

Ammonia Decomposition to Hydrogen on Carbon Supported Cobalt Catalysts

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ABSTRACT

Multi-wall carbon nanotubes (CNTs) and three types of active carbon (AC) were used as supports for cobalt based catalysts. The catalysts were prepared by incipient wetness impregnation method. The activity of the prepared catalysts in ammonia decomposition (AD) was tested in a fixed-bed reactor microreactor. The reaction conditions were as follows: reaction temperature = 400-500°C, pressure = 1 atmosphere and GHSV = 6000 to 24000 h⁻¹. The prepared catalysts were characterized by N₂ adsorption-desorption (BET), Transmission electron microscopy (TEM) and CO chemisorption. It was found that for Co/AC catalysts, crystallite size decreased with increasing surface area of the AC support while their activity increased. On the other hand, Co/CNTs catalyst has a much higher activity than the Co/AC catalysts. The higher activity of Co/CNTs is attributed to higher electron donation ability of the CNTs.

Keywords: Cobalt catalysts, ammonia decomposition, hydrogen

1 INTRODUCTION

Liquid ammonia, as a hydrogen carrier, has the advantages of both high energy density and high hydrogen storage capacity (17.7%) [1]. This makes ammonia suitable for on-board generation of CO_x free hydrogen by catalytic ammonia decomposition (AD). Unfortunately, the obtained results from studies of this process have low potential to be applied in practice due to the difficulty of achieving a high degree of conversion of ammonia at the working temperatures of the fuel cells. Therefore, much efforts are needed to obtain more understanding about the AD reaction with the aim of developing a highly active at low temperature, stable and cheap solid catalysts for AD reaction [2-4]. Thus, the objective of this work was to explore the effect of support textural properties on the activity of cobalt based catalyst. For this purpose three types of activated carbon and a Multi-wall carbon nanotubes were selected for this study.

2 EXPERIMENTAL

2.1 Catalyst Preparation

Carbon supported cobalt catalysts were prepared by conventional incipient wetness impregnation of CNTs and three types AC using solutions of cobalt nitrate in water-ethanol mixture. After impregnation, the catalyst samples were dried at 80 °C under vacuum for 10 h followed by calcination at 450 °C for 5 h under nitrogen flow. The obtained samples were denoted as Co/CNTs for Co supported on carbon nanotubes, and Co/AC-1, Co/AC-2 and Co/AC-3 for those supported on AC. Cobalt loading of 5 wt % was always used for all studied catalysts.

2.2 Catalyst Characterizations

The specific surface areas, total pore volume and average pore diameter of carbon materials used were determined from N₂ adsorption/desorption isotherms at -196 °C, using an automated gas sorption system (Quantachrome NOVA 1000e apparatus). Before each measurement, the sample was degassed in vacuum at 300 °C for 3 h.

CO chemisorption experiments were performed at 40 °C using ChemBET Pulsar Automatic Chemisorption Analyzer (Quantachrome Instruments) equipped with a thermal conductivity detector (TCD). Measurements were commenced by loading the catalyst (100 mg) in the sample holder. The catalyst was initially reduced in hydrogen for 2 hours at 500°C followed by flushing with helium while gradually reducing the temperature to 40 °C till a stable baseline is obtained from the TCD detector. A number of successive pulses of a fixed amount of CO (37µL) were then introduced into the catalyst until saturation with CO is achieved as indicated by the TCD signal. The metal surface area and the average crystallite size were then calculated assuming the stoichiometry of CO:Co = 1:1.

The size of cobalt particles was also determined by transmission electron microscopy (TEM) using JEM 2011 (JEOL) instrument. The accelerating voltage was 200 kV. The samples were dispersed in ethanol assisted by ultrasonic technique. The average particle size are

calculated from 100 particles of different areas of each sample in TEM images.

2.3 Catalytic Activity Measurements

Ammonia decomposition was carried out in a microreactor unit (PID Eng&Tech, Spain) equipped with a quartz reactor. Prior to the reaction, 100 mg catalyst sample (125-180 μm particles size) was activated in flow of H_2/N_2 mixture (25 % H_2) at 500 $^\circ\text{C}$ for 2 h. After activation, NH_3 gas was introduced into the reactor at 400 $^\circ\text{C}$ for 1 h. The reaction conditions were as follows: reaction temperature = 400-500 $^\circ\text{C}$, pressure = 1 atm and GHSV= 6000 to 24000 h^{-1} . The analysis of the reactor effluent was made using an on-line GC-450 (Varian, USA) equipped with a thermal conductivity detector and a Poropak Q column. NH_3 conversion in an empty reactor and in reactor charged with CNTs and AC were negligible under the experimental conditions used in this study.

