# COBALT SUPPORTED ON CARBON NANOTUBES. AN EFFICIENT CATALYST FOR AMMONIA DECOMPOSITION

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**Abstract**

Cobalt supported on carbon nanotubes catalyst is much more active in reaction of ammonia decomposition than nickel and iron catalysts. The observed low temperature activity of Co/carbon nanotubes catalysts is promising option for creating of ammonia decomposition catalysts with low working temperatures.

**Key words:** ammonia decomposition, cobalt catalysts, carbon nanotube

**1. Introduction.** Catalytic ammonia decomposition is an alternative route to produce $CO_x$-free hydrogen for use in PEMFCs [1, 2]. However, until this moment, the obtained results from studies of this process have no potential to be applied in practice. The reason is that high degree of conversion of ammonia is achieved only at temperatures much higher than the working temperatures of the fuel cells. Therefore, it is important to develop a cheap and active catalyst suitable for low temperature ammonia decomposition.

Much research has been focused on developing better catalysts for this process [3–6]. Monometallic or bimetallic Ru, Fe and Ni are often used as active components for ammonia decomposition catalysts because they are efficient catalysts in ammonia synthesis. Among these catalysts, Ru is the most active catalyst for ammonia decomposition [7, 8]. However, the limited availability of Ru makes it necessary to develop less expensive catalysts based on non-noble metals. Therefore, transition metal based catalysts such as Ni, Fe and Co seem to be the most promising candidates as active catalyst components.

Ample evidence in the literature has demonstrated that support has significant influence on the catalyst structure and properties. Studies reported in the literature data about the performance of Ru-based catalysts in ammonia decomposition using different supports [7], i.e. $Al_2O_3$, $SiO_2$, activated carbon (AC), meso- and microporous materials, carbon nanotubes (CNTs), etc. It is found that the ammonia conversion decreases in the following order: RuCNTs > RuMgO > $RuTiO_2 \approx RuAl_2O_3 \approx RuZrO_2$ > RuAC. The high ammonia conversion obtained with Ru/CNTs catalyst was attributed to a great extent to the excellent electronic conductivity of the CNTs support [7].

CNT is a novel material of the carbon family and has been used extensively as catalytic support. The Co/CNTs catalysts [9, 10] demonstrate high catalytic activity in Fischer–Tropsch synthesis, which is attributed to high cobalt dispersion and its easy reducibility. Recently, ZHANG and co-authors [11] have reported high ammonia conversion and good catalytic stability with Co-promoted Fe/CNTs catalyst. It can be expected that the combination of cobalt with CNTs will lead to a good catalytic performance for ammonia decomposition.

**2. Experimental.** A cobalt catalyst was prepared via aqueous incipient wetness impregnation of multi-wall CNTs (-COOH groups 2.56 wt.%, Chengdu Ltd Company of Organic Chemistry, Academy of Science of China) with the aqueous and ethanol solutions of cobalt nitrate under vacuum condition. After impregnation, the catalysts were dried in nitrogen flow at 433 K for 1 h, and then calcined at 723 K for 5 h. The calcined cobalt catalyst on carbon nanotubes was denoted as CoCNTs. For the purpose of comparison, monometallic Fe and Ni catalysts supported on CNTs were also prepared by the same method, which were denoted as FeCNTs and NiCNTs respectively. The samples were characterized by temperature programmed reduction ($H_2$-TPR) and temperature programmed surface reaction ($NH_3$-TPSR). The catalytic performance for ammonia decomposition was evaluated in a fixed bed quartz reactor charged with 100 mg catalyst (particle size lager than 180 µm) at atmospheric pressure. Prior to the test, the sample was reduced in situ for 2 h with 25% $H_2/N_2$ mixture. Then the reactor was purged with $N_2$ for 1 h. The reaction temperature and space velocity were varied in the range from 673 to 773 K, and 6000 to 24 000 $h^{-1}$ respectively. The analysis of the effluent from the reactor was performed with an on-line Varian 450 gas chromatograph equipped with a Porapak-Q column and a thermal conductivity detector.

