第 24 卷第 6 期 无 机 化 学 学 报 Vol.24 No.6
2008 年 6 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 848~855

$CuO/TiO_2/\gamma$-Al_2O_3 催化剂表征及对 NO+CO 反应性能研究

李惠娟 蒋晓原* 张 旭 郑小明
(浙江大学理学院化学系催化研究所,杭州 310028)

摘要: 采用色谱-微反流动法反应装置考察了 $w\%CuO/15\%TiO_2/\gamma$-Al_2O_3 催化剂对 NO+CO 的反应活性; 催化剂经空气氛或氢气氛预处理后,NO 转化率达 100%的反应温度分别是 325 和 275 ℃;XRD 仅能检测到 γ-Al_2O_3 晶相, 负载 15%CuO 后可以检测到微弱的 CuO 晶相;H_2-TPR 能检测到 2 个 CuO 的还原峰(α 和 β 峰),将其归属于高度分散的 CuO 分别在裸露的 γ-Al_2O_3 和 TiO_2/γ-Al_2O_3 载体上的还原;原位红外分析结果表明催化剂经空气氛或氢气氛预处理后,吸附 NO+CO 反应气后,反应的中间产物 N_2O 出现的温度分别为 200 和 150 ℃。

关键词: CuO-TiO_2/γ-Al_2O_3; NO+CO 反应; NO+CO 吸附; 原位红外表征
中图分类号: O614.41; O614.121; O611.62 **文献标识码**: A **文章编号**: 1001-4861(2008)06-0848-08

Characterization and Catalytic Properties of $CuO/TiO_2/\gamma$-Al_2O_3 for NO+CO Reaction

LI Hui-Juan JIANG Xiao-Yuan* ZHANG Xu ZHENG Xiao-Ming
(*Institute of Catalysis, Department of Chemistry, Faculty of Science, Zhejiang University, Hangzhou* 310028)

Abstract: The catalytic activity and properties of $w\%CuO/15\%TiO_2/\gamma$-Al_2O_3 in NO+CO reaction were examined using a micro-reactor gas chromatography reaction system. When pretreated by air and H_2, the catalysts had 100% NO conversion at 325 and 275 ℃, respectively. The XRD analysis could only detect γ-Al_2O_3 crystal diffraction and weak CuO crystal diffraction peaks after 15%CuO loading. There were two H_2-TPR reduction peaks in CuO-TiO_2/γ-Al_2O_3, the α peak due to the highly dispersed CuO which spread on γ-Al_2O_3 surface and the other peak due to the highly dispersed CuO which dispersed on $15\%TiO_2/\gamma$-Al_2O_3 surface. The DRIFTS analysis showed that catalysts with pretreatment in air or H_2 atmosphere adsorbed NO+CO gases, and the N_2O adsorption peaks appeared at 200 and 150 ℃, respectively.

Key words: CuO-TiO_2/γ-Al_2O_3; NO+CO reaction; NO+CO adsorption; DRIFTS characterization

The emission of NO_x from both mobile and fixed stationary sources is a serious environmental problem because it causes the formation of smog, acid rain, global warming and depletion of the stratospheric ozone layer[1~3]. It is urgent to eliminate NO_x pollution and improve environmental quality[4~12]. A lot of studies sug-gest that TiO_2 catalysts have more unique intrinsic activities than γ-Al_2O_3 catalysts [13~15]. However, low spe-cific surface area and poor thermal stability restrict the widespread use of titania as a catalyst support. To overcome these shortcomings, many mixed oxides containing TiO_2 (e.g. TiO_2-SiO_2, TiO_2-ZrO_2 and TiO_2-γ-Al_2O_3) were synthesized[16~19].

CuO is a good catalytic component for eliminating NO_x. When CuO is loaded on the TiO_2-mixed oxides, it has excellent catalytic activity for the

收稿日期:2007-09-23。收修改稿日期:2008-03-04。
浙江省自然科学基金(No.Y504131)资助项目。
*通讯联系人。E-mail:xyjiang@mail.hz.zj.cn; Tel:0571-88273283
第一作者:李惠娟,女,30 岁,博士研究生;研究方向:多相催化与环境催化。

removal of NO_x [20,21]. Amano et al [22] investigated the activity of CuO/γ-Al_2O_3 in NO+CO reaction and found that the catalyst had high one-electron reducibility ($Cu^{2+} \longrightarrow Cu^{+}$), suggesting the redox enhanced NO+CO reaction. Luo Mengfei et al [23] prepared CuO/γ-Al_2O_3 catalysts at different CuO loadings by impregnation method, and found that the activity of CuO/γ-Al_2O_3 in CO oxidation increased with CuO loading. Jiang et al[24] examined the activities of CuO/TiO_2 using a fixed-bed continuous flow reactor and reported 99% NO conversion at 325 ℃ after pretreatment with H_2 at 500 ℃ for 2 h.

