

## NO Decomposition on Rh Supported CNTs

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**Abstract:** The decomposition of NO has been studied in a steady flow reactor on fresh carbon nanotubes (CNTs), purified CNTs, Rh/*p*-CNTs and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> between 573 K and 973 K. NO decomposition at 573 K was initially complete over a reduced surface. The amount of NO absorption increased at temperature below 773 K. 100% NO conversion and more than 100% N<sub>2</sub> activity was achieved at 973 K for 150 min on *p*-CNTs and *f*-CNTs.

**Keywords:** NO decomposition, NO absorption, carbon nanotubes, rhodium.

It is well known that NO is one of the most predominant pollutants. It is the main source of acid rain and has strong carcinogenicity. Therefore, removal of NO is one of the key environmental subjects in the world nowadays. With the discovery of carbon nanotubes and their large-scale synthesis<sup>1-2</sup>, attention is now being focused on their potential application in various fields of materials research. In the field of heterogeneous catalysis, numerous carbon materials have been used to disperse and stabilize metallic particles<sup>3</sup>. CNTs was a good electron donor, so strong interaction would be found to exist between rhodium clusters and CNTs, and rhodium could be kept in low oxidation state easily.

None has reported regarding NO decomposition over Rh/CNTs. Therefore, this study will examine the steady catalytic activity of fresh CNTs (*f*-CNTs), purified-CNTs (*p*-CNTs), Rh/*p*-CNTs, and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for NO decomposition.

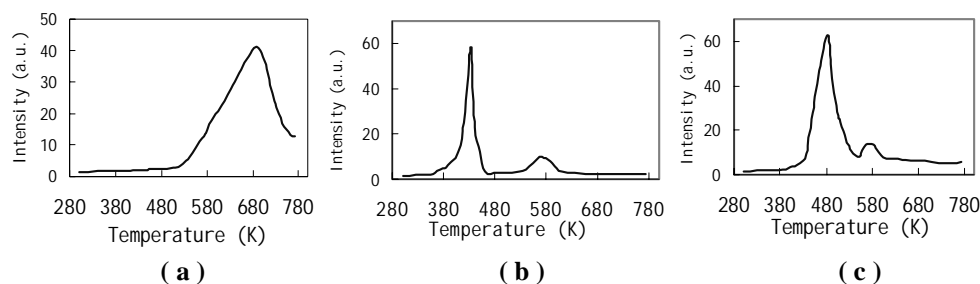
CNTs were synthesized *in situ* by means of CH<sub>4</sub> decomposition on H<sub>2</sub>-reduced LaCoO<sub>3</sub> at 973 K for two hours. Fresh CNTs were obtained and the yield of CNTs was about 200 g/g<sub>Co</sub>. Purified CNTs were carried out by treating the fresh CNTs with concentrated HCl at 353 K for 2 h, then washed with de-ionized water till the value of pH was approximately 7, dried at 373 K and calcined in air at 773 K for 4 h. Purified CNTs-supported rhodium was prepared by impregnating CNTs with RhCl<sub>3</sub> solution for 48 h, then the materials were dried at 373 K and calcined at 773 K in air for 4 h. The loading of Rh in the Rh/CNTs obtained was 1 wt%. For comparison, we also prepared 1 wt% Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Measurements of catalytic activity of catalyst for the NO decomposition reaction were conducted at atmospheric pressure in a micro-reactor under steady-state conditions. The feed gas, containing 6000 ppm NO in He, was passed downward at a total flow rate of 20 ml/min through the reactor, which contained 30 mg of the catalyst. The samples were heated in H<sub>2</sub> or He flows to 573 K and kept at 573 K for 2 h, then the feed gas

introduced. The reaction time was 2 h at 573 K and 1 h at 673 K, 773 K, 873 K, respectively. At last, the NO decomposition reaction was carried out for 150 min at 973 K. Sampled every 10 minutes in the whole process. The temperature was raised at the rate of 10 K min<sup>-1</sup>. The reactor effluent was analyzed by on-line gas chromatography. H<sub>2</sub>-TPR experiments were performed in a U-shaped quartz micro-reactor by using a 5% H<sub>2</sub>-95% N<sub>2</sub> (v/v) gas mixture. Before performing the TPR experiment, the sample was first calcined *in situ* at 423 K for 1 h in Ar flow of 45 ml/min followed by cooling in Ar to room temperature.

