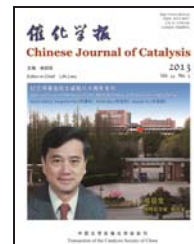




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Article (Special Issue in Memory of the 80th Birthday of Professor Jingfa Deng)

Deactivation mechanism of PdCl₂-CuCl₂/Al₂O₃ catalysts for CO oxidation at low temperatures

FENG Yafen, WANG Li, ZHANG Yanhui, GUO Yun *, GUO Yanglong, LU Guanzhong

Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, China

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ABSTRACT

Supported Wacker catalysts exhibited high activity for low temperature CO oxidation, but high concentrations of water in the reaction gas could lead to the deactivation of the catalyst. The PdCl₂-CuCl₂/Al₂O₃ catalysts were prepared, and a high relative humidity deactivation mechanism was suggested after characterizing the fresh and spent catalyst by X-ray diffraction, N₂ absorption-desorption, X-ray photoelectron spectroscopy, H₂-temperature programmed reduction and in situ diffuse reflectance infrared Fourier transform spectroscopy. The results showed that the water could adsorb and condense on the surface of the catalyst, which arouses the aggregation and transfer of Cu species into the internal pores of the catalyst. This weakens the interactions between the Pd and Cu species and reduces the re-oxidation ability of Pd⁰ to Pd²⁺, which blocks redox cycling and results in the decrease of CO oxidation activity.

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1. Introduction

CO is a toxic gas that is usually generated from chemical production processes, vehicles exhausting emissions, and incomplete combustion of fossil fuels. Catalytic oxidation is an efficient method for CO removal, especially at low temperatures. CO oxidation at lower temperatures has received wide attention as important practical applications in CO gas sensors, air purification, gas masks and closed system ventilation such as in submarines and spacecraft [1].

Composite oxides and noble metal catalysts can be used in CO oxidation. Oxide catalysts such as Hopcalite catalyst and Co₃O₄ can improve the CO oxidation activity. Co₃O₄ can oxidize CO even at -77 °C [2], but the trace water may cause catalyst deactivation [3]. Au, a typical noble catalyst, not only shows excellent CO oxidation activity [4], but also resists water [5].

Problems with Au catalysts, such as sensitivity to preparation conditions, halogen poisoning [6] and potential deactivation during storage [7], still limit its wider applications. Supported Pd catalysts show excellent performance for CO oxidation. When the Pd loading amount was 4 wt%, CO could be completely converted at -15 °C [8]. The supported Pd catalyst also has water resistance and halogen tolerance.

Supported Wacker-type catalysts (PdCl₂-CuCl₂) have high CO oxidation activity. PdCl₂-CuCl₂/Al₂O₃ prepared by NH₃ coordination-impregnation can completely convert CO at -30 °C [9] in 0.04% CO and 0.1% H₂O. The reaction mechanism for CO oxidation on supported Wacker-type catalysts was similar with that of homogeneous catalysts [10]:



* Corresponding author. Tel: +86-21-64253703; E-mail: yunguo@ecust.edu.cn

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The active phases of Pd and Cu are the Pd²⁺ and Cu₂Cl(OH)₃ species. Cu₂Cl(OH)₃ can accelerate the oxidation of lower valence Pd that would promote the redox cycle [11]. In this reaction cycle, some results showed that the rate determining step (RDS) was of the re-oxidation of Cu⁺ [12]. Pd⁰ oxidation to Pd⁺ by Cu²⁺ was also suggested to be a RDS [13].

Having water in the feed gas is inevitable for most practical applications. However, the presence of water has been reported to promote CO oxidation on supported Wacker-type catalysts [14]. The presence of water increases the CO oxidation rate by 2–3 times [15], but the excess water could adsorb onto the catalyst surface, covering the active sites and increasing the mass transfer resistant. For the hydrophilic support (such as Al₂O₃), capillary condensation of water can also occur inside the pores, which causes deactivation of the catalyst [12]. It was also reported that losing Cl⁻ ions can also cause catalyst deactivation as Cl⁻ ions are essential to maintain the redox cycle. CO oxidation activity is directly related to the coordination number of Cl⁻ ions surrounded Pd²⁺ [16]. Previous research also confirmed that the deactivation of the catalyst was related to the state of the Cu species [17].

In this paper, differences in the structure, surface and redox prosperities of fresh and spent catalysts are studied to investigate the deactivation mechanism for CO oxidation on PdCl₂-CuCl₂/Al₂O₃ catalysts at high relative humidity (100%).

2. Experimental

2.1. Catalyst preparation

Supported Wacker-type catalyst (PdCl₂-CuCl₂/Al₂O₃) was prepared by the NH₃ coordination-impregnation method, where the content of PdCl₂ and CuCl₂ was represented by their weight ratios, which was 1.5% and 3.3% respectively. The catalyst was labeled as 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃. CO oxidation activity of a fresh catalyst, denoted as F, was evaluated at 25 °C, with 100% relative humidity of feed gas, and a weight hourly space velocity (WHSV) of 15000 ml/(g·h). When CO conversion decreased to 10%, the deactivated catalyst was regenerated in air at 50 °C for 10 h, and then the same evaluation experiment was repeated. After several deactivation-regeneration cycles, the obtained catalyst was labeled as D. The same preparation were employed on both catalysts PdCl₂/Al₂O₃ and CuCl₂/Al₂O₃, denoted as 1.5 wt% Pd/Al₂O₃ and 3.3 wt% Cu/Al₂O₃.

2.2. Water adsorption experiment

A water adsorption experiment was conducted at ambient temperature in a quartz U-tube reactor; 0.2 g catalyst was used. 50 ml/min N₂ was directed through a water vapor saturator, and then flowed into reactor. The weight of the reactor was measured at a fixed time to obtain the water adsorption rate.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of sample were performed on a Brook D8 focus diffraction spectrometer with Cu K_α radiation at room temperature. The following parameters were used; incident wave length 0.15 nm, electric current 40 mA, power voltage 40 kV, scanning angle 10°–80°, scanning rate 2°/min.

