

Oxidation of Carbon Monoxide over Cu/CeO₂ Catalysts Prepared by SMAI

Wei Ping HUANG, Xiu Cheng ZHENG, Shou Min ZHANG,
Xiao Hang QIU, Wei WEI, Bao Qing LI, Shi Hua WU*

Department of Chemistry, NanKai University Tianjin 300071

Abstract: Supported Cu catalysts for low-temperature CO oxidation were prepared by solvated metal atom impregnation (SMAI). X-ray photoelectron spectroscopy (XPS) investigations indicated that the copper in all the samples was in a metallic state. XRD measurements showed that the mean diameters of Cu particles prepared by SMAI were small. Catalytical tests showed that the SMAI catalyst had high CO oxidation activity.

Keywords: CO oxidation, copper catalysts, solvated metal atom impregnation, conventional im-pregnation .

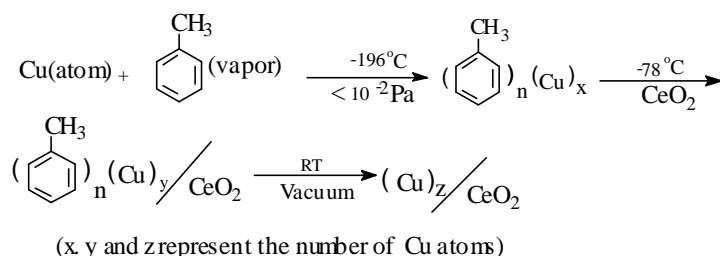
Introduction

Carbon monoxide is ubiquitous air pollutants emitted by many sources. Total oxidation of carbon monoxide to carbon dioxide is employed to meet environmental regulations in an economic way. Precious metals (Pt, Pd) are well-known oxidation catalysts with high activity and stability, and are widely used for exhaust gas emission control. However, the high cost of precious metals and their sensitivity to sulfur poisoning have long motivated the search for substitute catalysts. It was reported that high active and resistant to poisoning catalysts for CO oxidations were achieved by doping some oxides, such as ceria, zirconia, and thoria with transition metals, such as copper, cobalt, or nickel¹. The catalysts for fundamental studies are prepared by various conventional techniques, such as impregnation, ion exchange, anchoring/grafting, spreading and wetting, hydrolysis, homogenous deposition precipitation, and solution combustion²⁻³. Presently, there has been trended forwards the novel methods of preparation. The solvated metal atom impregnation (SMAI) method had been found to be unique for obtaining high dispersed metallic catalysts⁴. In this article we report the first study on CO oxidation over Cu/CeO₂ catalyst prepared by SMAI method.

Experimental

The procedures for preparing Cu/ CeO₂ catalysts by SMAI method are as follows:

* E-mail: wushihuae@eyou.cn



The support CeO_2 was dehydrated under vacuum (1.3×10^{-2} Pa) at 400°C for 8 h. Toluene used as the solvating medium was carefully dehydrated and degassed by "freeze-haw" process. The design of the static metal atom reactor for the preparation of the precursor solution of bis(toluene) copper(0) has been described elsewhere⁵. In a typical experiment, approximately 1 g of copper chop (99.9%) was evaporated and cocondensed with 130 mL of toluene at -196°C under a dynamic vacuum of less than 1.33×10^{-2} Pa over a period about 1 h. After finishing the cocondensation, the condensate was allowed to be warmed up to -78°C and melted down to the bottom of the reactor, the bis(toluene) copper (0) complex prepared in this way is extremely air sensitive and thermally unstable, which decomposes into copper(0) and toluene at about -100°C . The precursor solution was transferred to the precooled (-78°C) CeO_2 through a stainless steel tube. The CeO_2 (20 g) was impregnated with solvated Cu atom (cluster) solution for 5 h at -78°C under stirring. Then the Cu-toluene/ CeO_2 slurry was gradually warmed to room temperature. The colorless excess toluene was removed by a syringe and the Cu/ CeO_2 catalysts were dried under vacuum at room temperature for several hours. The dry sample was stored and handled in the nitrogen filled glovebox.

X-ray diffraction of the supported copper particles was performed on a D/MAX-III A X-ray diffraction spectrometer. Diffraction patterns were recorded with $\text{CuK}\alpha$ radiation and graphite monochromator over a 2θ - range of 20° to 70° . The working voltage and current of X-ray tube were 45kV and 170 mA.