**Figure 1** shows the TPR profiles of *p*-CNTs, Rh/*p*-CNTs and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. There is one peak, which centers at 680 K for *p*-CNTs. This peak can be ascribed to the uptake of hydrogen. There are two peaks for Rh/*p*-CNTs, the peak at 423 K is ascribed to the reduction of Rh<sup>3+</sup> to metallic Rh, and the one of 563 K is assigned to the uptake of hydrogen by CNTs. The peak area of 563 K is smaller than the one of *p*-CNTs. There are also two peaks for Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which center at 493 K and 573 K, they are assigned to the reduction of Rh<sup>3+</sup> to metallic Rh and the spillover of hydrogen, respectively.

**Figure 1** The TPR profile (a) *p*-CNTs (b) Rh/*p*-CNTs (c) Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



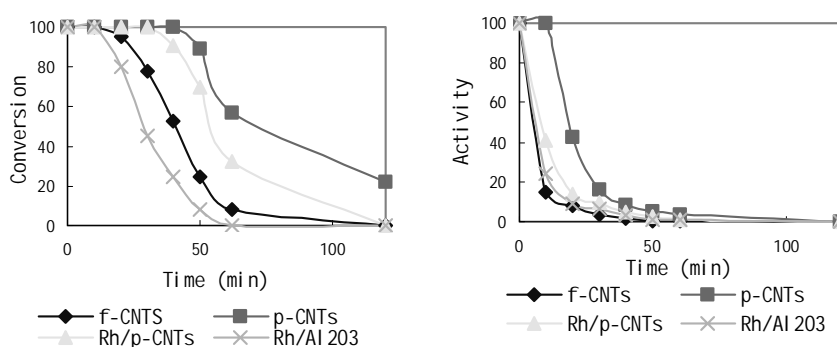
The results of NO conversion and N<sub>2</sub> activity at different time at 573 K were shown in **Figure 2**. NO decomposition at 573 K was initially complete over a reduced surface, but it rapidly slowed down and almost totally stopped after a period of 20-30 min. N<sub>2</sub> was the unique product observed. This was in much agreement with the report by Gigola<sup>4</sup>. Later, no N<sub>2</sub> was detected, but NO conversion was above zero. At 573 K on H<sub>2</sub>-reduced samples, we regarded that three factors existed in the reaction: first, H<sub>2</sub> was absorbed in CNTs, so NO was reduced by H<sub>2</sub>; second, Rh was reduced, then NO decomposed on metallic Rh; third, NO can be uptaken by CNTs.

At 573 K, the main role for N<sub>2</sub> formation was the availability of absorbed hydrogen. In line with previous studies, gas phase oxygen was never observed, thus the poisoning of reduced catalyst must be due to the build-up of oxygen atoms on the metal surface<sup>5</sup>. This interpretation was supported by our experimental data. The oxygen formed during NO decomposition was removed by H<sub>2</sub>, thus N<sub>2</sub> was the sole N-containing product detected. With the amount of hydrogen uptaking decreasing, the concentration of N<sub>2</sub> was decreased. When H<sub>2</sub> was consumed completely, no N<sub>2</sub> was detected. This can also be supported by the results of activity of NO decomposition over He-pretreated catalysts. No N<sub>2</sub> was detected on *p*-CNTs, which was treated in He flow. The results were not shown in this paper.

After the hydrogen uptaking was ceased completely, NO can absorb on CNTs or

metallic rhodium, so we observed that  $N_2$  activity was zero, while NO conversion was above zero. After about 60 min, the equilibrium of NO absorption was achieved at 573K.

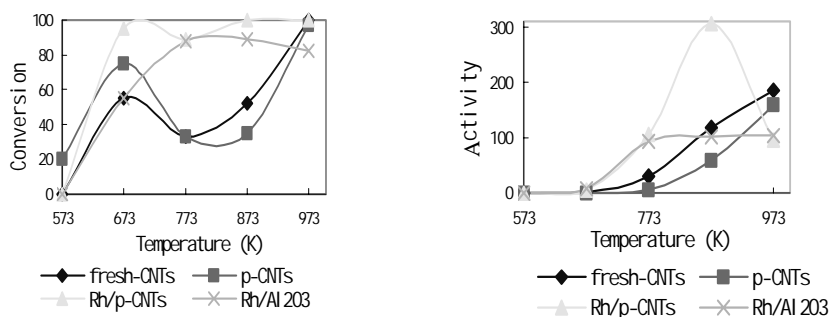
**Figure 2** NO conversion and  $N_2$  activity versus reaction time at 573 K



The results of catalytic activities at different temperatures over  $H_2$ -reduced fresh-CNTs, purified-CNTs, Rh/*p*-CNTs, Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, were shown in **Figure 3**.