Elemental analysis of Pd and Cu was carried out with inductively coupled plasma-atomic emission spectrometry (ICP-AES) instruments (Varian 710ES, Varian Co. Palo Alto, US).

X-ray photoelectron spectroscopy (XPS) spectra were acquired with an AXIS Ultra DLD spectrometer using Mg-K_α (hν = 1253.6 eV) radiation. Charged samples were avoided by setting the binding energy of adventitious carbon (C 1s) to 284.8 eV.

N₂ adsorption-desorption isotherms were measured using an ASAP 2010 apparatus at 77 K, where the samples were degassed at 200 °C before each measurement.

Temperature-programmed reduction (H₂-TPR) of an unreduced catalyst was carried out in equipment made by Penxiang Co. (Tianjing, China). A sample of 100 mg was used and the experiments were performed by heating the sample under 5% H₂/N₂ flow rate (45 ml/min) from ambient temperature to 450°C at a rate of 10°C/min. A TCD detector recorder the H₂ consumption with CuO used as the reference for calculation.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO adsorbed onto the catalyst was measured on a Nicolet Nexus 670 spectrometer. The DRIFTS spectra were obtained at 25°C. (1) The mixture gases of 0.15% CO + Ar flowed through the sample cell and the spectra recorded every 2–5 min; (2) O₂ (5% and 20%) was added to the mixture gas (1) above, and the spectra recorded every 2–5 min; (3) ~0.6% H₂O was added to the mixture gases (2) above, and the spectra recorded every 2–5 min.

3. Results and discussion

3.1. Testing of the catalyst

A 0.15% CO was completely oxidized at –10 °C using fresh catalyst (1.5 wt% Pd-3.3 wt% Cu/Al₂O₃-F) when the content of H₂O in the feed gas was 0.1% H₂O and the WHSV was 15000 ml/(g·h). The stability of the catalyst was investigated at 25 °C, 100% relative humidity and WHSV 15000 ml/(g·h), with the results shown in Fig. 1. The CO oxidation rate gradually decreased with increased reaction time, decreasing from 93% to 10% in 25 h. The activity of deactivated catalyst could be recovered after their regeneration in dry air and the stability of the regenerated and fresh catalysts were similar as a function of reaction time. Although the initial CO conversion on the regenerated catalyst did not noticeably decrease after several deactivation-regeneration cycles, the deactivation rate of catalyst was found to accelerate.

3.2. Water adsorption rate on catalysts with different composition

The water adsorption rates of catalysts with different compositions are shown in Fig. 2. For the pure Al₂O₃ support, the

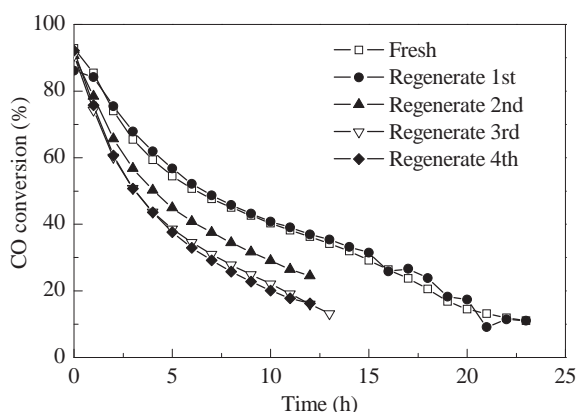


Fig. 1. Stability of 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalyst. Reaction conditions: 25 °C, 0.15% CO, ~3.1% H₂O, WHSV 15000 ml/(g·h).

water adsorption rate reached 9% in the first 2 h. With increasing adsorption time, water adsorption also increased slowly. Saturated water adsorption (10%) was obtained after 10 h. The saturated water adsorption was 13% on PdCl₂/Al₂O₃ and 20% on 3.3 wt% Cu/Al₂O₃, which was induced by the high solubility and easy melting of CuCl₂. The saturated water adsorption of 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ was between that of Pd/Al₂O₃ and Cu/Al₂O₃, which suggested that the deposition of Pd species inhibited Cu species in adsorbing water.

3.3. XRD characterization

The XRD patterns of fresh and spent 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalysts are shown in Fig. 3. For fresh catalysts, only the characteristic peaks of the γ -Al₂O₃ phase could be observed, and no Pd or Cu species were detected. It was indicated that the Pd and Cu species were highly dispersed on the alumina surface. Some Pd loading may be below the detection limit of the XRD equipment. On spent catalysts, Cu₂(OH)₃Cl and CuCl could be clearly detected, indicating highly dispersed Cu species are aggregated on the support surface. The presence of CuCl may be caused by the reduction of CO.

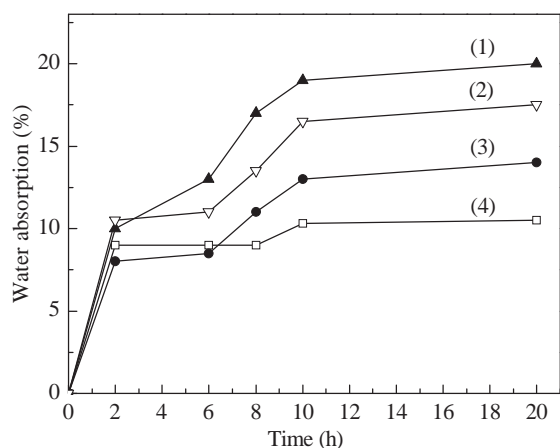


Fig. 2. Water adsorption rate of the catalysts with different composition: (1) 3.3 wt% Cu/Al₂O₃, (2) 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃, (3) 1.5 wt% Pd/Al₂O₃, (4) Al₂O₃.

