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Article

Stability of Pd-Cu-Cl_x/Al₂O₃ catalyst for CO oxidation

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ARTICLE INFO

Article history:

Received 20 March 2018

Accepted 28 April 2018

Published 5 September 2018

Keywords:

CO oxidation

Stability

Moisture

Hydrophobicity

Supported Wacker catalyst

ABSTRACT

By taking advantage of silylanization, Al₂O₃ support was modified by organosilane and supported Pd-Cu-Cl_x/Al₂O₃ catalysts were prepared. The effects of hydrophobicity on catalyst stability during CO oxidation were investigated. The physicochemical properties and redox potential of the catalyst were characterized by N₂ adsorption-desorption, XRD, H₂-TPR, and XPS. In order to understand the relationship between the oxidation stability of CO and the presence of water, the CO oxidation mechanism was studied by in situ DRIFT. Support pretreatment markedly promoted catalyst stability during CO oxidation; CO conversion was 78% after 150 h at saturated humidity and freezing point. Modification led to an obvious decrease in chloride ion concentration and enhancement in hydrophobicity. The role of water in CO oxidation was complicated. The presence of water favored CO oxidation over active Pd⁺ species and Pd⁰ reoxidation by Cu²⁺ species. Meanwhile, water also inhibited the formation of the active Pd⁺ species and helped to produce carbonate species. Compared with the form of the carbonate species, the inhibition of water to produce active Pd⁺ species played the main detrimental role in catalyst stability.

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1. Introduction

Catalytic oxidation of carbon monoxide (CO) has been widely applied in air purification, automotive exhaust emission control, and CO gas sensors [1]. Environmental concerns need to be considered in the design of a catalyst for CO oxidation, such as high temperature (200–600 °C) for industrial and vehicle exhaust emission control and ambient temperature and high humidity for air purification of semi-enclosed space (underground tunnel or parking lot). Slow speed and frequency/cold start of vehicle results in the accumulation of CO that is usually beyond the normal emission level. It is a challenge to design a CO oxidation catalyst with high activity and stability at

ambient temperature and high humidity.

Metal oxides, Co₃O₄ or Hopcalite catalyst with outstanding CO activity, are sensitive to moisture and quickly deactivated in the presence of trace water [2–4]. The weak stability of Hopcalite catalyst against vapor is caused by the strong adsorption of water on the catalyst surface relative to oxygen and CO adsorption [5,6]. The deactivation of Co₃O₄ is ascribed to the hydrogenation of lattice oxygen and the formation of stable bicarbonates [7]. On the contrary, water facilitates CO oxidation on supported Pt/Pd catalysts [8–12], because OH is more active than lattice oxygen in reacting with CO to yield COOH on account of a smaller energy barrier [7].

Supported Wacker catalyst revealed excellent performance

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This work was supported by the National Key Research and Development Program of China (2016YFC0204300), National Natural Science Foundation of China (21207037, 21333003, 21571061), the "Shu Guang" Project of the Shanghai Municipal Education Commission (12SG29), and the Commission of Science and Technology of Shanghai Municipality (15DZ1205305).

DOI: 10.1016/S1872-2067(18)63112-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 9, September 2018

in CO oxidation, especially in the presence of water, and the CO oxidation rate increased 2–3 times compared to that of the case without water [13]. CO could be completely oxidized even at a temperature as low as $-40\text{ }^{\circ}\text{C}$ over the supported Wacker catalyst prepared by using the NH_3 -coordination-impregnation method [14]; however, unfortunately, a continuous loss in activity was still observed at $0\text{ }^{\circ}\text{C}$, 0.6% H_2O after 5 h [15]. A further study confirmed that the low temperature and high humidity rendered the whole reaction system unstable [16]. The presence of water facilitates Cu transfer from the surface to the pores, which impaired the contact between the Pd and Cu species [17] and inhibited the re-oxidization of Pd^0 species [18].

To suppress the performance deterioration of catalysts by water, many methods have been proposed and attempted. One such technique involves the use of an hydrophobic coating for the catalysts for stable operation. Amorphous carbon-coated Mn/Cu-based Hopcalite nanoparticle catalysts showed a certain level of water vapor resistance for CO oxidation [5]. A proper coating of gas-permeable vapor-resistant polymers with a layer of nanofilm for the vapor-sensitive Co-Fe-based nanoparticle catalyst played a major role in its high stability observed during CO oxidation [19].