In this study, high specific surface area TiO_2/γ-Al_2O_3 was synthesized by co-precipitation method. The catalytic properties and activity of $CuO/TiO_2/\gamma$-Al_2O_3 in NO+CO reaction were examined using the XRD, TPR and FTIR techniques.

1 Experimental

1.1 TiO_2/γ-Al_2O_3 preparation

TiO_2/γ-Al_2O_3 was synthesized by co-precipitation method. First $Al(NO_3)_3 \cdot 9H_2O$ crystallite was dissolved in double distilled water to prepare 3.0 $mol \cdot L^{-1}$ $Al(NO_3)_3$ aqueous solution and then slowly added to 0.1 $mol \cdot L^{-1}$ $TiCl_4$ solution . With vigorous stirring, the dilute $NH_3 \cdot H_2O$(1∶1, *v*/*v*) was dropped into the mixed solution until pH=10.5. The precipitation was laid in the solution for 24 h, then washed with distilled water until free from Cl^- ions. The solid materials were dried at 110 ℃ overnight and calcined at 500 ℃ for 2 h , after that, cooled to room temperature in air to obtain the TiO_2/γ-Al_2O_3 mixed oxide.

1.2 Catalyst preparation

$CuO/TiO_2/\gamma$-Al_2O_3 catalysts were prepared by wetness impregnation method. An amount of $Cu(NO_3)_2$ aqueous solution was added to TiO_2/γ-Al_2O_3 to yield certain metal loading. All the catalysts were dried at 110 ℃ in oven overnight and calcined at 500 ℃ for 2 h, denoted as w% CuO/15% TiO_2/γ-Al_2O_3, where w% and 15% represent the weight percentage of CuO and TiO_2, respectively.

1.3 Catalytic activity in NO+CO reaction

Catalytic activity was determined under the steady state in a fixed-bed quartz reactor (Φ=5 mm). The reaction gas consisted of 6.0%NO, 6.0%CO and 88%He (*V*/*V*). 60 mg of catalyst with particle size of 40~60 mesh (420~250 μm) was used. The reactions occurred at different temperatures with a space velocity of 1 000 0 h^{-1}. The analysis of the gases concentration in the reactor effluent was performed using a gas chromatography (GC) equipped with a TCD detector (the detector temperature was 200 ℃). A molecular sieve 13X column (2 m×4 mm×0.30 μm, stainless steel, controlled at 40 ℃) was used to separate N_2, NO and CO, and a Paropark Q column(2 m×4 mm×0.33 μm, stainless steel, controlled at 40 ℃) to analyze N_2O and CO_2. the GC carrier gas was H_2 and its flow rate was 25 $mL \cdot min^{-1}$.

1.4 Catalytic characterization

X-ray diffraction (XRD) data were obtained using a horizontal Rigaku B/Max Ⅲ B powder diffractometer with Cu *Kα* radiation(λ=0.154 18 nm) obtained by using Ni filter and a power of 40 kV×30 mA. The diffraction angles were 2θ(20°~70°).

H_2-temperature programmed reduction (TPR) was done by the GC method using a thermal conductivity detector. Sample was put into a quartz tube, with 95% N_2 and 5%H_2 mixtures(*V*/*V*) at flow rate of 15 $mL \cdot min^{-1}$. After the base line was stabilized, temperature increased at a rate of 10 $℃ \cdot min^{-1}$.

Specific surface area was determined by the BET method with N_2 adsorption at the liquid-nitrogen temperature using Coulter OMNISORP-100CX instrument. The samples were degassed in vacuum (10^{-5} Pa) for 2 h at 200 ℃.

Transmission electron microscopy(TEM) was done on a JEOL JEM-2010 (HR) microscope at 200 kV, The powder was ultrasonically suspended in alcohol for 5 min, and the suspension was deposited on a copper grid previously covered with a thin layer of carbon, and the TEM observations were carried out after drying the mesh.