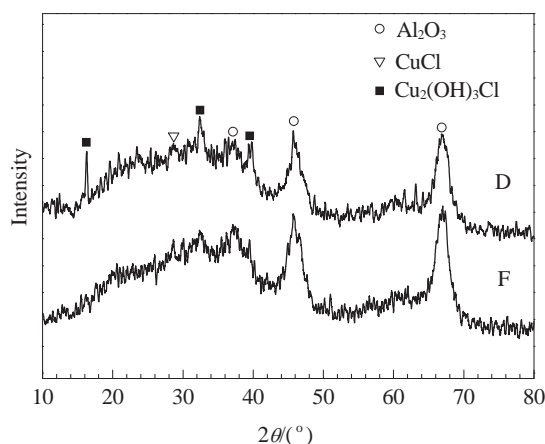


Fig. 3. XRD patterns of fresh (F) and deactivated (D) 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalysts.

3.4. BET surface area and composition of catalyst

The surface area of the catalysts were measured by N₂ adsorption-desorption, and are listed in Table 1. The surface area of the fresh catalyst (173 m²/g) was smaller than that of the support (200 m²/g), which is likely to be attributed to the active species blocking some pores of the catalyst. The surface area of the spent catalyst (197 m²/g) was larger than the that of the fresh catalyst. From the results in Figs. 2 and 3, it can be noted that the adsorption and condensation of water on the catalyst surface may induce the dissolution and aggregation of Cu species. Simultaneously, partial Cu species transferred from the surface opens the internal pores blocked by the active species, which increases the surface area of the spent catalyst. The loadings of Pd and Cu species onto the fresh and spent catalysts are kept the same, as shown in Table 1. This indicates that the active components were not lost during the reaction.

The XPS spectra of Pd and Cu on the fresh and spent 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalyst are shown in Fig. 4, and the surface composition and the chemical state are listed on Table 1. For the fresh catalyst, Pd exists in the form of Pd²⁺ and Cu exists in the forms of Cu⁺ and Cu²⁺. The molar ratio of Cu/Pd on the surface (3.35) was close to the catalyst composition (3.68), which suggests that there is a uniform distribution of Pd and Cu species on the fresh catalyst surface.

There were obvious differences in the chemical state of Pd and Cu between the fresh and spent catalysts. As well as Pd²⁺, Pd⁺ and Pd⁰ were also detected on the spent catalyst surface. This was because of the partial reduction of the catalyst by CO in the feed gas. Simultaneously, the surface concentration of Pd increased from 0.23% to 0.72%, while the concentration of Cu decreased from 0.77% to 0.59%. With the BET results, it can be suggested that some Cu species dissolved in the condensed water on the surface and migrated into the pores. This would expose the previously covered Pd species. The aggregation and migration of Cu species can break the close-knit structure of the Pd-Cu species and decrease their interactions. This can hinder the oxidation of Pd by Cu²⁺, which then blocks the recycling of CO oxidation [11]. There was no noticeable difference in the

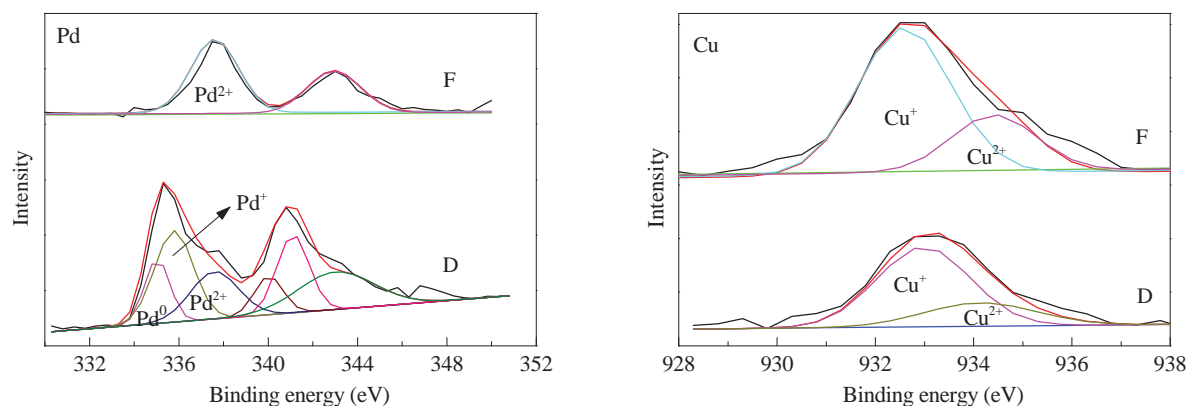


Fig. 4. Pd 3d and Cu 2p XPS spectra of fresh catalyst (F) and deactivated 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalyst inactive (D).

Table 1

Specific surface area and composition of fresh (F) and deactivated (D) 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalysts.

Sample	A_{BET} (m ² /g)	Pd ^a (wt%)	Cu ^a (wt%)	Pd ²⁺ ^b (at%)	Pd ⁺ ^b (at%)	Pd ⁰ ^b (at%)	Cu ²⁺ ^b (at%)	Cu ⁺ ^b (at%)	Cu ²⁺ /Cu ⁺ ^b	Cu/Pd ^b (mol/mol)	Cl ^b (at%)
F	173	1.5	3.3	0.23	—	—	0.2	0.57	0.35	3.35	2.08
D	197	1.4	3.2	0.22	0.35	0.15	0.15	0.44	0.34	0.82	2.09

^a Obtained by ICP-AES analysis. ^b Obtained by XPS analysis.

amount of Cl⁻ for the fresh and spent catalysts, which suggests that loss of Cl⁻ was not the main reason for deactivation.

