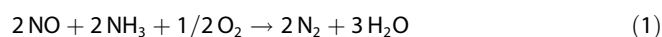


A Highly Distributed Cu_xAu_y-Deposited Nanotube Carbon for Selective Reduction of NO in the Presence of NH₃ at Very Low Temperature

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Cu_xAu_y Deposited on carbon nanotubes prepared by solution plasma sputtering was used for first time as a catalyst for selective reduction of NO, in the presence of NH₃, at low temperature. N₂ and H₂O are desirable during the NO reduction process; however, N₂O is totally absent from the obtained products.

Selective catalytic reduction (SCR) is considered to be the most efficient technology for reducing NO_x emissions from stationary sources. The reaction can be achieved efficiently by conventional catalysts such as V₂O₅-WO₃/TiO₂ [Eq. (1)].^[1]



The most effective reaction temperature for this process is known to be in the range of 300–400 °C.^[2,3] However, many studies have been performed to develop new low temperature SCR catalysts that can work well around 250 °C or even below. In this case the SCR unit could be placed behind the electric precipitation and desulfurizer in a power plant to efficiently remove NO_x over a wider temperature range and for NO_x control in diesel engines.^[4] According to our literature overview, many catalysts, e.g., modified carbon fibers^[5] and metal-activated carbon,^[6] have been tested for the SCR of NO at low temperatures (<250 °C), however, such catalysts exhibited lower catalytic activity for a commercial process. On the other hand, catalysts containing transition metals such as Mn, V, Fe, and Rh-Sn^[7–10] exhibited good low-temperature SCR activity. Among them, the nano-MnO_x catalyst has been studied extensively, as it contains various types of labile oxygen species required for low-temperature SCR.^[4,11] Several accounts have been reported for the SCR of NO conversion; Cu/CeO₂, Cu-Fe and Au/MgO, Au/SiO₂, and Au/Al₂O₃^[12–14] catalysts display

higher activities in SCR of NO with NH₃, H₂, CO, and hydrocarbons.

The aim of this work is to study SCR of NO with NH₃ over novel Cu_xAu_y/CNTs catalysts synthesized by solution plasma sputtering (SPS) process and the detailed preparation conditions and characterization results are given in the Supporting Information.

Moreover, the measurements of the SCR activity were performed in a self-designed SCR reactor.^[15] Four gas streams, 700 ppm of NO, 4% of O₂ and 10% of H₂O steam and with He in balance were used to simulate the flue gas. Mass flow controller was used to control NO, and gas rotameters were used to control the stream of NH₃ and O₂. In all the runs, the total gas flow rate was maintained at 300 mL min⁻¹ over 1 g of catalyst to adjust W/F as 3.2 × 10⁻³ g/(mL min⁻¹), where W denotes the weight of catalyst and F denotes the flow of the feed gases. The feed gases were mixed in a chamber and then pre-heated before entering the reactor. Catalytic activity data was collected at low temperature range of about 30–65 °C. The NO concentrations at the inlet and outlet of the reactor were monitored by using an on-line Flue Gas Analyzer KM900 equipped with NO sensor. To avoid the effect of the adsorption characters, the catalysts were purged with reaction gas for 2 h at first.

Here we report a rare example of SCR of NO using Cu_xAu_y/CNTs catalysts. Figure 1 shows the catalytic activities of Cu_xAu_y/

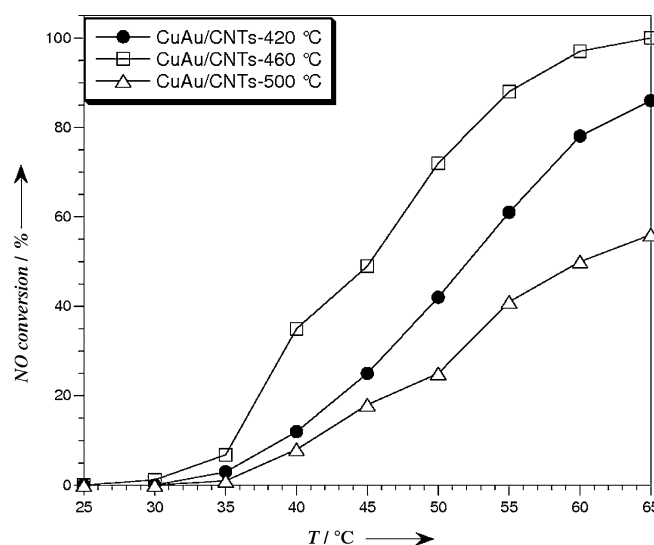


Figure 1. Catalytic activity of Cu_xAu_y/CNTs catalysts calcined at different temperatures. Reaction conditions: 700 ppm of NO, 750 ppm of NH₃, 4% of O₂ and 10% of H₂O steam, He to balance, W/F = 3.2 × 10⁻³ g/(mL min⁻¹).