Another approach is to take advantage of organosilane to form oxane bonds of Si–O–metal and alkyl chain attached onto the surface of metal oxide. Polydimethylsiloxane (PDMS)-coated nanostructured manganese oxide materials exhibited a high selective adsorption of organic molecules in the presence of water [20]. Besides preventing the excess water from adsorbing on the surface of the catalyst [21], the pretreatment of Al_2O_3 support enhanced the metal-support interactions and benefited support reduction, which led to exceptional activity and stability for CH_4 combustion [22].

The above results triggered our interest in the study of how to enhance the stability of supported Wacker catalyst, therefore, a silane coupling agent (diethoxy dimethyl silane) was used to modify the support, and the stability of CO oxidation on Pd-Cu- $\text{Cl}_x/\text{Al}_2\text{O}_3$ catalysts was investigated for 0.6% H_2O at $0\text{ }^{\circ}\text{C}$.

2. Experimental

2.1. Catalyst preparation and testing

After dissolving diethoxy dimethyl silane in 40 mL ethanol, Al_2O_3 was added and refluxed at $80\text{ }^{\circ}\text{C}$ under stirring for 3 h; it was then washed with ethanol and dried at $120\text{ }^{\circ}\text{C}$ for 2 h to obtain modified Al_2O_3 , which was labeled as $\text{Al}_2\text{O}_3\text{-M}$ (M = modified). Supported Wacker catalysts (Pd-Cu- $\text{Cl}_x/\text{Al}_2\text{O}_3$) were prepared by the NH_3 coordination-impregnation method using $\text{PdCl}_2\cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ as precursors [14]. Cu was introduced first and calcined at $350\text{ }^{\circ}\text{C}$ for 4 h before the impregnation of $\text{PdCl}_2\cdot 2\text{H}_2\text{O}$. The catalysts prepared from pristine Al_2O_3 and $\text{Al}_2\text{O}_3\text{-M}$ were respectively denoted as R and M.

2.2. Catalyst characterization

The surface areas of the samples were measured by N_2 adsorption-desorption at a low temperature ($-196\text{ }^{\circ}\text{C}$) on a NOVA

4200e surface area and porosity analyzer. The catalysts were degassed at $200\text{ }^{\circ}\text{C}$ before the measurement.

The powder X-ray diffraction (XRD) patterns of the samples were obtained on a Brook D8 focus diffraction spectrometer with Cu- K_α radiation (40 kV, 40 mA, $\lambda = 0.15406\text{ nm}$) at the scanning rate of $6^\circ/\text{min}$. The average crystallite sizes of the catalysts were estimated using the Scherrer equation.

The contents of Pd and Cu were measured by an inductively coupled plasma-atomic emission spectrometry (ICP-AES) instrument (Varian 710-ES). The results showed that the pristine catalyst (R) consisted of 1.5 wt% Pd and 4.3 wt% Cu and the modified catalyst (M) contained 1.5 wt% Pd and 4.5 wt% Cu. ICP-AES analysis showed similar loadings of Pd and Cu on the catalysts.

H_2 -temperature programmed reduction (H_2 -TPR) was effected using a suitable equipment (Penxiang Co., Tianjin, China). The sample was heated in a flow of 5% H_2 -95% N_2 from ambient temperature to $800\text{ }^{\circ}\text{C}$ at the rate of $10\text{ }^{\circ}\text{C}/\text{min}$. The amount of H_2 consumed was measured by a thermal conductivity detector (TCD) using H_2 consumption with CuO as the reference for quantitative analysis.

X-ray photoelectron spectroscopy (XPS) was performed at $25\text{ }^{\circ}\text{C}$ with an AXIS Ultra DLD spectrometer using Mg K_α ($h\nu = 1253.6\text{ eV}$) radiation. Charged samples were avoided by setting the binding energy of adventitious carbon (C 1s) to 284.8 eV.

The in situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) of the CO adsorbed onto the catalyst were recorded on a Nicolet Nexus 670 spectrometer at $25\text{ }^{\circ}\text{C}$ every 2 min. The process followed this sequence: (1) mixture gas (0.15% CO/N_2) flowed into the reactor at the rate of 50 mL/min, (2) the gas passed through a water vapor saturator to the reactor, and (3) O_2 was added to the mixture gas.