3.5. H₂-TPR

To further investigate the interactions between the Pd and Cu species, the effects of Cu content on the redox properties of the catalysts were studied under the same conditions as those used for fixed Pd loading, with the results shown in Fig. 5 and

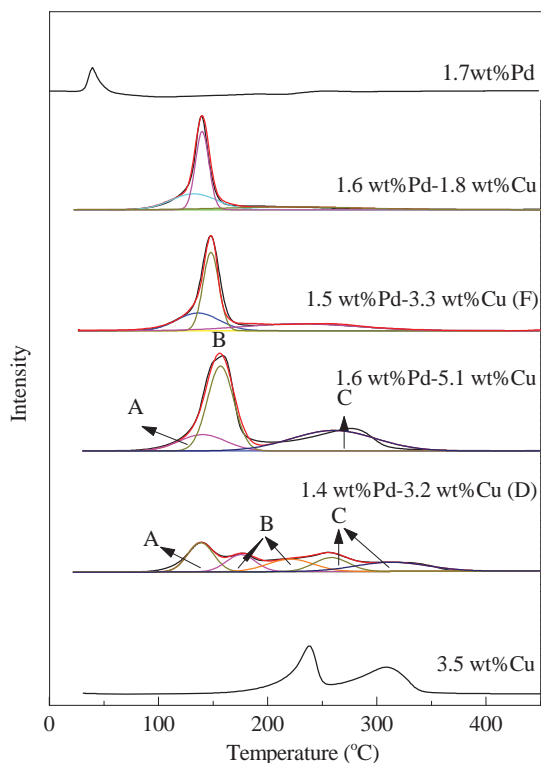


Fig. 5. TPR profiles of Pd-Cu/Al₂O₃ with different compositions.

Table 2.

The TPR of Pd/Al₂O₃ reveals a peak around 39 °C. Two reduction peaks (237 and 308 °C) found for CuCl₂/Al₂O₃ can be ascribed to the reduction of Cu²⁺ to Cu⁺ and Cu⁺ to Cu. The TPR of the Pd-Cu/Al₂O₃ samples exhibited two peaks in the range of 100–200 °C and 200–350 °C. The lower temperature peak can be attributed to the reduction of the Pd species (peak A) and the strong interaction of the Cu and Pd species (peak B), while the higher temperature peak (Peak C) indicates the reduction of the isolated Cu species [9]. It was indicated that introducing the Cu species decreased the reduction of the Pd species and enhanced the reduction of Cu species. With increased Cu loading, the reduction peaks of the catalysts were shifted to a higher temperature.

It was indicated that for all the catalysts, the H₂ consumption of the Pd species were kept constant with the same Pd loading. The calculated H₂ consumption of the catalysts with different composition showed that the amount of Cu species is strongly related to that of the Pd species. With increased Cu amount, the Pd species was also increased (Peak B). Combined with the CO oxidation activities of the catalysts, it was suggested that the rate of activity increases with an increased amount of Cu species, which corresponds to Peak B.

Compared with the H₂-TPR profile of the fresh catalyst, the

Table 2

H₂ consumption amount in TPR and catalytic activity for Pd-Cu/Al₂O₃ with different compositions.

Sample	H ₂ uptake (μmol/g)			CO conversion ^a (%)	
	A	B	C		
1.6%Pd-1.8%Cu	122	177	61	1.45	80.7
1.5%Pd-3.3%Cu (F)	127	211	132	1.66	82.5
1.6%Pd-5.1%Cu	128	378	292	2.95	83.3
1.4%Pd-3.2%Cu (D)	127	180	191	1.42	—

^a CO reaction conditions: 0.15% CO, 0.6% H₂O, WHSV 15000 ml/(g·h), temperature 0 °C.

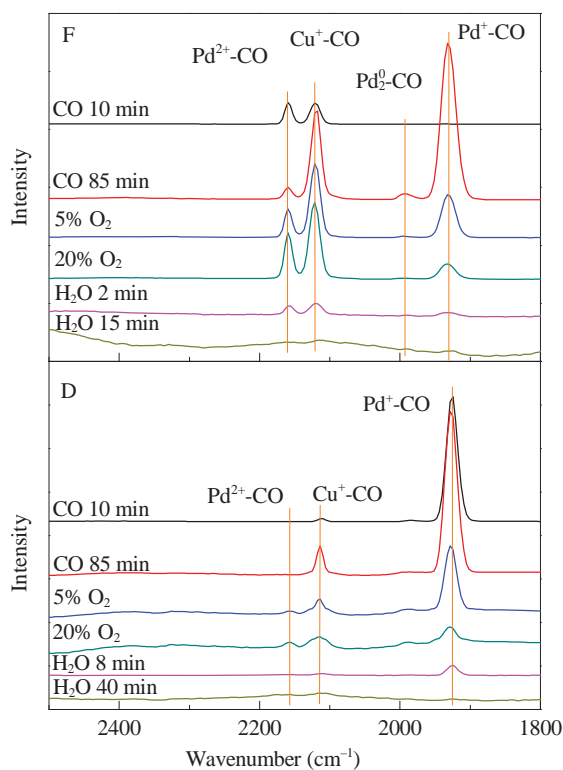


Fig. 6. In situ DRIFTS spectra of fresh (F) and inactive (D) 1.5 wt% Pd-3.3 wt% Cu/Al₂O₃ catalysts.

spent catalyst showed more complex reduction behaviors because of a significant difference in the chemical states of Pd and Cu species. The aggregation and transformation of Cu species in the presence of H₂O decreased the interactions between the Pd and Cu species, and inhibited CO oxidation.

3.6. In situ DRIFTS

To further investigate the deactivation mechanism of the catalysts, in situ DRIFTS technology was employed to study the properties of CO adsorption and oxidation on fresh and spent catalysts, with the results shown in Fig. 6.

Figure 6(F) shows that the CO adsorption peaks of Pd²⁺-CO (2160 cm⁻¹) [18] and Cu⁺-CO (2120 cm⁻¹) were observed on the fresh catalyst in the presence of 0.15% CO/Ar. With increased contact time, the Pd²⁺-CO peak decreased, but new peaks of Pd₂⁰-CO (1993 cm⁻¹) and Pd⁺-CO (1933 cm⁻¹) [19] were detected. The peak intensity of Cu⁺-CO also significantly increased. This could be ascribed to the partial reduction of the Pd and Cu species by CO in the reaction gas. The adsorption of Cu²⁺-CO could not be observed as the adsorption of CO on Cu²⁺ was unstable [20].