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CNTs catalysts calcined at different temperatures. As expected, $\text{Cu}_x\text{Au}_y/\text{CNTs}$ catalyst calcined at 460°C displays a much higher activity than that calcined at 420 and 500°C . In fact, the $\text{Cu}_x\text{Au}_y/\text{CNTs}$ (460°C) catalyst achieved totally NO conversion to 100% at very low temperature range 30 – 65°C . The NO conversion on $\text{Cu}_x\text{Au}_y/\text{CNTs}$ catalysts decreased in the order: $\text{Cu}_x\text{Au}_y/\text{CNTs}$ (460°C) > $\text{Cu}_x\text{Au}_y/\text{CNTs}$ (420°C) > $\text{Cu}_x\text{Au}_y/\text{CNTs}$ (500°C). Based on our literature overview, when copper and gold salt precursors were calcined at different temperatures, the main states of both noble metals were Au, Cu, and CuO, whereas for the samples calcined at 460°C , the main states would appear to be Cu and Au.^[16]

To further investigate the effect of Cu/Au mass contents on NO conversion, seven different loadings of copper and gold have been prepared on $\text{Cu}_x\text{Au}_y/\text{CNTs}$ catalysts and calcined at 460°C . These catalysts have the same total mass content of 1%. The NO conversion as a function of temperature, in the range of 30 – 65°C , is shown in Figure 2 over different mass

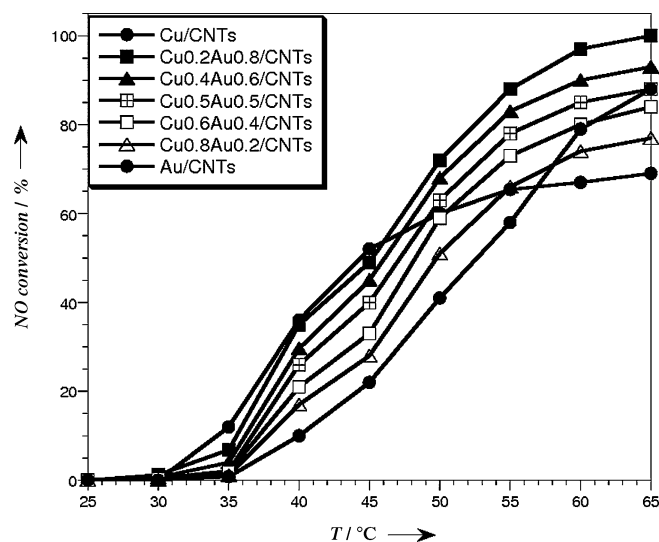


Figure 2. Catalytic activity of $\text{Cu}_x\text{Au}_y/\text{CNTs}$ catalysts with different Cu and Au mass contents. Reaction conditions: 700 ppm of NO, 750 ppm of NH_3 , 4% of O_2 and 10% of H_2O steam, He to balance, $W/F = 3.2 \times 10^{-3} \text{ g}/(\text{mL min}^{-1})$.

contents of $\text{Cu}_x\text{Au}_y/\text{CNTs}$ catalysts. Among these catalysts, $\text{Cu}_{0.2}\text{Au}_{0.8}/\text{CNTs}$ (460°C) catalyst shows the highest NO conversion of 100% at 65°C and it was the most suitable for this application. Then, the Cu/CNTs catalyst is more active at low temperature but less selective in comparison with Au/CNTs catalyst, which exhibits a lower activity at low temperature, but which is more selective at high temperature. The catalytic activity of $\text{Cu}_x\text{Au}_y/\text{CNTs}$ catalysts was much higher than those reported in literature overview,^[4,7–9,17,18] such as catalysts containing transitional metal: Fe, V, Cr, Cu, Co, and Mn.

