关键词: 铜锰氧化物; 选择性刻蚀; 氧化-还原性能; 一氧化碳氧化; 共沉淀

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