2.3. Test of catalytic stability

The stability test for CO oxidation was performed in a quartz tubular U-tube fixed-bed reactor at $0\text{ }^{\circ}\text{C}$, and a 0.2 g sample (20–40 mesh) was used in each test. The mixture 0.15% CO -20% O_2 /balanced N_2 at the weight hour space velocity (WHSV) of 15000 mL/(g·h) was directed through a water vapor saturator immersed in a $0\text{ }^{\circ}\text{C}$ water bath into the reactor. The water concentration in the feed gas was about 0.6%. The CO concentration was analyzed by an on-line gas chromatograph equipped with a FID detector and a methanator.

The water adsorption experiment was conducted at $10\text{ }^{\circ}\text{C}$; 0.2 g of the catalyst was used. N_2 was directed at the rate of 50 mL/min through a water vapor saturator at $0\text{ }^{\circ}\text{C}$, and the mass of the catalyst was measured at different time to obtain the amount of water adsorbed.

3. Results and discussion

3.1. Test of the stability of catalysts

The stability of the pristine and modified catalysts are shown in Fig. 1. CO conversion on the pristine catalyst was equal to that of the modified catalyst after the first 1 h, which

Fig. 1. Stability of pristine (R) and modified (M) catalysts during CO oxidation.

indicated that support silylation did not have an effect on catalyst activity. Although a slightly increased CO conversion was observed for the modified catalyst, the CO conversions finally became similar after 4 h. With a further increase in time, an obvious difference is observed in Fig. 1. The CO conversion of the pristine catalyst displayed a decreasing trend, and the value of the conversion sharply dropped from 86% to 52% even after 23 h. On the contrary, the conversion was rather stable after 150 h in the case of the modified catalyst. These experiments illustrated that support silylation was an efficient way to improve catalyst stability in the presence of water at a low temperature (0 °C).

3.2. Water adsorption test

Water adsorption experiments were conducted at 100% relative humidity and 0 °C, and the results are shown in Fig. 2. During the initial time, the water adsorption amount on the modified catalyst was higher than that on the pristine catalyst, but with further exposure to water, the water adsorption rate on the pristine catalyst was four times that on the modified catalyst after the first 5 h. When water adsorption reached the saturation level, the saturated water adsorption amount on the

Fig. 2. Water adsorption rate of pristine (R) and modified (M) catalysts.

modified catalyst was only one-third that on the pristine catalyst. The water adsorption rate and saturation amount significantly decreased after support silylation, which confirmed that support silylation made the surface hydrophilic.

3.3. Physical and chemical properties of catalysts

The surface areas of the samples are provided in Table 1. The surface areas of both pristine and modified catalysts have similar values, suggesting that support pretreatment had no effect on the surface area.

The XRD patterns of the pristine/modified catalysts and support are shown in Fig. 3. No characteristic Pd diffraction peaks were observed, indicating that either the Pd species was highly dispersed on the support surface or Pd loading was below the detection limit of the XRD equipment.

The XRD patterns of the pristine and modified supports reveal that silylation has no effect on the phase structure. The characteristic diffraction peaks at 16.3°, 32.7°, and 40.2° were attributed to the $\text{Cu}_2(\text{OH})_3\text{Cl}$ species. The crystallite sizes are 26 and 40 nm for the pristine and modified catalysts, according to the Scherrer equation, based on the (101) peak of $\text{Cu}_2(\text{OH})_3\text{Cl}$. Compared with the pristine catalyst, support silylation increased the crystallite sizes of $\text{Cu}_2(\text{OH})_3\text{Cl}$ in the case of the modified catalyst.

3.4. H_2 -TPR

The H_2 -TPR profiles and H_2 consumption of catalysts are shown in Fig. 4, and Table 2, respectively. $\text{Pd}/\text{Al}_2\text{O}_3$ had an obvious H_2 reduction peak at 38 °C, while $\text{Cu}/\text{Al}_2\text{O}_3$ revealed two

Table 1
Physicochemical properties of catalysts.