FTIR experiments were performed using Nicolet 560 spectrometer with a MCT detector and a high-pressure, high temperature DRIFTS cell (Thermo Spectra-Tech) fitted with ZnSe windows. Spectra were acquired at a resolution of 4 cm^{-1} typically averaging

100 scans. The sample was pretreated in oxygen or hydrogen at 400 ℃ for 1 h, then cooled down to room temperature in the same gas to obtain the background. The oxygen or hydrogen was pumped off, and the absorbed gas was led to the IR cell. All spectra were taken at different temperatures. The flow rate through the IR cell was 15 mL·min^{-1}. The absorbed gas contained 10%NO+90%He, 10%CO+90%He or 6%NO+6%CO+88%He(*V*/*V*).

2 Results and discussion

2.1 Specific surface areas of TiO_2/γ-Al_2O_3 and *w*%CuO/15%TiO_2/γ-Al_2O_3

Specific surface areas of *w*% CuO/15% TiO_2/γ-Al_2O_3 decrease with CuO loading (Table 1). The pore structure data and 15%TiO_2/γ-Al_2O_3 catalysts calcined at different temperatures are shown in Table 2. Specific surface area is the largest after TiO_2/γ-Al_2O_3 is calcined at 500 ℃ and changes little from 600 to 700 ℃, but decreases with further increase in calcination temperature, which is consistent with previous studies[25]. After TiO_2/γ-Al_2O_3 is calcined at high temperature, from the TEM micrograph, we can see that the particles of TiO_2 and Al_2O_3 are enlarged and aggregated with increasing in calcination temperature, many pores are disappeared and the spacing of particles grows larger, this may result in the great specific surface area decreasing. The evolution of pore structure is strongly affected by calcination temperature. In all cases, the average pore size increases with increasing calcination temperature. For the most of materials, surface area reduction accompanies the pore size increase due to the removal of materials from the convex grain to the more concave necks. After calcinations at 500 to 900 ℃, the average pore sizes are 9.42 nm, 9.75 nm, 10.48 nm, 12.53 nm, 16.76 nm, respectively. This results are in the same trend as the study of Choi et al[26].

Table 1 Specific surface areas at different loadings of *w*%CuO/15%TiO_2/γ-Al_2O_3 (500 ℃, 2 h)

CuO / %	0	3	6	9	12	15
Specific surface area / ($m^2 \cdot g^{-1}$)	266	246	206	192	179	165

Table 2 Specific surface areas of TiO_2/γ-Al_2O_3 calcined at different temperatures

Temperature / ℃	500	600	700	800	900	1 000
Specific surface areas/($m^2 \cdot g^{-1}$)	266	196	199	142	100	45
Pore volume / ($mL \cdot g^{-1}$)	0.352	0.349	0.413	0.396	0.390	0.138
Average pore size / nm	9.42	9.75	10.48	12.53	16.76	23.74
Volume adsorbed / ($mL \cdot g^{-1}$) (STP)	61.09	43.26	45.65	32.73	23.06	9.36

2.2 TEM results

TEM is also employed to observe the shape and the size of the 15%TiO_2/γ-Al_2O_3 mixed oxides calcined at 500 and 1 000 ℃ for 2 h(Fig.1). From the two micrograph, we can see that there are many pores dispersed on the 15%TiO_2/γ-Al_2O_3 mixed oxides calcined at 500 ℃. But for the 15%TiO_2/γ-Al_2O_3 calcined at 1 000 ℃, the sintering of TiO_2 and Al_2O_3 particles are detected, a lot of pores of the mixed oxide are disappeared. We think that the structure of the TiO_2/γ -Al_2O_3 mixed oxide aggregates and collapses with increasing calcined temperature, and then produces large space among the primary particles. The TEM results agree well with our BET results.