The effect of the initial NH_3 concentration on the NO conversion is shown in Figure 3. The NO conversion increased with the NH_3 concentration. When the initial NH_3 concentration was 400 ppm, the SCR of NO attained 96% conversion of NO. The NO conversion tended to be a constant value with further increase of NH_3 concentration. Therefore, in practical application

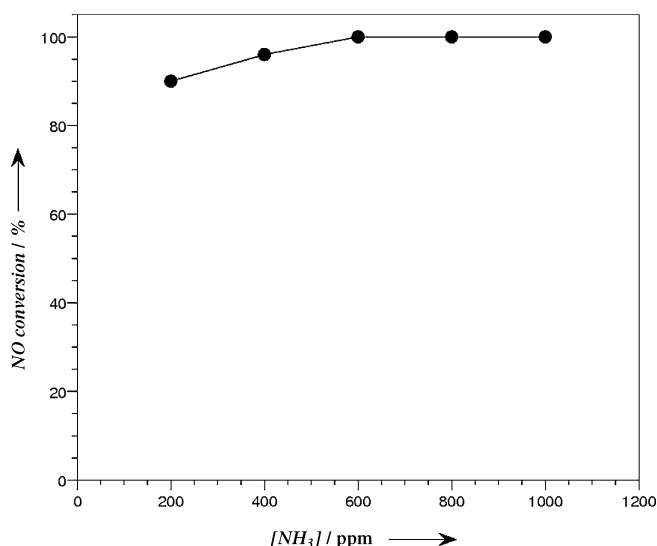


Figure 3. Effect of initial NH_3 concentration on the catalytic performance on $\text{Cu}_{0.2}\text{Au}_{0.8}/\text{CNTs}$ catalyst calcined at 460°C . Reaction conditions: $T = 65^\circ\text{C}$, 700 ppm of NO, 4% of O_2 and 10% of H_2O steam, He to balance, $W/F = 3.2 \times 10^{-3} \text{ g}/(\text{mL min}^{-1})$.

of SCR of NO with NH_3 , NH_3 in excess should be treated to avoid secondary pollution.^[19,20]

Figure 4 shows the effects of initial NO concentration on the NO conversion. There is a lesser effect of initial NO concentration on the NO conversion. With initial NO concentration be-

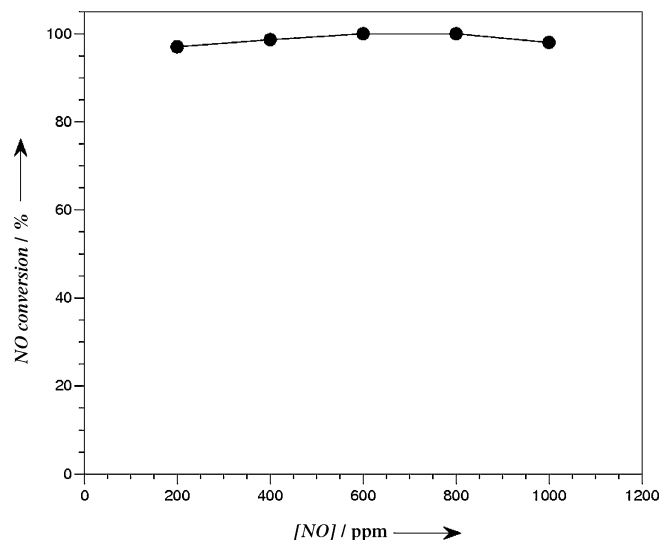


Figure 4. Effect of NO concentration on the catalytic performance on $\text{Cu}_{0.2}\text{Au}_{0.8}/\text{CNTs}$ catalyst calcined at 460°C . Reaction conditions: $T = 65^\circ\text{C}$, 750 ppm of NH_3 and He to balance, $W/F = 3.2 \times 10^{-3} \text{ g}/(\text{mL min}^{-1})$.

tween 600 and 800 ppm, NO conversion remained constant at 100%. With the initial NO concentration of 400 ppm, the SCR of NO attained more than 97% conversion of NO. Moreover, it was previously reported that O_2 presents significant effect on SCR performance. Indeed, the effect of O_2 concentration on