**3. Results and discussion.** The catalytic performances of CoCNTs, NiCNTs and FeCNTs catalysts for ammonia decomposition as a function of the temperature and space velocity are presented in Fig. 1. The different reaction temperature resulted in remarkable varieties of $NH_3$ conversion (Fig. 1a). The activity in terms of $NH_3$ conversion increased with reaction temperature, in agreement with the endothermic character of the $NH_3$ decomposition reaction. At 773 K, $NH_3$ conversion of CoCNTs, NiCNTs and FeCNTs catalysts were 60.8%, 25.4%
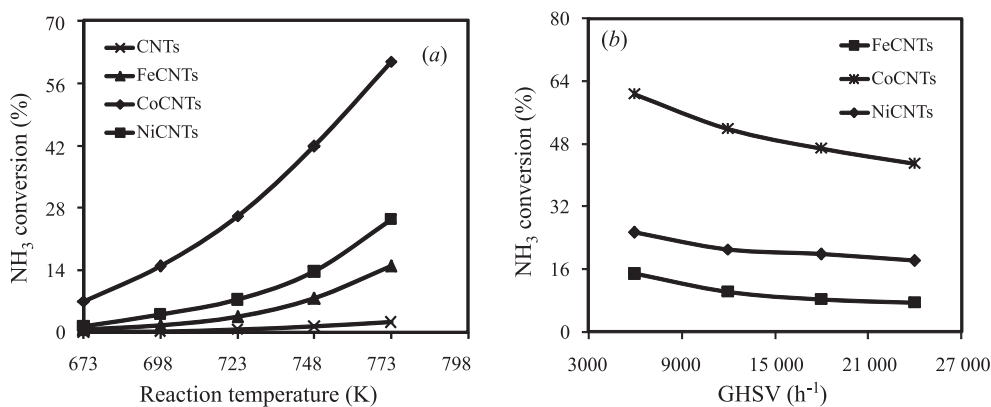
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Fig. 1. $NH_3$ conversion on CNTs supported catalysts: (*a*) at different reaction temperatures at $NH_3$ GHSV of 6000 $h^{-1}$; (*b*) at different $NH_3$ GHSV at temperature 773 K

and 14.8%, respectively. For CoCNTs catalyst, when the reaction temperature was fixed at 773 K, even at a space velocity as high as 12 000 $h^{-1}$, the ammonia conversion of CoCNTs was still as high as 51.9%. Further increase of space velocity to 24 000 $h^{-1}$ resulted in a slight decrease in ammonia conversion, as it is shown in Fig. 1*b*. A similar dependence on $NH_3$ conversion was observed over NiCNTs and FeCNTs catalysts. Table 1 shows a comparison of the activity of catalysts used in this work with those reported in the literature. Commercial Co-containing CNTs catalyst, reported by ZHANG [9], and catalysts containing Ni or Fe [7, 11] are less active to our catalyst. Cobalt-carbon nanotube catalyst prepared in this study by incipient wetness impregnation method showed superior activity to that of NiCNTs and FeCNTs.

The apparent activation energies Ea calculated by the Arrhenius equation are listed on Table 1. The apparent activation energies were calculated for data obtained at the following conditions: temperatures between 673 K and 773 K and GHSV of ammonia of 6000 $h^{-1}$. The Ea values of CoCNTs, NiCNTs and FeCNTs were 93.0 kJ/mol, 120.8 kJ/mol and 142.2 kJ/mol, respectively, which was consistent with the results that were reported by YIN and co-workers [1].

TPR data for cobalt reducibility in prepared CoCNTs catalysts are presented in Fig. 2. The $H_2$-TPR patterns on CoCNTs (curve *1*) show four hydrogen consumption peaks: (i) at temperature lower than 550 K; (ii) at temperature region of 550–650; (iii) at temperature region of 650–750 K; (iv) at temperature region higher than 750 K. The low temperature reduction peak below 550 K was due to the decomposition of residual nitrate species. The reduction peaks at 550–750 K were attributed to two-step reduction of $Co_3O_4$ to metallic cobalt that proceeded via intermediate formation of CoO [13–15]. The high temperature broad peak is a result of the gasification of carbon. This was confirmed by comparing the result of two consecutive experiments of $H_2$-TPR on CoCNTs, curves *1* and *2*. In the second experiment (curve *2*) only a high temperature peak is

Gaussian fitting curves results
Peak  Area  Centre  Width Height
1     3264.3540.65139.7418.639
2     1088.1606.4142.75120.308
3     2626.9690.0567.44631.076
4     19143 824.86177.0686.264

Intensity (a.u.)

(3)

(2)

(1)

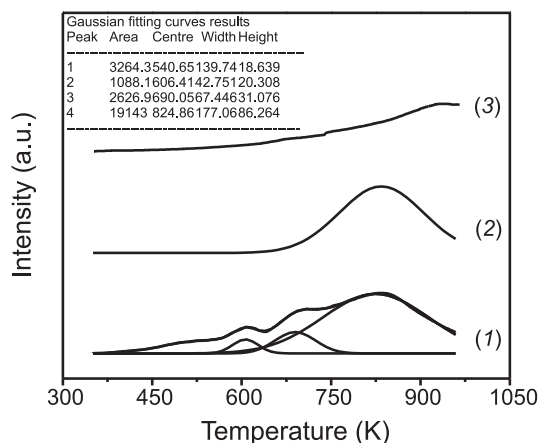300  450  600  750  900  1050
Temperature (K)

Fig. 2. $H_2$-TPR spectra of CoCNTs catalysts: (1) CoCNTs; (2) Second TPR scan of CoCNTs; (3) CNTs. The table in the figure shows the detailed results of the fitted curves by Gaussian method

observed. The hydrogen consumption peak at high temperature region for CNTs support (curve 3) was registered, but it had much lower intensity compared to that of CoCNTs catalyst. The intensity of the broad peak attributed to carbon gasification remained almost unchanged even at a second TPR scan of CoCNTs. Therefore, metallic cobalt seems to act as a catalyst for the methane formation at high temperature. After subtraction of the contribution of carbon gasification, the ratio of hydrogen consumption from peaks responsible for reduction of $Co_3O_4$ amount of metallic Co was 2.4, which was close to the value predicted from the stoichiometry of reactions (1) and (2)