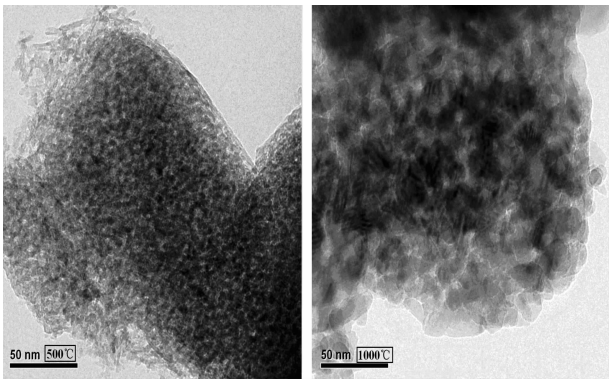


Fig.1 TEM micrograph of the 15%TiO_2/γ-Al_2O_3 calcined at 500 ℃ and 1 000 ℃ for 2 h

2.3 TG-DTA results

The DTA profile show three endothermic peaks at around 90, 440 and 600 ℃ (Fig.2), corresponding to three weight losses in the TG curve. According to the literature[27], it is presumed that the 90 ℃ peak is due to the removal of physically absorbed water molecules. The 440 ℃ peak is the result of phase transformation of boehmite to γ-Al_2O_3, and the peak at 600 ℃ is deemed

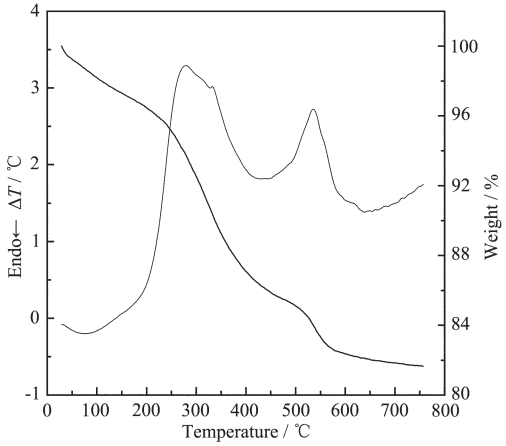
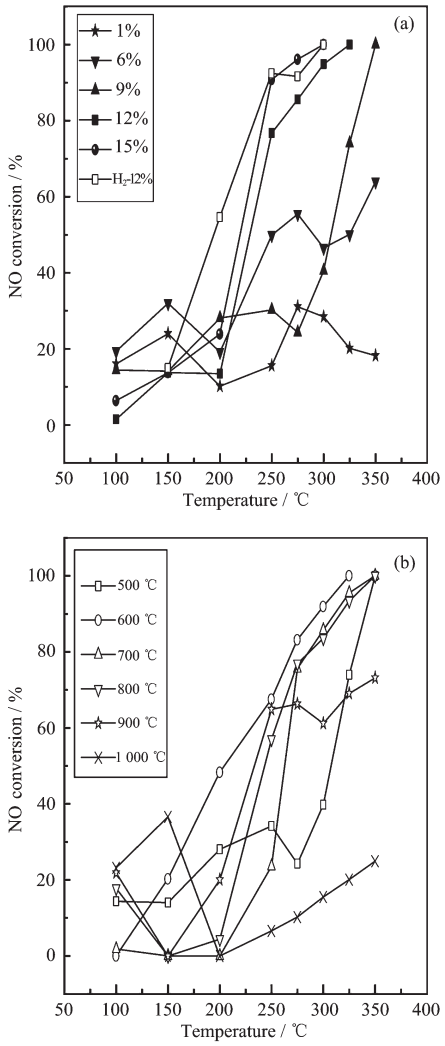


Fig.2　TG-DTA curves of TiO_2/γ-Al_2O_3

to the γ-Al_2O_3 phase formed completely[28].

2.4　Catalytic activity of NO

The activity of *w*% CuO/15% TiO_2/γ-Al_2O_3 with different CuO loadings calcined at 500 ℃ for 2 h are shown in Fig.3a. From the curve, it can be observed that there is a twist for every catalysts appeared at 150 ~ 200 ℃ except for the catalyst pretreated by H_2. We speculate that this phenomena is caused by NO adsorption and desorption on the catalysts. Compared with FTIR spectra in section 2.7, a lot of NO molecules could adsorbed on the catalysts at low temperatures, which results in very quick increase in NO conversion from 100 to 150 ℃. However, with increasing the temperature, the NO molecules desorbe from the catalyst, and the detected NO conversion decreases, thus bringing about a twist. But when the reaction temperature continues to increase, the NO+CO reaction initializes, this can also be seen from FTIR spectra in section 2.7, the intermediate products N_2O become larger at 200 ℃. Then the NO conversion goes up rapidly from 200 ℃ on. Because there may be some difference in the NO adsorption and desorption on different catalysts , the temperature range for twists to appear might not be the same. When talking about the reaction temperature from 200 to 400 ℃, it could be seen that the NO conversion increases rapidly with temperature. And the more CuO loading, the lower temperature for the total NO conversion. According to our XRD results, there is no CuO phase detected from *w*% CuO/15% TiO_2/γ-Al_2O_3 (500 ℃, 2 h) catalysts. And our TPR has merely one peak