After 5% O₂ was introduced into the feed gas, the adsorp-

tion peaks of Cu⁺-CO, Pd₂⁰-CO and Pd⁺-CO decreased noticeably, particularly for the Pd₂⁰-CO and Pd⁺-CO peaks. However, the Pd²⁺-CO peak increased. With O₂ concentration increasing to 20%, the peaks of Pd₂⁰-CO and Pd⁺-CO further decreased, but the Pd²⁺-CO peak continued to increase while the Cu⁺-CO peak was almost the same. It was indicated that the presence of O₂ in the feed gas promoted the oxidation of Cu⁺ to Cu²⁺, which further accelerated the oxidation of the Pd species with low valences, namely Cu²⁺ + Pd⁺/Pd⁰ → Cu⁺ + Pd²⁺.

When ~0.6% water was introduced into the mixture gases, all the CO adsorption peaks decreased rapidly. Only weak Pd²⁺-CO peak and broad peaks of Cu⁺-CO and Pd⁺-CO were observable after 15 min.

Figure 6(D) showed that only the Cu⁺-CO and Pd⁺-CO peaks were observed for the spent catalyst in the presence of 0.15% CO/Ar, and peaks intensified with contact time. XPS results showed the presence of 0.22% Pd²⁺ on the surface of the catalyst, but no Pd²⁺-CO peak was detected; this may be induced by the reduction of Pd²⁺ by CO. The aggregation of the Cu species weakens the interactions between the Pd and Cu species, which blocks the re-oxidation of Pd species by Cu species and leads to the disappearance of the Pd²⁺-CO peak.

After 5% O₂ was added in the gas mixture, the peaks of Cu⁺-CO and Pd⁺-CO decreased noticeably. However, Pd²⁺-CO peak could still be observed. When the CO concentration increased to 20%, the Pd²⁺-CO peak was strengthened, while the peaks of Cu⁺-CO and Pd⁺-CO gradually decreased, Pd⁺-CO in particular. Similar trends were noted for the fresh catalyst where the presence of water promoted the oxidation of Cu⁺. With the XRD and XPS results, it was suggested that the presence of water leads to the aggregation and migration of Cu species, which decreases the surface concentration of Cu²⁺ and weakens the interactions between Pd and Cu species. This reduces the re-oxidation ability of the Pd species, blocking the redox cycle and accelerating the deactivation of the catalyst.

4. Conclusions

This paper studied the stability of PdCl₂-CuCl₂/Al₂O₃ for CO oxidation under high relative humidity. The structure and surface properties of fresh and spent catalysts were characterized to determine their deactivation mechanism. At high relative humidity (100%), the water in the feed gases could be adsorbed and condensed on the catalyst surface, which promoted the aggregation and migration of the Cu species. A suggested migration model is shown in Fig. 7. The transfer of the Cu species into the internal pores decreased the surface Cu/Pd ratio on the catalysts and weakened the interaction between Pd and Cu species. This reduces the redox properties of the catalyst. It can be concluded that the existence of Pd species with lower chemical valence on the catalyst surface and decreasing of the

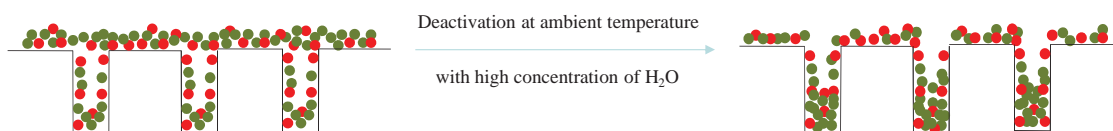


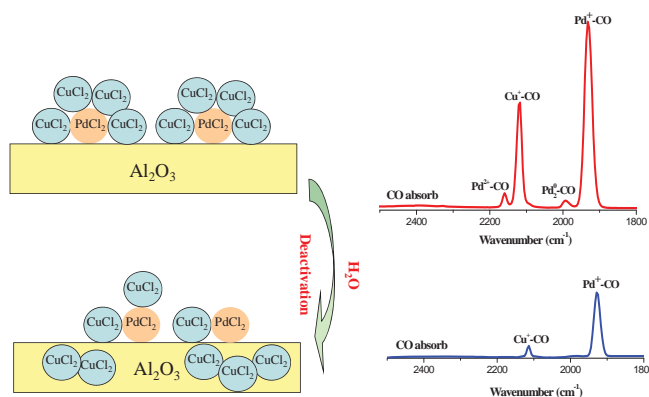
Fig. 7. Deactivation mechanism model diagram.

Graphical Abstract

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Deactivation mechanism of PdCl₂-CuCl₂/Al₂O₃ catalyst for CO oxidation at low temperatures

FENG Yafen, WANG Li, ZHANG Yanhui, GUO Yun*, GUO Yanglong, LU Guanzhong
East China University of Science and Technology



The transfer of Cu species to the internal pores of the support in the presence of water weakens the Pd and Cu species interactions, which causes catalyst deactivation.

Pd to Pd²⁺ re-oxidation rate inhibit the redox cycle and decrease the CO oxidation activity. This leads to the deactivation of the catalyst.