3 RESULTS AND DISCUSSIONS

3.1 Catalytic Activity

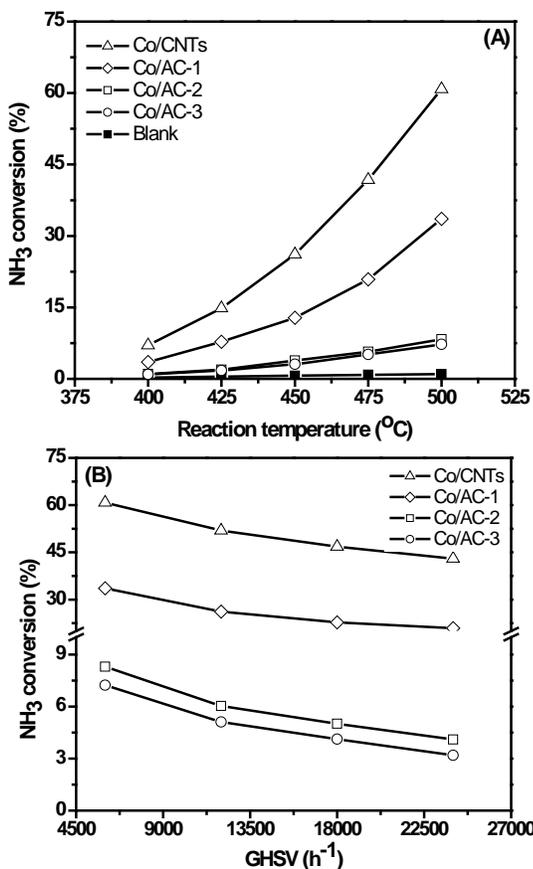


Figure 1: (A) Effect of reaction temperature on NH_3 conversion: NH_3 feed, GHSV= 6000 h^{-1} . (B) Effect of GHSV on NH_3 conversion (B): NH_3 feed, GHSV=6000 h^{-1} , reaction temperature = 500 $^\circ\text{C}$.

Figure 1 shows the effect of reaction temperature (A) and GHSV (B) on ammonia conversion for the different catalysts. Regardless of reaction temperature or GHSV, the activity of these catalysts are ranked in the following order: $\text{Co/CNTs} > \text{Co/AC-1} > \text{Co/AC-2} > \text{Co/AC-3}$. It should be noted that for AC supported catalysts, Co/AC-1 has the largest surface area and Co/AC-3 has the smallest surface area. The Co/CNTs catalyst shows a much higher activity compared to AC supported catalyst. Since NH_3 decomposition is endothermic, an increase in reaction temperature would result in an increase in NH_3 conversion as it is evident from Figure 1(A). NH_3 conversion over all the cobalt catalyst used decreases with the increase of space velocities as shown in Figure 1(B).

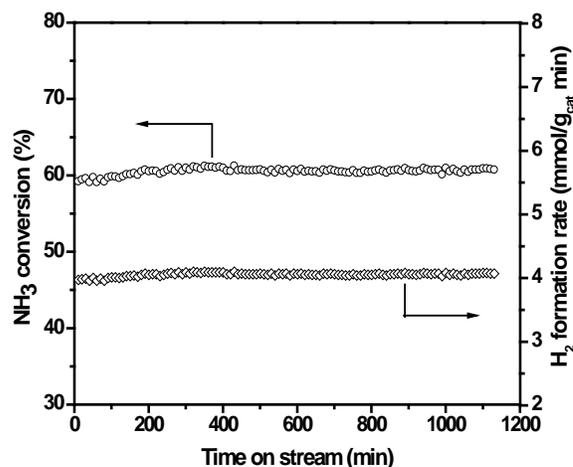


Figure 2: NH_3 conversion and H_2 formation rate with time on stream for Co/CNTs catalyst. Reaction conditions: 100 mg catalyst, NH_3 feed, GHSV=6000 h^{-1} , $T=500^\circ\text{C}$.

Furthermore, tests using the Co/CNTs catalyst shows an excellent stability of this catalyst as shown in Figure 2. Stability tests (Figure 2) performed at 500 $^\circ\text{C}$ and GHSV = 6000 h^{-1} shows that NH_3 conversion and H_2 formation rate were stable over a reaction time period of 1200 min.

3.2 Catalysts Characterization

3.2.1 Textural Properties of Supports

The specific surface area, pore volume and average pore diameter of the AC and CNTs supports are summarized in Table 1. The selected three types of AC have wide variation in their textural characteristics. The surface area and pore volume of AC-1 (2954 m^2/g , 1.6 cm^3/g , respectively), are much larger than that of the other two types of AC supports. AC-3 has the smallest surface area and pore volume (71.3 m^2/g and 0.08 cm^3/g , respectively) while its average pore diameter (4.51 nm) was the largest among the three types of AC used in this study. It should be noted that although the surface area of CNTs was much smaller than that for AC-2 (169.3 m^2/g compared to 695.2 m^2/g) their pore volumes

were exactly the same equal to $0.41 \text{ cm}^3/\text{g}$. Thus, as shown in Table 1, CNTs support is ought to have a larger average pore diameter of 9.65 nm compared to 2.37 nm for AC-2.