(a) *w*%CuO/15%TiO_2/γ-Al_2O_3 catalysts with different CuO loadings;
(b) 12%CuO/15%TiO_2/γ-Al_2O_3 calcined at different temperatures

Fig.3　Activity of catalysts in NO+CO reaction

for all catalysts, we suggest that the highly dispersed CuO might be the NO+CO reaction active component. When the catalysts has higher CuO loading, there are more highly dispersed CuO, so they have better catalytic activity. As for the catalyst pretreated by H_2 at 400 ℃ for 1 h, the catalytic activity increases and its 100% NO conversion temperature is 300 ℃, and at the same time the twist at 200 ℃ is also disappeared. There might be two reasons responsible for the above observations. The catalysts have adsorbed H_2 during pretreatment with H_2 at 400 ℃ for 1 h. According to Lietti et al[29], H_2 could evolve in the NO+CO reaction, the NO elimination is a reduction reaction, and the desorption of H_2 favors for the reductions, thus decreasing the temperature for 100%

NO conversion . Similar results were also reported by Wu et al[30].

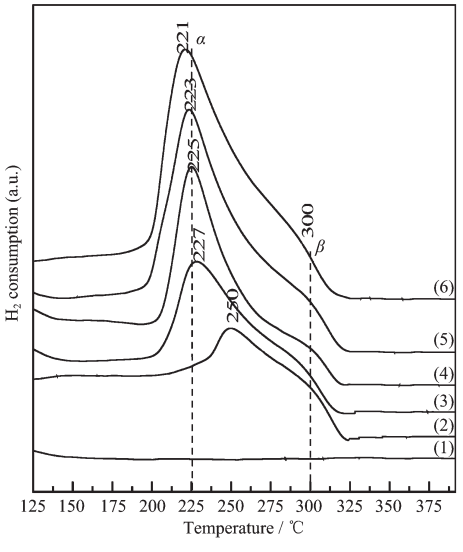
For the catalysts calcined at different temperatures, 12%CuO/15%TiO_2/γ-Al_2O_3 (600 ℃, 2 h) has the highest activity in NO +CO reaction, with 100% NO conversion at 325 ℃(Fig.3b). Although catalysts calcined at 500, 700 and 800 ℃ have some differences in catalytic activity at low temperature, they all reach 100% NO conversion at 350 ℃. However, when the catalyst is calcined at 900 ℃ for 2 h, 100% NO conversion occurs at 450 ℃, and for the catalyst calcined at 1 000 ℃ only has lower than 20% NO conversion at 450 ℃. In general, w%CuO/15%TiO_2/γ-Al_2O_3 catalysts have better thermal stability, despite a limitation of calcination temperature. The best calcination temperature is 600 ℃.

2.5 H_2-TPR results

Our previous work showed a strong reduction peak at 356 ℃ for CuO, two reduction peaks at 240 and 289 ℃ for 12%CuO/γ-Al_2O_3, and two reduction peaks at 318.9 and 387.5 ℃ for 12% CuO/TiO_2 [31]. In this study, there is no reduction peak for 15%TiO_2/γ-Al_2O_3, but a broad reduction peak (α=250 ℃) appears when 3%CuO is loaded(Fig.4). As CuO loading increases, the α peak becomes larger, especially for the 12% and 15% CuO loading catalysts. As for 6%, 9%CuO loading, the other reduction peak (β=300 ℃) appears. From XRD results, there is no CuO phase for the most of catalysts, so these two peaks might be due to the reduction of highly dispersed CuO catalysts. According to Xu et al[32] and our previous result , we assign this α peak to the highly dispersed CuO on γ-Al_2O_3 surface, the other β peak due to the highly dispersed CuO on 15%TiO_2/γ-Al_2O_3 surface.