Sample	Surface area (m^2/g)	d^a (nm)	$\text{Pd}^{2+}/\text{Pd}^+^b$ (at%)	$\text{Cu}^{2+}/\text{Cu}^+^b$ (at%)	Cl^b (at%)	$(\text{Cu}/\text{Pd})^b$
R	132	26	0.24/0.08	0.73/0.58	4.30	4.10
M	131	40	0.22/0.05	0.94/0.57	2.80	5.60

^a Crystallite size of $\text{Cu}_2(\text{OH})_3\text{Cl}$ as obtained from XRD (Fig. 3)

^b Obtained from XPS.

Fig. 3. XRD patterns of pristine (R) and modified (M) catalysts.

Fig. 4. H₂-TPR profiles of pristine (R), modified (M), and single metal catalysts.

Table 2

Reduction temperature and H₂ consumption of catalysts.

Sample	H ₂ consumption (mmol/g)/Reduction temperature (°C)			B/(B+C)
	Peak A	Peak B	Peak C	
R	0.196/148	0.215/172	0.269/275	0.44
M	0.190/143	0.302/174	0.260/272	0.54

such peaks at 239 and 311 °C. With the introduction of Cu to Pd/Al₂O₃, two distinct reduction peaks at 100–250 °C and 250–400 °C were observed. Compared with the single metal catalysts, it was known that the presence of Pd promoted the reduction of Cu species. The intense reduction peak with a

shoulder in the temperature range 100–250 °C can be de-convoluted into two reduction peaks: one (peak A) was ascribed to the reduction of Pd species and the other (peak B) to the reduction of copper species, which was in close contact with the Pd species. The high-temperature reduction peak (peak C) at 250–400 °C was attributed to the reduction of isolated copper species [23,24].

Owing to the same Pd loading amounts, the H₂ consumption during low-temperature reduction was dominated by the amount of Cu species in close contact with the Pd species. The lower reduction temperature and higher H₂ consumption values demonstrated the higher reducibility of the catalyst.

Although the reduction temperature of peak B slightly shifted to a higher value, its H₂ consumption value increased from 0.215 mmol/g (pristine catalyst) to 0.302 mmol/g (modified catalyst). Support pretreatment decreased the amount of isolated Cu species, and the reduction temperature was shifted to a low value. The H₂ consumption ratio of peak B/(B+C) increased from 0.44 to 0.54, indicating that most Cu species were in close contact with Pd species after support pretreatment.

3.5. XPS

The XPS patterns of Pd 3d, Cu 2p, and Auger Cu LMM spectra for the reference and modified catalysts are shown in Fig. 5, and the surface compositions and chemical states listed in Table 1.

The Pd 3d spectrum exhibited Pd²⁺ and Pd⁰ peaks at 337.5 and 335.7 eV, respectively, while the Cu 2p spectrum shows two peaks at 934.4 and 932.4 eV, respectively. It is easy to infer that the peak at 934.4 eV is attributable to Cu²⁺, however, it is difficult to distinguish the Cu⁰ and Cu⁺ species due to their similar binding energies in the Cu 2p XPS pattern. Auger electron spectroscopy of the Cu species was performed, and the results

Fig. 5. Pd 3d, Cu 2p, and Cu LMM spectra of pristine (R) and modified (M) catalysts.

are shown in Fig. 5. The binding energies of Cu^+ and Cu^0 are 570 and 568 eV, respectively, in Auger Cu LMM spectroscopy [25]. Only one peak at 570 eV was detected in all the samples, so the presence of the metal Cu species on the catalyst surface was excluded. The Cu species existed in the form of Cu^{2+} and Cu^+ .

As shown in Table 1, the effects of support modification on Cu ion distribution are more obvious than those on Pd ion distribution. The ratio Cu/Pd even increased after support modification. A higher ratio of Cu/Pd indicated closer contact between the Pd and Cu species. This closer contact facilitated the reduction of the Cu species, as confirmed by H_2 -TPR. It is worth mentioning that the surface concentration of Cl decreased from 4.3% to 2.8% after support pretreatment, indicating less residual Cl on the modified catalyst.