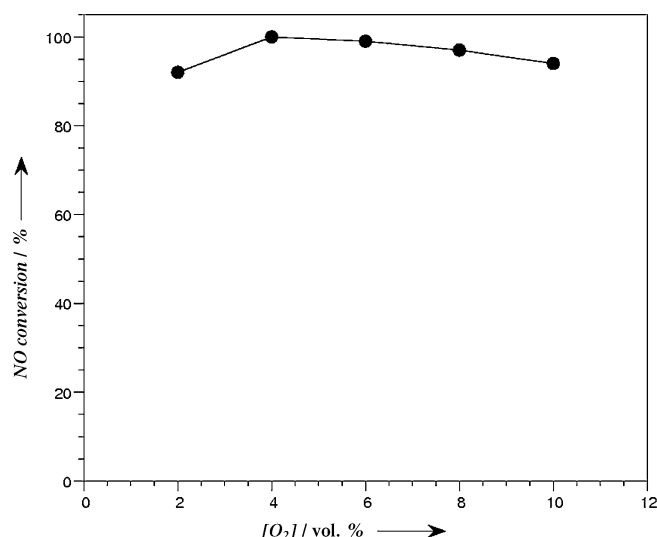


Figure 5. Effect of O_2 concentration on the catalytic performance on $Cu_{0.2}Au_{0.8}/CNTs$ catalyst calcined at $460^\circ C$. Reaction conditions: $T = 65^\circ C$, 700 ppm of NO, 750 ppm of NH_3 and 10% of H_2O steam, He to balance, $W/F = 3.2 \times 10^{-3} \text{ g}/(\text{mL min}^{-1})$.

the NO conversion has been performed and is shown in Figure 5.

When the O_2 concentration was less than 4%, the NO conversion increased; however, NO conversion decreased slightly when O_2 concentration was above 4%. This can be explained by the oxidation of NH_3 to NO. With the O_2 concentration of 2, 4, 7, and 10%, the NO conversion reached 92, 100, 97, and 94%, respectively. Gongshin et al.^[21] also found a similar observation that the NO conversion increased sharply when a low O_2 concentration (less than 4%) was introduced to the initial reactants in SCR evaluation.

For SCR of NO conversion, re-startability is another key parameter to be considered. Figure 6 shows that the activity

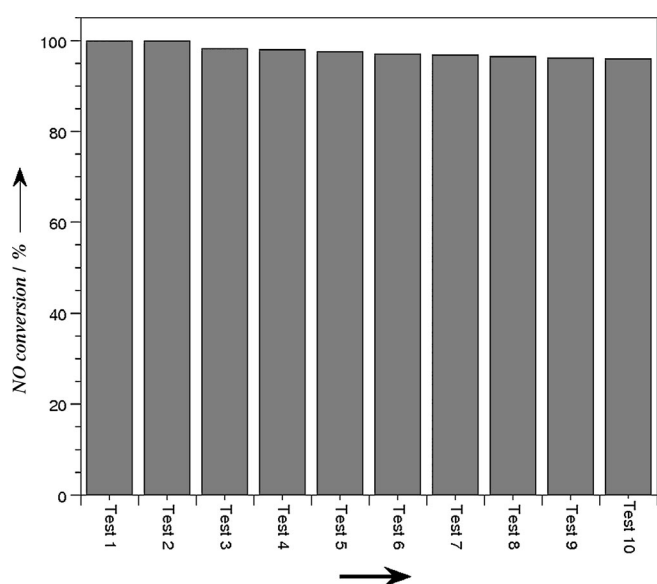


Figure 6. Catalytic activity for re-startability of $Cu_{0.2}Au_{0.8}/CNTs$ for SCR of NO.

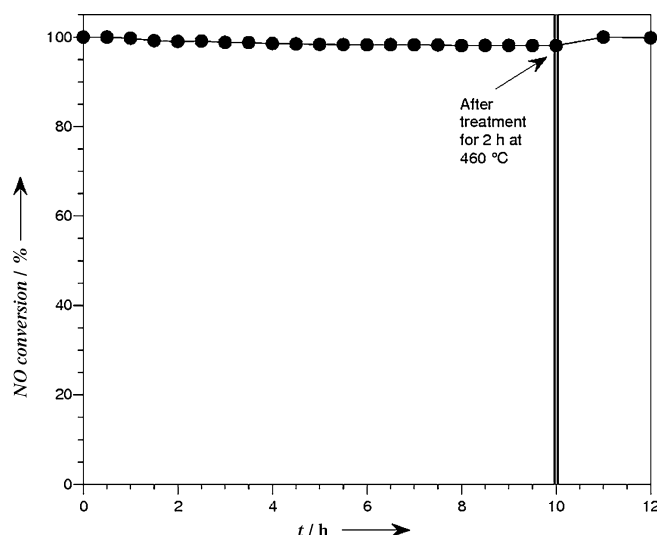


Figure 7. Long-term durability test of catalytic activity of $Cu_{0.2}Au_{0.8}/CNTs$ for SCR of NO.

slightly decreased (about 4%), after ten tests, from 100 to 96%, demonstrating a good re-startability of $Cu_{0.2}Au_{0.8}/CNTs$ catalysts at $30\text{--}65^\circ C$ temperature range.