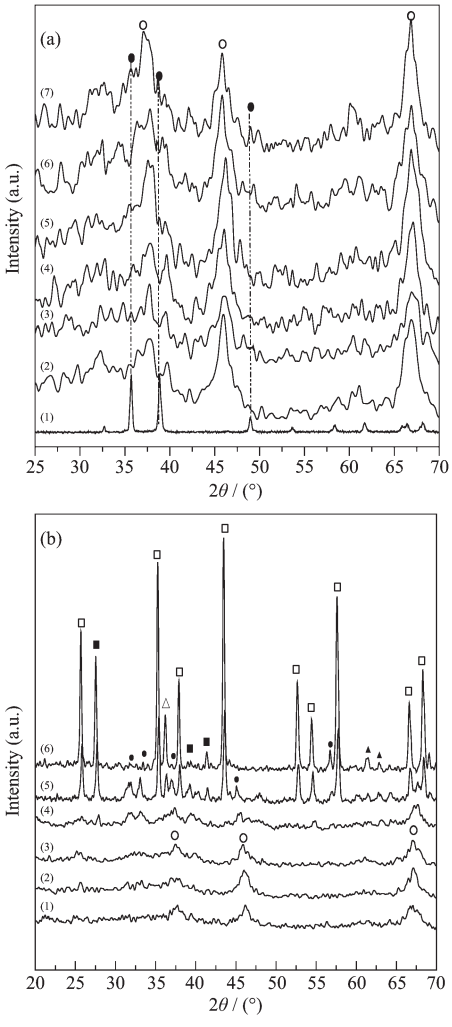
2.6 XRD results

With increasing CuO loading, the XRD patterns of *w*% CuO/15% TiO_2/γ-Al_2O_3 change little and TiO_2 crystallite diffraction peaks are not detected, but γ-Al_2O_3 diffraction peaks are observed(Fig.5a). Weak CuO



(1) 15%TiO_2/γ-Al_2O_3; (2)3%CuO/15%TiO_2/γ-Al_2O_3;
(3) 6%CuO/15%TiO_2/γ-Al_2O_3; (4)9%CuO/15%TiO_2/γ-Al_2O_3;
(5) 12%CuO/15%TiO_2/γ-Al_2O_3; (6)15%CuO/15%TiO_2/γ-Al_2O_3

Fig.4 H_2-TPR profiles of catalysts calcined at 500 ℃ for 2 h



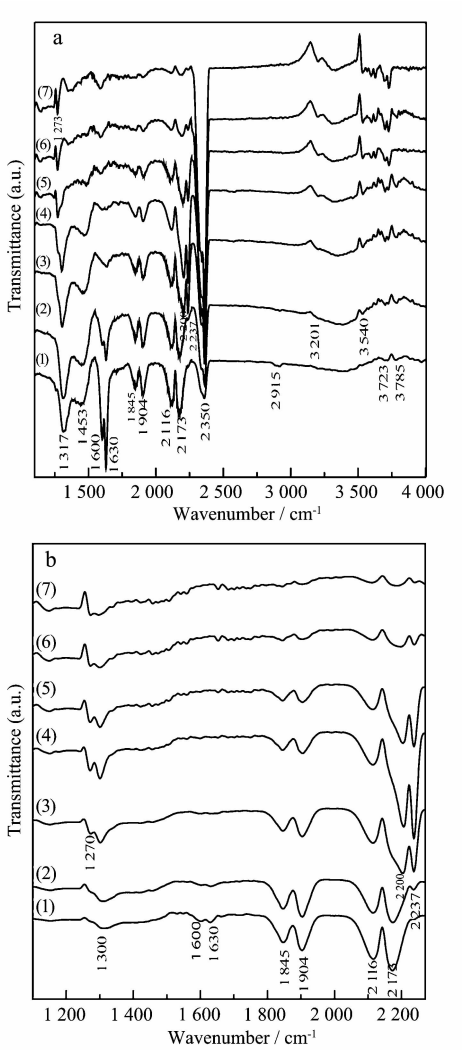
w%CuO/TiO_2/γ-Al_2O_3 with different CuO loadings (a): (1) CuO; (2) 0%; (3)3%; (4)6%; (5) 9%; (6) 12%; (7) 15% (● CuO ○γ-Al_2O_3) and TiO_2/γ-Al_2O_3 calcined at different temperatures (b):100 ℃; (2) 600 ℃; (3) 700 ℃; (4) 800 ℃; (5) 900 ℃; (6) 1 000 ℃(■ rutile TiO_2, ▲ $TiAl_2O_5$, ○γ-Al_2O_3, □ α-Al_2O_3, △ δ-Al_2O_3, ● θ-Al_2O_3)