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PdCl₂-CuCl₂/Al₂O₃催化剂低温催化CO氧化的失活机理

封雅芬, 王 丽, 张艳慧, 郭 耘*, 郭杨龙, 卢冠忠

华东理工大学工业催化研究所, 上海200237

摘要: 采用X射线衍射、N₂吸-脱附、X射线光电子能谱分析、氢气-程序升温还原和原位红外漫反射等方法对新鲜和失活的PdCl₂-CuCl₂/Al₂O₃低温催化CO氧化催化剂进行表征, 研究了高相对湿度(100%)下催化剂的失活机理. 结果表明, 催化剂表面沉积的水使得活性铜物种容易从催化剂表面向载体孔道内部迁移, 由于Pd、Cu相互作用弱化从而减弱了Pd与Cu物种间的相互作用, 使得催化剂的氧化还原性能受到影响, 抑制了Pd⁰再氧化为Pd²⁺的过程, 从而因CO氧化反应中催化剂氧化还原循环受阻而导致失活.

关键词: 低温一氧化碳氧化; 氯化钯; 氯化铜; 三氧化二铝; 失活

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*通讯联系人. 电话: (021)64253703; 电子邮箱: yunguo@ecust.edu.cn

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1. 前言

工业生产、机动车尾气排放以及化石燃料的不完全燃烧都会产生有毒气体CO, 催化氧化是一种有效的脱除CO方法. 低温CO催化氧化在传感器、空气净化器、防毒面罩以及潜水艇、航天器等密闭系统方面都有着较高的实用价值和广阔的应用前景, 受到研究者的广泛关注^[1].

用于CO氧化的催化剂主要有复合氧化物催化剂和贵金属催化剂等. 氧化物催化剂有Hopcalite催化剂和Co₃O₄催化剂等, 具有良好的CO催化氧化性能, 如Co₃O₄催化剂在-77 °C时即可使CO完全转化^[3], 但该类催化剂的抗水性能差, 即使微量水的存在也可导致催化剂迅速失活^[2,3]. 贵金属催化剂最具代表性的是纳米Au催化剂, 不仅具有很高的CO催化氧化活性^[4], 而且具有良好的抗水稳定性^[5], 但其制备条件敏感, 易被卤素毒化^[6], 在存放和使用过程中容易失活^[7]. 负载的钯催化剂也具有良好的低温CO氧化活性, 当Pd负载量为4%时, CO完全转化温度可达-15 °C^[8]. 另外, 钯基催化剂具有一定的抗水性和抗卤素毒化能力.

负载型Wacker催化剂(PdCl₂-CuCl₂)对CO氧化也具有很高的催化活性, 在前期工作中采用氨络合浸渍法制备了PdCl₂-CuCl₂/Al₂O₃催化剂, 在含有0.04% CO和0.1% H₂O的反应气氛下, CO完全转化温度最低可达-30 °C^[9]. 负载型Wacker催化剂上CO氧化的反应机理与均相Wacker催化剂的相似^[10]:



其中, 反应的活性中心为Pd离子, 活性Cu物种通常认为是以Cu₂Cl(OH)₃形式存在, 它的存在有利于低价态Pd的氧化, 从而保证催化循环的进行^[11]. 研究表明, 反应的控速步骤是Cu⁺被氧气氧化^[12], 也有人认为是Pd⁰被Cu²⁺氧化成活性Pd⁺物种^[13].

在实际使用时, 反应气氛中不可避免存在H₂O, 对于负载型Wacker催化剂而言, 微量水的存在可以促进反应的进行^[14], 在水汽条件下CO氧化反应速率较干燥条件下提高2~3倍^[15]. 而过量的水汽存在, 则会导致H₂O在载

体表面吸附和凝结, 覆盖活性中心, 反应气体的扩散阻力增加; 同时H₂O还可在亲水性的载体(如Al₂O₃)的孔道内发生毛细凝结, 堵塞催化剂孔道, 进而引起失活^[12]. 也有研究表明, 氯离子的流失也是导致催化剂失活的原因之一, 认为氯离子是保证催化氧化循环所必需的, 而且催化剂活性与Pd周围Cl的配位数直接相关^[16]. 我们前期工作表明, 催化剂的失活与表面Cu物种的存在状态密切相关^[17], 活性铜物种Cu₂(OH)₃Cl的聚集以及其转化成CuCl都会导致催化剂活性降低.

在前期工作基础上, 本文研究高相对湿度(100%)的反应条件下PdCl₂-CuCl₂/Al₂O₃失活前后的结构、表面状态和氧化还原性能的差别, 以探讨催化剂失活的机理.

2. 实验部分

2.1. 催化剂的制备

采用氨络合浸渍法制备了Wacker催化剂PdCl₂-CuCl₂/Al₂O₃, 其中Pd和Cu的质量百分含量分别为1.5%和3.3%, 标记为1.5% Pd-3.3% Cu/Al₂O₃. 新鲜催化剂标记为F. 将新鲜催化剂在25 °C, 相对湿度100%, 空速15000 ml/(g·h)条件下进行CO氧化实验, 当CO转化率降为10%后停止反应. 然后将催化剂在50 °C空气中干燥10 h, 继续在相同条件下进行CO氧化性能. 经过多次失活-活化的循环, 取出催化剂, 标记为D. 同方法制得吸水实验的1.5% Pd/Al₂O₃和3.3% Cu/Al₂O₃催化剂.

2.2. 催化剂吸水实验

室温下, 将50 ml/min的N₂通过水汽饱和器, 然后进入装有0.2 g样品的U形石英反应管, 每隔一段时间对反应管进行称重, 得到相应的吸水率.

2.3. 催化剂的表征

采用Brook D8型X衍射仪(XRD)对催化剂进行了分析, Cu K_α靶射线源(λ = 0.15 nm), 管流40 mA, 管压40 kV, 广角扫描范围10°~80°, 扫描速率2°/min.

采用Varian 710ES型等离子体发射光谱(ICP-AES)仪器测定催化剂上Pd和Cu含量.

采用AXIS Ultra DLD型X射线光电子能谱分析仪(XPS)对催化剂的表面元素进行了分析, 使用单色Mg K_α (hν = 1253.6 eV)为激发源, 室温下采集图谱, 使用沾污碳的C 1s = 284.8 eV为内标校正样品表面的电荷效应.