With the temperature increasing, the capacity of NO was enhanced below 773 K. The amount of NO absorption attained the maximum at 773 K for *p*-CNTs, but 673 K for *f*-CNTs, Rh/*p*-CNTs, as well as Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Mahzoul *et al*<sup>6</sup> reported that the NO<sub>x</sub> storage was at a maximum at 350°C over a catalyst, containing 0.72% Pt, 0.14% Rh, Ba and La supported on a wash-coat base. Our results were in agreement with theirs.

**Figure 3** NO conversion and  $N_2$  activity versus temperature



No  $N_2$  was observed below 873 K on *p*-CNTs. At 873 K, the  $N_2$  activity was improved to almost 70%, but NO conversion was below 40%. At 973 K,  $N_2$  activity was above 100%, and NO conversion was 100%. NO conversion and  $N_2$  activity were calculated based on the following formula expression.

NO conversion = 1 - NO detected in experiment / NO in the feed gas

$N_2$  activity =  $N_2$  detected in experiment / The theoretical amount of  $N_2$  by NO decomposition in feed gas

When temperature increased up to 773 K, part of NO decomposed into  $N_2$  and  $O_2$ . The outlet was  $N_2$  and NO, no  $O_2$  was detected and this was in agreement with the previous studies<sup>5</sup>.  $N_2$  activity was above 100% for Rh/*p*-CNTs already, but it was below

100% for *f*-CNTs and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 773 K. At 873 K, NO conversion and N<sub>2</sub> activity were further enhanced, as compared to those at 773 K. A constant amount of CO appeared over Rh/*p*-CNTs. The sequence of N<sub>2</sub> activity was as follows: Rh/*p*-CNTs > Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > *f*-CNTs. We can conclude that rhodium is much more active than cobalt and La<sub>2</sub>O<sub>3</sub> (According to the results of XRD, the *f*-CNTs contain few cobalt and a small amount of La<sub>2</sub>O<sub>3</sub>.), and the metal-support interaction existed in Rh/*p*-CNTs was much stronger than in Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The amount of oxygen vacancies determines the reaction rate and N<sub>2</sub> activity at higher temperature.

Strong interactions exist between Rh and CNTs, as we know. The bonds of Rh-C were intensified and the bond of C-C near Rh particles will be weakened more. NO decomposed on Rh, and N<sub>2</sub> and O<sub>2</sub> were produced, N<sub>2</sub> was released in the gas phase, but O<sub>2</sub> was built-up on the surface. At higher temperatures, the bond vibration was intensified, thus the carbon-carbon bond activated by Rh was able to react with oxygen to produce CO at 873 K. The interaction between Rh and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was not so strong as the one between Rh and CNTs. The oxygen formation in NO decomposition can not be easily transferred to the oxygen vacancies on the surface. This will define the rate of reaction and N<sub>2</sub> activity. Therefore, NO conversion and N<sub>2</sub> activity on Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were lower than that on Rh/*p*-CNTs.

Above 773 K, NO can be decomposed on the *f*-CNTs. At 573 K, NO conversion and N<sub>2</sub> activity for *f*-CNTs are lower than that for Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. This can be attributed to that the Rh was more active than Co, and NO could not be decomposed on CNTs at 573 K. At 873 K, the activities of N<sub>2</sub> were almost equal for *f*-CNTs and Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. But *f*-CNTs was more active than Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 973 K. This is due to the big  $\pi$  electron exist in CNTs, which could facilitate oxygen to transfer to oxygen vacancies.

At higher temperature, the rate of reaction and reactivity were determined by the amount of oxygen vacancies rather than metallic rhodium. The behaviors of four samples have no discrepancies over H<sub>2</sub> or He pretreated surfaces above 773 K, the results were not shown in this paper. This will be a powerful proof for the oxygen vacancy mechanism.

It is proved that CNTs have the ability of storing large amount of hydrogen<sup>7</sup>. NO can be reduced by H<sub>2</sub> uptaking in CNTs at 573 K and even lower temperatures. Above 873 K, the CNTs exhibit high activity for NO decomposition, even surpass the catalysts containing Rh. They behave the high-temperature stability and will not be oxidized by the oxygen generation during NO decomposition. The CNTs will be a high efficient material for the removal of NO. The price of CNTs is low.

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