3.6. DRIFTS

In order to further investigate the effect of support pretreatment on CO oxidation stability, CO adsorption and oxidation were further investigated by DRIFT. In situ DRIFT spectra, the bands at 2300–2400 cm^{-1} are ascribed to gaseous CO_2 [26–28], while the bands in the regions 1600–1700 and 1500–1300 cm^{-1} are assigned to the OH groups and carbonates, respectively [29,30]. The bands at 2126 and 2162 cm^{-1} correspond to the adsorbed CO in the Cu^+ complex ($\text{Cu}^+\text{-CO}$) and the terminal CO groups in the Pd^{2+} complex ($\text{Pd}^{2+}\text{-CO}$). The bands at 1991, 1934, and 1810 cm^{-1} originate from the bridge-bonded CO on the Pd metal surface ($\text{Pd}_2\text{-CO}$), bridged carbonyl ligands in the Pd^+ complexes ($\text{Pd}^+\text{-CO}$), and triply bonded CO on metallic Pd ($\text{Pd}_3\text{-CO}$) [31–33].

In situ DRIFT spectra of CO adsorbed over catalysts in CO/Ar as functions of time are illustrated in Fig. 6. Weak bands for $\text{Pd}^{2+}\text{-CO}$ (2158 cm^{-1}) and $\text{Cu}^+\text{-CO}$ (2126 cm^{-1}) appeared first after 4 min exposure to CO on the pristine catalyst. The appearance of $\text{Pd}_2\text{-CO}$ (1991 cm^{-1}), lagging behind $\text{Pd}^+\text{-CO}$ (1934 cm^{-1}), indicated that the Pd metal originated from the reduction of the Pd^+ species by CO. Meanwhile, the carbonate species (1300–1500 cm^{-1}) kept intensive with increasing con-

centration of $\text{Pd}_2\text{-CO}$, suggesting that this species originated from the transformation of Pd^+ to Pd metal.

Unlike CO adsorption on the pristine catalyst, $\text{Pd}^{2+}\text{-CO}$, $\text{Cu}^+\text{-CO}$, and $\text{Pd}^+\text{-CO}$ were clearly observed simultaneously after introducing CO for 4 min on the modified catalyst. $\text{Pd}_2\text{-CO}$ appeared after exposure in CO for 8 min, and no bands corresponding to the carbonate were observed. However, it is worth mentioning that the band ratio of $\text{Cu}^+\text{-CO}/\text{Pd}^+\text{-CO}$ over the pristine catalyst was higher than that over the modified catalyst. The intense CO adsorption on the Cu^+ species indicated the facile oxidation of the metallic Pd by high-valence Cu species.

Water was introduced after CO adsorption equilibrium, and the results are shown in Fig. 7. $\text{Pd}^{2+}\text{-CO}$ and $\text{Cu}^+\text{-CO}$ maintained their peak intensities with the increase in the exposure time to water, while $\text{Pd}^+\text{-CO}$ revealed an opposite trend. The disappearance of $\text{Pd}^+\text{-CO}$ was accompanied by the intensification of CO adsorption on metallic Pd ($\text{Pd}_2\text{-CO}$, $\text{Pd}_3\text{-CO}$). As a result of the admission of water, the carbonate species was further enhanced in amount compared to that observed in the absence of water in the feed gas.

Oxygen gas was introduced after exposure to water for 20 min, which stabilized the bands of $\text{Pd}^{2+}\text{-CO}$ and $\text{Cu}^+\text{-CO}$ quickly. Because the redox potential of $\text{Cu}^+/\text{Cu}^{2+}$ (0.15 V) was much lower than that of $\text{Pd}^0/\text{Pd}^{2+}$ (0.92 V), O_2 would oxidize Cu^+ first rather than Pd^0 . Shen et al. [18] also confirmed the fast oxidation of Cu^+ to Cu^{2+} by O_2 .

Although the absorption bands for the two catalysts displayed similar tendencies, compared with the modified catalyst, a faster disappearance of $\text{Pd}^+\text{-CO}$ over the reference catalyst was still observed. Combined with Fig. 6, it further confirmed that the presence of water favored the oxidation of metallic Pd by the Cu^{2+} species. The gradually intensifying $\text{Pd}_2\text{-CO}$ band seemed to contradict the competitive adsorption between CO and water on active sites. Considering the first step in CO oxidation, which is the fast reduction of Pd^{2+} to Pd^+ by CO, it is suggested that the presence of water strongly inhibited the reduction of Pd^{2+} by CO, which led to the deactivation.

3.7. Discussion

Fig. 6. In situ DRIFT spectra of CO adsorbed over pristine (R) and modified (M) catalysts.