As shown in Figure 7, the NO conversion was very slightly decreases from its original level 100% to 98.08% after 10 h of NO conversion, but the NO conversion almost stabilizes. When the catalyst was heated for 2 h at $500^\circ C$ in Ar, the activity quickly restores to its initial level. This indicates that the $Cu_{0.2}Au_{0.8}/CNTs$ catalyst is resistant to water vapor. The decreased activity in the process is mainly caused by the competing adsorption of H_2O and reaction gases on the catalyst.

The carbon nanotubes and $Cu_{0.2}Au_{0.8}/CNTs$ catalysts were also characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The obtained results were presented in the Supporting Information.

In conclusion, the current study reveals that novel highly distributed $Cu_{0.2}Au_{0.8}/CNTs$ catalysts can act as encouraging catalysts for very low temperature for SCR of NO and it is also resistant to water vapor.

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Keywords: copper • gold • low temperature • NO • nanotubes • reduction • solution plasma sputtering

- [1] G. Busca, L. Lietti, G. Ramis, F. Berti, *Appl. Catal. B* **1998**, *18*, 1–36.
- [2] A. Bahamonde, A. Beretta, P. Avila, E. Troconi, *Ind. Eng. Chem. Res.* **1996**, *35*, 2516–2521.
- [3] A. Beretta, C. Orsenigo, N. Ferlazzo, E. Troconi, P. Forzattti, *Ind. Eng. Chem. Res.* **1998**, *37*, 2623–2633.
- [4] T. S. Park, S. K. Jeong, S. H. Hong, S. C. Hong, *Ind. Eng. Chem. Res.* **2001**, *40*, 4491–4495.

- [5] J. Muñiz, G. Marban, A. B. Fuertes, *Appl. Catal. B* **1999**, *23*, 25–35.
- [6] E. Zhu, Z. Liu, S. Liu, H. Niu, T. Hu, T. Liu, Y. Xie, *Appl. Catal. B* **2000**, *26*, 25–35.
- [7] L. Singoredjo, R. Korver, F. Kapteijn, J. Moulijn, *Appl. Catal. B* **1992**, *1*, 297–316.
- [8] B. Huang, R. Huang, D. Jin, D. Ye, *Catal. Today* **2007**, *126*, 279–283.
- [9] R. Q. Long, R. T. Yang, R. Chang, *Chem. Commun.* **2002**, 452–453.
- [10] K. Tomishige, K. Asakura, Y. Iwasawa, *J. Chem. Soc. Chem. Commun.* **1993**, 184–185.
- [11] J. Li, H. Chang, L. Ma, J. Hao, R. T. Yang, *Catal. Today* **2011**, *175*, 147–156.
- [12] P. Bera, S. T. Aruna, K. C. Patil, M. S. Hegde, *J. Catal.* **1999**, *186*, 36–44.
- [13] T. Ishihara, M. Kagawa, F. Hamada, Y. Takita, *J. Catal.* **1997**, *169*, 93–102.
- [14] J. Y. Lee, J. Schwank, *J. Catal.* **1986**, *102*, 207–215.
- [15] E. Seker, E. Gulari, R. H. Hammerle, C. Lambert, J. Leerat, S. Osuwan, *Appl. Catal. A* **2002**, *226*, 183–192.
- [16] X. Liao, W. Chub, X. Daib, V. Pitchona, *Appl. Catal. B* **2013**, *142*, 25–37.
- [17] J. H. Park, H. J. Park, J. H. Baik, I. S. Nam, C. H. Shin, J. H. Lee, B. K. Cho, S. H. Oh, *J. Catal.* **2006**, *240*, 47–57.
- [18] J. Y. Yan, G.-D. Lei, W. M. H. Sachtler, H. H. Kung, *J. Catal.* **1996**, *161*, 43–54.
- [19] F. Kapteijn, L. Singoredjo, A. Andreini, J. A. Moulijn, *Appl. Catal. B* **1994**, *3*, 173–189.
- [20] Y. Masaaki, Y. Akinori, M. Isao, *Appl. Catal. A* **1998**, *173*, 239–245.
- [21] G. S. Qi, R. T. Yang, *J. Catal.* **2003**, *217*, 434–441.

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