Fig.5 XRD patterns of catalysts

diffraction peaks are detected only for 15% CuO/15% TiO_2/γ-Al_2O_3. When TiO_2/γ-Al_2O_3 is calcined at low temperature, γ-Al_2O_3 diffraction peaks are detected without a trace of TiO_2 diffraction peaks(Fig.5b). Calcined at 900 ℃, many diffraction peaks of TiO_2 rutile phase are observed. It is known that titania mainly exists in two forms, anatase and rutile, with transformation temperatures at the range of 600~800 ℃[34]. For 15%TiO_2/γ-Al_2O_3, the transformation temperature increases to 900 ℃, indicating that the addition of TiO_2 to γ-Al_2O_3 increases TiO_2 transformation temperature. It is common that TiO_2 anatase phase helps catalyze the NO+CO reaction. The preparation of 15%TiO_2/γ-Al_2O_3 by co-precipitation might have improved thermal stability. When 15%TiO_2/γ-Al_2O_3 is calcined at 900 ℃, δ-Al_2O_3 and θ-Al_2O_3 phases appear and γ-Al_2O_3 phase weakens. Calcined at 1 000 ℃, the α-Al_2O_3 phase is observed.

2.7 DRIFT analysis

Under flow of reaction mixture NO(6%) and CO (6%) in balance with He, DRIFT spectra taken over 12%CuO/15%TiO_2/γ-Al_2O_3 catalysts at different temperatures are shown in Fig.6a. The catalyst was first oxidized in O_2 at 400 ℃ for 1h and then cooled to 25 ℃ before exposing to the reaction mixture. The bands at 1 845 cm^{-1} is attributed to Cu(Ⅰ)-NO species and 1 904 cm^{-1} due to Cu(Ⅱ)-NO. As the surface temperature increases, the peak intensities of NO adsorption bands decrease gradually. After the sample contacts with NO+CO at 100 and 200 ℃, the Cu^{2+} sites are reduced and, as a result, no Cu^{2+}-CO(2 192 cm^{-1}[35]) species are detected. Scarano et al[36] suggested that $Cu^+(CO)_2$ species were produced during low-temperature CO adsorption on Cu/SiO_2, and they proposed a band at ca. 2 115 cm^{-1} to correspond to ν_{as} and ν_s, a band at ca. 2 160 cm^{-1} to the modes of the $Cu^+(CO)_2$ species. According to these literatures, we propose that the bands at 2 116 and 2 173 cm^{-1} are assigned to the ν_{as} and ν_s of $Cu^+(CO)_2$ species. The different results given here could be due to the lower interaction temperature and/or the different support and sample preparation technique. The 2 116 cm^{-1} peak intensity decreases with temperature but the 2 173 cm^{-1} peak becomes smaller at 150 ℃



(1) 100 ℃; (2) 150 ℃; (3) 200 ℃; (4) 250 ℃; (5) 300 ℃; (6) 350 ℃; (7) 400 ℃

(a) pretreated by air for 1 h at 400 ℃;

(b) pretreated by H_2 for 1 h at 400 ℃

Fig.6　DRIFTS spectra of 12%CuO/15%TiO_2/γ-Al_2O_3 absorbing NO+CO

and disappears at 200 ℃. At the same time a new peak at 2 200 cm^{-1} appears. 2 352 cm^{-1} band belongs to the CO_2 adsorption and its intensity becomes larger with temperature. 1 630, 2 915 and 3 540 cm^{-1} are due to stretching vibrations of O-C-O, C-H and O-H, respectively. These three bands might be caused by the HCOOH($CO+H_2O \rightarrow HCOOH$) existed on the surface of catalysts[37]. The bands at 1 600 cm^{-1} are NO_2 adsorption peaks. And the bands at 1 270, 1 300 $cm^{-1}$are assigned to monodentrate and bidentrate symmetric stretching vibrations of the NO_x (x =2 ~3)[38]. These three peaks (1 600, 1 270 and 1 300 cm^{-1}) weaken rapidly with

temperature. The N_2O adsorption peak (2 237 cm^{-1}) appears at 200 ℃, it goes bigger at 250 ℃ and becomes smaller and smaller when the surface temperature of catalysts is higher than 300 ℃.