采用NOVA 4200e型N₂吸附-脱附分析仪对催化剂的比表面积进行测定。N₂吸-脱附实验在液氮温度(77 K)下进行,样品先经过200 °C的脱气预处理。

氢气-程序升温还原实验(H₂-TPR)在天津鹏翔科技有限公司催化剂表征系统实验装置进行。称取0.1 g样品于反应管内,在5% H₂/N₂ (45 ml·min⁻¹)混合气中,以10 °C/min程序升温至450 °C。TCD检测耗氢量,并以CuO为参比,定量计算催化剂在还原过程中的耗氢量。

采用原位红外漫反射光谱(DRIFTS)研究了失活前后催化剂吸附CO性能,实验在Nicoler 6700型红外光谱仪上进行,在25 °C时采集谱图。将0.15% CO/Ar混合气体通入样品池后,每隔2~5 min采集谱图一次;吸附饱和后,在上述混合气中加入O₂,并考察O₂浓度(5%和20%)对催化剂吸附CO性能的影响;最后在反应气体中引入~0.6%水蒸气,观察H₂O对催化剂吸附CO性能的影响。

3. 结果与讨论

3.1. 催化剂的催化性能

在0.15% CO, 0.1% H₂O, 空速15000 ml/(g·h)反应条件下,新鲜的1.5% Pd-3.3% Cu/Al₂O₃-F催化剂上CO完全氧化的温度为-10 °C。进一步考察了在25 °C,相对湿度100%,空速15000 ml/(g·h)条件下催化剂上CO氧化反应的稳定性,结果见图1。可以看出,随着反应时间的延长,CO转化率在25 h内从93%逐渐降到10%。对失活催化剂进行活化处理,在相同条件下再次进行稳定性测试,其稳定性曲线与新鲜催化剂的基本相同。多次失活-活化循环后发现,虽然活化后催化剂的初活性基本不变,但其失活速率加快。

3.2. 组成对催化剂吸水率的影响

不同组成催化剂吸水率的实验结果见图2。可以看出,Al₂O₃载体吸附2 h时吸水率达到9%;继续延长吸附时间,吸水率的增加幅度降低,至10 h后基本达到饱和,饱和吸水率为10%。负载PdCl₂后,催化剂的吸水能力略有提高,饱和吸水率为13%。由于CuCl₂的溶解度大,容易吸潮,因此3.3% Cu/Al₂O₃的饱和吸水率20%。而1.5% Pd-3.3% Cu/Al₂O₃的吸水能力介于Pd/Al₂O₃和Cu/Al₂O₃催化剂之间,说明Pd物种的引入在某种程度上降低了Cu物种的吸水能力。

3.3. 催化剂失活前后XRD表征

新鲜催化剂(1.5% Pd-3.3% Cu/Al₂O₃-F)和失活催化剂(1.5% Pd-3.3% Cu/Al₂O₃-D)的XRD谱见图3。可以看出,新鲜催化剂上只检测到了γ-Al₂O₃的特征衍射峰,这

可能是因为Pd和Cu物种高度分散在Al₂O₃载体表面,也可能是因为Pd含量太少低超出XRD的检测限所致。对于失活催化剂,除了γ-Al₂O₃以外,还观察到了Cu₂(OH)₃Cl和CuCl的衍射峰。这说明高度分散在载体表面的Cu物种由于受到反应气氛中水分的影响,在载体表面发生了聚集和相分离。CuCl的出现可能是由于催化剂被反应气中CO还原所致。

3.4. 催化剂的比表面积及组成分析

采用N₂吸-脱附测定了1.5% Pd-3.3% Cu/Al₂O₃催化剂的比表面积,结果列于表1。可以看出,新鲜催化剂的比表面积为173 m²/g,较载体氧化铝(200 m²/g)有所降低。这可能是因为催化剂表面被活性组分覆盖,导致部分孔道被堵塞所致。然而失活催化剂比表面积(197 m²/g)则有所增加。结合图2和图3可以认为,反应气氛中水在催化剂表面凝结和沉积后,不仅可使活性相Cu物种的粒子增大和团聚,而且可导致部分铜物种的溶解并向孔道内迁移,从而使原有被堵塞的部分孔道又重新暴露出来,进而增大了催化剂的比表面积。ICP结果表明,反应前后催化剂中Pd和Cu含量基本一致(见表1),说明反应气氛中的水分虽然导致了活性组分的迁移,但并未使其流失。

图4为失活前后1.5% Pd-3.3% Cu/Al₂O₃催化剂表面Pd和Cu的XPS谱,其表面组成列于表1。可以看出,新鲜催化剂表面Pd以Pd²⁺形式存在,Cu物种以Cu⁺和Cu²⁺形式存在;表面Cu/Pd摩尔比为3.35,与催化剂体相组成(3.68)较接近,这说明新鲜催化剂上Pd和Cu的分散均匀。

失活催化剂表面Pd物种除了Pd²⁺外,还观测到Pd⁺和Pd⁰的存在,可认为是反应过程中CO使催化剂发生部分还原所致;同时表面Pd含量显著升高,从新鲜催化剂的0.23%增至0.72%,而表面总Cu含量从0.77%降至0.59%,表面Cu/Pd比明显降低。这可能是部分Cu物种在表面沉积的水中溶解并向孔道内部迁移,导致原本被Cu物种覆盖的Pd暴露在表面。结合反应机理可以认为,由于Cu物种在催化剂表面的团聚和迁移,削弱了它与Pd物种之间的接触和相互作用,不利于低价态Pd被Cu²⁺氧化成高价态Pd,抑制了CO催化氧化循环的进行,进而导致催化剂活性降低^[11]。XPS结果表明,失活前后催化剂表面Cl⁻浓度变化不大,因此催化剂失活的主要原因不是由于Cl⁻的流失所致。