(1)  $$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \quad (550{-}650\ K)$$

(2)  $$CoO + H_2 \rightarrow Co^0 + H_2O \qquad (650{-}750\ K)$$
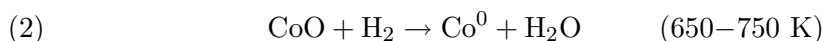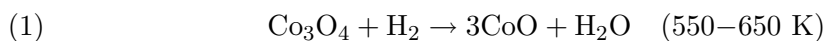
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Catalytic activity of CNTs supported transition metal catalysts for $NH_3$ decomposition

| Catalyst | Metal loading, wt% | Reaction temperature, K | GHSV, $h^{-1}$ | $NH_3$ conversion, % | Activation energy, ($E_a$, kJ/mol) |
|---|---|---|---|---|---|
| CoCNTs* | 5 | 773 | 6000 | 60.8 | 93 |
| CoCNTs* | 5 | 773 | 24 000 | 43.0 | — |
| FeCNTs* | 5 | 773 | 6000 | 14.8 | 142.2 |
| NiCNTs* | 5 | 773 | 6000 | 25.4 | 120.8 |
| CoCNTs[9] | 4.1 | 973 | 20 000 | 100 | — |
| FeCNTs[9] | 2.8 | 973 | 5000 | 75.1 | — |
| NiCNTs[7] | 2.8 | 773 | 30 000 | < 10 | 90.3 |
| FeCNTs[11] | 5 | 873 | 36 000 | ~ 45 | 147 |
| FeCNTs[7] | 2.7 | 773 | 30 000 | < 10 | 148.5 |

*result from this study

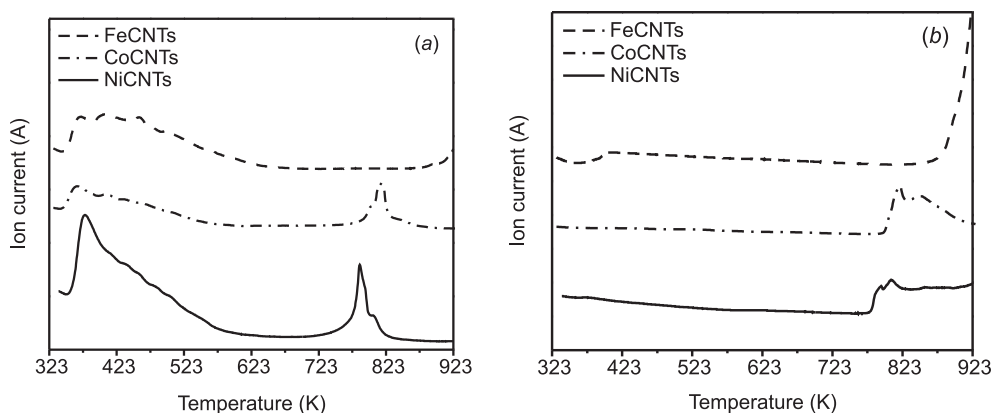*H. Zhang, Y. A. Alhamed, Y. Kojima et al.*

Fig. 3. $NH_3$ desorption (*a*) and $N_2$ formation (*b*) obtained from $NH_3$-TPSR spectra at a ramping rate of 10 K/min

TPR results showed that the formation of methane due to methanation of carbon at high temperature was possible in the presence of hydrogen. However, no $CH_4$ was detected under the operating conditions for catalytic tests performed in this study.

To evaluate the catalyst surface adsorption, reaction and desorption behaviour, temperature programmed surface reaction was performed (see Fig. 3). $NH_3$ desorption peaks occurred mainly in two regions: low temperature region (323–623 K) and high temperature region (higher than 723 K), which were respectively attributed to the physically and chemically adsorbed $NH_3$. In ammonia decomposition, the recombinative desorption of nitrogen atoms was considered as the rate limiting reaction step [1, 7]. Figure 3*b* shows the spectra of $N_2$ signals from $NH_3$-TPSR. From Figure 3*b*, the formation of $N_2$ occurred mainly around 823 K over CoCNTs and NiCNTs catalysts. The $N_2$ desorption peak intensity from CoCNTs was higher than that of NiCNTs catalyst. It indicated that the recombined desorption of nitrogen adatoms on the surface of CoCNTs catalyst became more facile.

**4. Conclusions.** In conclusion, we have prepared cobalt catalyst supported on CNTs, which exhibited a superior activity to those of Ni and Fe catalysts in ammonia decomposition.

The unique capacity of CNTs as electron reservoirs and the synergetic interaction between cobalt and CNTs seem likely to be the reasons responsible for high ammonia conversion over cobalt–carbon nanotube catalyst.

Further increasing of CoCNTs activity at low temperatures might be enhanced through the efficient design of cobalt-CNTs catalyst.

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