At low temperatures, 12% CuO/15% TiO_2/γ-Al_2O_3 had NO and CO adsorption peaks are at the same location regardless of pretreatments by air or H_2(Fig.5b) at 400 ℃ for 1 h. The peak at 1 600 cm^{-1} is weak, indicating only a few NO_2 species. The peaks at 1 270, 1 300 cm^{-1} are also small, and NO_3^- peak at 1 430 cm^{-1} is not detected. When 12% CuO/15% TiO_2/γ-Al_2O_3 is pretreated by air at 400 ℃ for 1 h, there are more oxygen species on the catalyst surface. The oxygen species react with NO+CO gases at low temperature to produce NO_2, NO_x and nitrate species. However, pretreatment by H_2 at 400 ℃ for 1 h offers fewer oxygen species on the catalyst and therefore produces fewer NO_x species. At 200 ℃ the bands at 2 173 cm^{-1} disappear but 2 210 cm^{-1} adsorption peak appears. The N_2O band at 2 237 cm^{-1} appears at 150 ℃, becomes the strongest at 250 ℃, weakens at 350 ℃, then disappears at 400 ℃. It is suggested that the N_2O intermediates are produced at low temperature, then turned into N_2 at higher temperature.

There have been many studies on the band peak at 2 210 cm^{-1}. Tamás Bánsági et al [39] investigated the adsorption of NO+CO gases by Rh/CeO_2 using FTIR techniques and assigned the band peak 2 210 cm^{-1} to Rh-NCO^- species adsorption. Venezia et al[40]studied the coadsorption of NO+CO on Pd/SiO_2 catalysts, and assigned 2 190 cm^{-1} band to Pd(-NCO). According to other authors [41,42], the 2 150~2 200 cm^{-1} adsorption bands belong to M-NCO species (M denotes metal or metal ions). Therefore when CO and NO are co-absorbed by the transition metal or the transition metal oxides at higher temperatures, NCO^- usually is prod-uced. By analogy with the results of Beloshapkin et al[43], they assigned the bands at 2 205 cm^{-1} to the asymmetric stretching of Cu^+-NCO species. In this study, the 2 210 cm^{-1} adsorption peak appears at 200 ℃ or higher temperatures, where CO reduces CuO into Cu^0 and Cu^+, and we only test the $Cu^+(CO)_2$ species. Above all, we attribute the band at 2 210 cm^{-1} to the Cu^+-NCO^- species adsorption.

After 12% CuO/15% TiO_2/γ-Al_2O_3 is pretreated by H_2 atmosphere, few oxygen species exist on the surface of catalyst and thus less NO_x and nitrate are produced in NO+CO reaction. Because N_2O is a very important intermediate in the NO+CO reaction, its appearing and disappearing temperatures could directly influence the rate of NO+CO reaction and NO conversion. This study has explained why catalysts pretreated by H_2 have higher activity than those pretreated by air atmosphere.

3 Conclusions

(1) *w*% CuO/15% TiO_2/γ-Al_2O_3 catalysts have high catalytic activity and thermal-stability for NO+CO reaction, the reaction temperature is 325 ℃ in air and 275 ℃ in H_2 for 100% NO conversion over 12% CuO/15%TiO_2/γ-Al_2O_3(500 ℃, 2 h).

(2) 15% TiO_2/γ-Al_2O_3 catalysts prepared by co-precipitation method have high BET surface area, its pore size increases with temperature. Only γ-Al_2O_3 crystallite diffraction peaks are detected and weak CuO crystal diffraction peaks could be detected for 15%CuO loading for w%CuO/15%TiO_2/γ-Al_2O_3(500 ℃, 2 h). Two TPR peaks(α, β) are detected when CuO is loaded on TiO_2/γ-Al_2O_3. The α and β peak are assigned to the highly dispersed CuO reduction on γ-Al_2O_3 and 15% TiO_2/γ-Al_2O_3, respectively.

(3) After catalysts are pretreated in air and H_2 atmosphere, DRIFT analysis detects the N_2O adsorption peaks in NO+CO reaction at 200 ℃ and 150 ℃, respectively.

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