3.5. H₂-TPR结果

为进一步了解活性Pd-Cu物种间相互作用,保持Pd含量不变,考察Cu含量对于Pd-Cu/Al₂O₃催化剂其氧化还原性能的影响,结果如图5和表2所示。

由图5可知, Pd/Al₂O₃催化剂的还原峰温度为39 °C; CuCl₂/Al₂O₃催化剂在237和308 °C出现了两个还原峰, 分别对应于Cu²⁺→Cu⁺, 和Cu⁺→Cu. 对于不同组成的Pd-Cu/Al₂O₃催化剂, 分别在100~200和200~350 °C的范围内检测到了两个还原峰: 低温还原峰可归属为Pd物种(峰A)以及与Pd间存在强相互作用的Cu物种(峰B)的还原; 高温还原峰(峰C)可归属为孤立Cu物种的还原^[9]. 这说明Cu的引入增强了Pd-Cu间的相互作用, 从而降低了Pd物种的还原性能, 却提高了Cu物种的还原性能. 随着Cu含量增加, 所得样品还原峰整体向高温方向移动.

通过计算各还原峰的耗氢量及比值可以发现, 由于催化剂中Pd含量相同, 因此Pd的耗氢量基本保持不变. 随着催化剂中Cu含量的增加, 虽然与Pd之间存在强相互作用的Cu物种(峰B)的量增加, 但其所占比例(B/(B+C))逐渐减小. 结合催化活性可以看到, 随着与Pd之间存在强相互作用的Cu物种数量增加(B/A比值增加), CO转化率略有增加.

然而, 失活后催化剂出现了多个还原峰. 这主要是因为催化剂表面Pd和Cu物种的存在状态发生了变化, 同时在反应气氛中水汽的作用下, Cu物种在催化剂表面的聚集和迁移, 减弱了它与Pd物种之间的接触和相互作用, 进而影响其催化活性.

3.6. 失活前后催化剂DRIFTS表征

为了进一步探讨催化剂的失活原因, 采用原位DRIFTS谱研究了失活前后催化剂表面CO的吸附和反应性能, 结果如图6所示.

由图6可知, 通入0.15% CO/Ar气体后, 在新鲜催化剂上检测到Pd²⁺-CO(2160 cm⁻¹)^[18]和Cu⁺-CO(2120 cm⁻¹)的振动峰; 随着反应时间的延长, Pd²⁺-CO的峰强度降低, 同时检测到了明显的Pd₂⁰-CO(1993 cm⁻¹)和Pd⁺-CO(1933 cm⁻¹)^[19]的振动峰, 并且Cu⁺-CO峰的强度也显著增加. 这说明反应气氛中的CO可使催化剂表面的Cu和Pd物种部分还原. 室温下, CO在Cu²⁺上的吸附不稳定, 因此观察不到Cu²⁺-CO吸附峰^[20].

在反应气氛中引入5% O₂后, 催化剂表面Cu⁺-CO, 特别是Pd₂⁰-CO和Pd⁺-CO振动峰明显变弱; 与此同时, Pd²⁺-CO吸附峰增强. 提高O₂浓度至20%, Pd₂⁰-CO和

Pd⁺-CO振动峰的强度进一步降低, 同时Pd²⁺-CO峰的强度继续增加, 而Cu⁺-CO振动峰的变化不明显. 这说明O₂的引入有利于Cu⁺被氧化成Cu²⁺物种, 而Cu²⁺物种的增多可促进低价态Pd的氧化, 即Cu²⁺ + Pd⁰/Pd⁺ → Cu⁺ + Pd²⁺.

当在反应气氛中引入~0.6%的水蒸气后发现, 所有的CO吸附峰均迅速变弱, 15 min后反应达到稳定, 仅观察到非常微弱的Pd²⁺-CO吸附峰及Cu⁺-CO和Pd⁺-CO形成的宽峰.

对于失活催化剂, 当通入0.15% CO后, 催化剂表面仅检测到Cu⁺-CO和Pd⁺-CO的振动峰, 且随着反应时间的延长而增强. 但由XPS结果可知, 催化剂表面存在Pd²⁺的表面浓度为0.22%. 这说明反应气中CO可导致Pd²⁺的还原. 由于失活催化剂表面Cu物种的聚集及其与Pd物种之间相互作用的减弱, 使得低价态的Pd难以被Cu物种氧化, 从而在表面上未出现Pd²⁺-CO振动峰.

引入5% O₂后, 失活催化剂上Cu⁺-CO和Pd⁺-CO吸附峰的强度显著降低, 同时检测到少量的Pd²⁺-CO. 继续增加O₂浓度至20%, Pd²⁺-CO吸收峰增强, 而Cu⁺-CO, 特别是Pd⁺-CO的强度进一步降低. 与新鲜催化剂相似, 水的引入会进一步加速Cu⁺的氧化, 同时所有的CO吸附峰均迅速变弱. 结合XRD和XPS的结果可以认为, 反应气氛中H₂O的存在导致了催化剂表面Cu物种的聚集和迁移, 表面Cu²⁺的含量降低; 同时减弱了Pd与Cu之间的相互作用, 使得催化剂表面低价态Pd物种再氧化的能力减弱, 阻碍了氧化还原循环的进行, 从而导致催化剂失活.

4. 结论

研究了在高相对湿度的条件下, PdCl₂-CuCl₂/Al₂O₃催化剂上CO氧化的稳定性, 通过对比失活前后催化剂的结构和表面性质, 结果表明高相对湿度(100%)条件下, 反应气氛中水可在催化剂表面吸附并凝结, 促进了活性Cu物种的聚集和向载体孔道内的迁移(其迁移模型见图7), 使得催化剂表面Cu/Pd比例降低, 并减弱了催化剂表面活性物种Pd与Cu间相互作用, 降低了催化剂的氧化还原性能, 从而导致活性物种Pd以较低价态存在于催化剂表面, 且使其再氧化成Pd²⁺的反应速率下降, 致使氧化还原循环受阻, 因而其氧化活性降低.