Fig. 7. In situ DRIFT spectra of CO/H₂O/O₂ adsorbed over pristine (R) and modified (M) catalysts.

Water cannot be avoided in the environment, so it is important to explore catalysts with high water tolerances. A hydrophobic catalyst or an active component inert to water revealed excellence performance in a moist environment. Although small amounts of water could promote CO oxidation over the supported Wacker catalyst, with the increase in the amount of deposited water, the active sites would be covered and the close-knit structure between the Pd and Cu species broken [16]. Such detrimental effects lead to both reversible and irreversible deactivation.

Considering the solubility of CuCl₂ in water, it seems that the decrease in the hydrophilic support will be efficient to control CuCl₂ transfer in the presence of water. Therefore, diethoxy dimethyl silane was used to form oxane bonds to increase the hydrophobicity of the support. Silylation made the surface of the modified catalyst more hydrophobic compared to that of the pristine catalyst. The catalyst based on the pretreated support revealed no obvious decline in activity even after 150 h at 0 °C and 100% relative humidity.

Support silylation had no effect on specific surface area (Table 1), but it increased the particle size of Cu₂(OH)₃Cl from 26 to 40 nm (Fig. 3 and Table 1). Meanwhile, the amount of the Cu species in close contact with the Pd species enhanced according to H₂-TPR and XPS analyses (Figs. 4 and 5). It should be mentioned that the concentration of chlorine in the case of the modified catalyst was much lower than that of the pristine catalyst (Table 1). With the increase in the amount of Cl species coordinated with the Pd species, the CO substitution energy will increase accordingly, which inhibits CO adsorption [34].

The water adsorption experiment showed that silylation inhibited water deposition on the modified support (Fig. 2). The CO oxidation stability was correlated with the water concentration, while the role of water could not be clearly

demonstrated. Therefore, in situ DRFTIR was used to clarify the relationship between them. The reaction mechanism for CO oxidation on supported Wacker-type catalysts was similar to that involving homogeneous catalysts: Pd species are the active sites for CO oxidation, and CO oxidation is achieved by the dual redox cycle of the Pd and Cu species. Although it is well accepted that Pd ions are the active component in CO oxidation, the nature of Pd itself is ambiguous. Choi et al. [35] thought that the structure of the Pd species was similar to that of PdCl₂, and was probably modified by a carbonyl ligand. DFT modulation suggested that it should exist as PdOH, based on the de-chlorination of PdCl₂ [36].

As shown in Fig. 6, the presence of CO accompanied by the appearance of the Pd⁺ species suggest the easily reduction of Pd²⁺ to Pd⁺ by CO. The faster disappearance of Pd⁺ indicated that this species was more active than Pd²⁺ during CO oxidation, especially in the presence of water (Fig. 7). Meanwhile, most of carbonate species accumulated with the transformation of Pd⁺ to Pd⁰, which had detrimental effects on the stability of CO oxidation. The high concentration of Cu⁺ on hydrophilic catalysts indicated that water favored the reoxidation of Pd⁰ by Cu²⁺. However, it is worth mentioning that the Pd²⁺ species intensified in the presence of water. Although the accumulated carbonate species had negative effects on CO oxidation, considering the important role of Pd⁺ in the oxidation, the deactivation in the presence of water was mainly due to its inhibition to produce Pd⁺.

4. Conclusions

Silylation is an efficient way to improve hydrophobicity, so diethoxy dimethyl silane (C₆H₁₆O₂Si) was used to modify Al₂O₃ and prepare the hydrophobic catalysts Pd-Cu-Cl_x/Al₂O₃.

This support pretreatment significantly promoted the CO oxidation stability, and CO conversion remained at 78% even after 150 h at saturated humidity and freezing point. Support silylation improved catalyst hydrophobicity and promoted the reduction of the Cu species. Compared with the pristine catalyst, the concentration of Cl ions decreased significantly, which benefited CO adsorption.