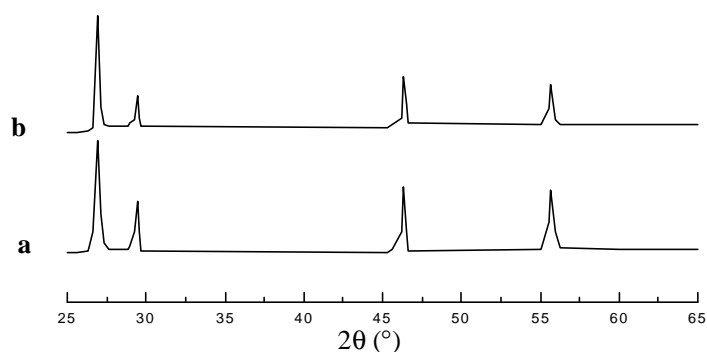
Steady- state catalytic test was carried out in a fixed - bed flow microreactor. The catalyst powder was embeded between glass wool plug in a 8 mm ID glass reactor tube. Experiments were performed in the temperature range 273 K - 393 K and at atmospheric pressure. For each experiment 200 mg catalyst was used which was transferred into the reactor under the protection of N_2 gas flow. The reaction gases contain 1.0% CO balanced with air, purified through a molecular sieve column and passed through the catalyst bed at a flow rate of 67 mL/min (sv = 20000 mL/h/g). Kinetic data were taken after 10 or 20 min on stream at specified conditions. The products were analyzed by a SP- 501 gas chromatograph.

Results and Discussion

Figure 1 shows the XRD Patterns for 4.6 wt% Cu/ CeO_2 catalyst and CeO_2 support. There are no Cu diffraction peaks (Cu (III), $2\theta = 43^\circ$) to be observed on the sample

prepared by SMAI method. This is because the Cu particles in the sample are so small that they go beyond the limit of the instrument sensitivity (~ 2.5 nm).

Figure 1 XRD Patterns of Cu/CeO₂ catalysts and CeO₂

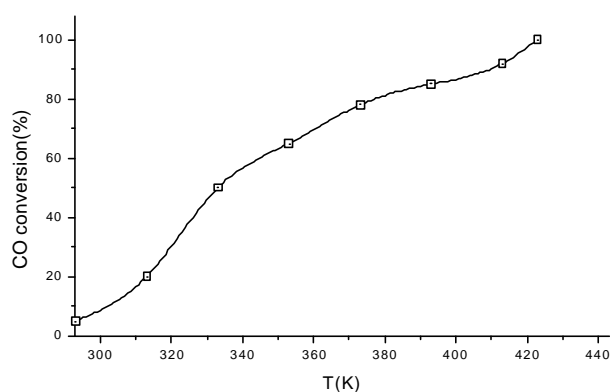


a. Support CeO₂ b. 4.6wt% Cu/CeO₂ catalysts (Cu content was measured by ICP)

Figure 2 depicts the catalytic activities (CO conversion) of the Cu catalysts for CO oxidation as a function of reaction temperature. It is to be noted that the conversion of CO increased as the temperature increased, the conversion of CO was 50%, 100% respectively at temperature 333 K and 423 K.

The results of this study showed that preparation of support copper particles *via* solvated metal atom impregnation affords highly active catalysts for the low temperature oxidation. SMAI is a very wise technique for preparing highly dispersed copper particles which makes CO oxidation at low temperature to be possible.

Figure 2 Catalytic activities of Cu catalysts in CO oxidation as a function of reaction temperature



References

1. W. Liu, A. L. Sarofim, Flytzani-Stephanopoulos, M., *App. Catal. B*, **1994**, *4*, 167.
2. F. J. Janssen, *Handbook of Heterogeneous Catalysts*, ed by G. Ertl, H. Knozinger, and J. Weitkamp, VCH, Weinheim **1977**, *4*, 1633.
3. B. Parthasarathi, S. T. Aruna, K. C. Patil, M. S. Hegde, *J. catal.*, **1999**, *36*, 186.
4. S. H. Wu, C. Y. Zhu, W. L. B., *Chinese J. catal.*, **1996**, *17* (4), 319.
5. S. H. Wu, *Chemistry* (in Chinese), **1989**, *8*, 40.

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