Pd^+ species was more active than Pd^{2+} species in CO oxidation, and the oxidation was achieved by the dual redox cycle of the Pd and Cu species. The presence of water favored CO oxidation over active Pd^+ and Pd^0 reoxidation by Cu^{2+} . Meanwhile, water also inhibited the formation of active Pd^+ species and helped to produce carbonate species. Compared with the form of the carbonate species, the inhibition of the production of the active Pd^+ species played a main detrimental role in determining the stability.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 1560–1567 doi: 10.1016/S1872-2067(18)63112-2

Stability of Pd-Cu-Cl_x/Al₂O₃ catalyst for CO oxidation

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Support silylation efficiently improved catalyst hydrophobicity and ensured stability after 150 h at 0 °C and 100% relative humidity. The detrimental role of water on stability through the inhibition of the production of the active Pd^+ species was overwhelmingly restrained.

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Pd-Cu-Cl_x/Al₂O₃催化剂对CO氧化的稳定性

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摘要: CO催化氧化广泛应用于空气净化、机动车尾气治理和CO气体传感器中。在CO氧化催化剂设计与制备过程中, 催化剂与使用环境密切相关。例如工业和机动车尾气净化需要在高温(200–600 °C)下进行, 而对于半密闭空间(隧道或者地下停车场)空气净化需要在室温和高相对湿度下进行。频繁冷启动导致半密闭空间CO浓度累积而超过排放控制标准, 因此制备室温、高相对湿度下CO氧化催化剂是面临的重要问题之一。

负载型Wacker催化剂对于CO低温催化氧化的研究一直受到广泛关注。环境中少量水的存在会促进负载型Wacker催化剂对CO的低温氧化性能, 但随着水沉积量的增加, 活性位点将被覆盖, 并且Pd和Cu活性组分之间的紧密结构被破坏, 从而导致催化剂的失活, 即催化剂的稳定性变差。因此, 为了提高催化剂在高相对湿度下的稳定性, 利用二乙氧基二甲基硅烷对Al₂O₃载体进行硅烷化处理, 以增加载体的疏水性, 考察载体疏水改性对CO低温氧化过程中催化剂稳定性的影响。

催化剂的稳定性测试结果表明, 在0 °C, 100%相对湿度条件下, 未改性催化剂在约20 h内CO转化率由81%下降到50%; 载体硅烷化后制备的催化剂在反应进行150 h后, CO转化率仍保持在78%, 即反应活性未见降低。由此表明催化剂载体经有机硅烷改性后, 可显著增强催化剂在低温、高相对湿度下的稳定性。N₂吸附/脱附和水吸附实验结果表明, 载体硅烷化改性并未对催化剂的比表面积产生影响, 但显著降低了催化剂上水沉积速度和沉积量, 未改性催化剂的初始吸水速度是改性后催化剂的4倍, 但改性后催化剂的饱和吸水率仅占未改性催化剂的1/3。X射线衍射结果表明, 载体预处理后活性物种Cu₂(OH)₃Cl晶粒尺寸有所增加。氢气程序升温还原、X射线光电子能谱结果表明, 载体硅烷化预处理改善了催化剂中Cu和Pd物种的化学分布及接触状态, 增加了与Pd物种紧密接触的Cu物种的量, 从而促进了Cu物种的还原。与此同时, 载体硅烷化显著降低了催化剂表面Cl⁻离子的浓度, 从而影响到对CO吸附。

为了进一步研究水与催化剂稳定性之间的关系, 采用原位红外漫反射(In situ DRIFT)对催化剂进行表征。负载型Wacker催化剂对CO氧化反应机理为: Pd是CO氧化反应的活性中心, 通过Pd和Cu物种之间的氧化还原循环来实现CO氧化, 且Pd⁺比Pd²⁺具有更高的CO氧化性能。反应气氛中水的存在, 有利于CO在Pd⁺上氧化、以及金属态Pd被Cu²⁺物种再氧化的过程, 同时水也显著促进了催化剂表面碳酸盐的生成以及抑制了活性物种Pd⁺生成。与表面碳酸盐累积相比, 水对于活性物种Pd⁺生成的抑制作用是导致催化剂活性降低的主要原因。

关键词: 一氧化碳氧化; 稳定性; 湿度; 疏水性; 负载型Wacker催化剂

收稿日期: 2018-03-20. 接受日期: 2018-04-28. 出版日期: 2018-09-05.

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基金来源: 国家重点研发计划(2016YFC0204300); 国家自然科学基金(21207037, 213333003, 21571061); 上海市教委“曙光”计划(12SG29); 上海市科学技术委员会(15DZ1205305).

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