Support	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
CNTs	169.3	0.41	9.65
AC-1	2954.0	1.56	2.11
AC-2	695.2	0.41	2.37
AC-3	71.3	0.08	4.51

Table 1: Texture properties of carbon material used

3.2.2 Cobalt particle size

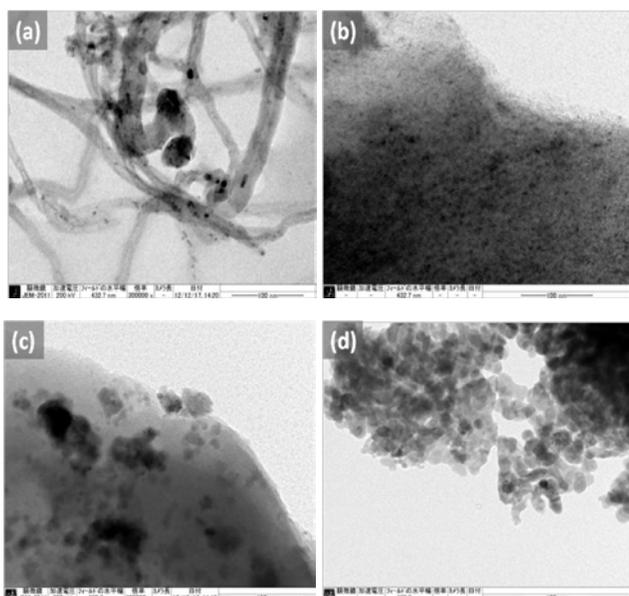


Figure 3: TEM images of cobalt catalysts supported on different carbon materials. (a)Co/CNTs; (b)Co/AC-1; (c)Co/AC-2;(d)Co/AC-3.

TEM images of cobalt catalysts supported on different carbon materials are shown in Figure 3. This figure shows that most of cobalt particles are dispersed on CNTs with average particle size of 4.8 nm. However, smaller cobalt particle size of 2.3 nm with narrower particle size distribution was observed on AC-1 support, which has the largest surface area among AC supports. For Co/AC-2 and Co/AC-3, the average size of cobalt particle was 19.9 nm and 21.4 nm, respectively. But some large cobalt clusters were also detected on the surface of AC-2 .

Catalyst	Co area $\text{m}^2/\text{g.cat}$	Co particle size, nm		Co dispersion %
		CO ads	TEM	
Co/CNTs	1.19	4.7	4.8	3.5
Co/AC-1	2.96	1.9	2.3	8.7
Co/AC-2	0.15	36.8	19.9	0.5
Co/AC-3	0.10	54.4	21.4	0.3

Table 2: Characteristics of Co crystallites

The metallic cobalt crystallites size was further characterized by CO pulse chemisorption at 40°C using the assumption of adsorption stoichiometric ratio of Co:CO =1:1. The results are displayed in Table 2. In agreement with TEM results, the Co/AC-1 catalyst gives the smallest cobalt crystallite size (1.9 nm) and the highest cobalt dispersion (8.7 %) among the four studied samples. The cobalt particle size and dispersion of Co/CNTs was 4.7 nm and 3.5 %, respectively. The metal surface area was $2.96 \text{ m}^2/\text{g}$, $0.15 \text{ m}^2/\text{g}$ and $0.10 \text{ m}^2/\text{g}$ for Co/AC-1, Co/AC-2 and Co/AC-3, respectively. The metal surface area of Co/CNTs was $1.19 \text{ m}^2/\text{g}$, which was lower than that of Co/AC-1, but higher than those of Co/AC-2 and Co/AC-3.

3.3 Discussion

3.3.1 Effect of Support Textural Properties on Cobalt Particle Size

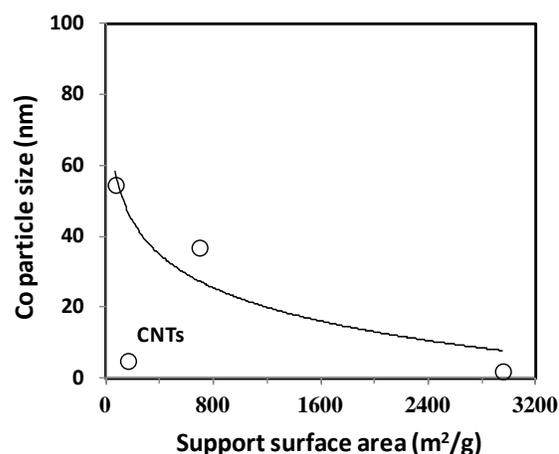


Figure 4: Relationship between support surface area and cobalt particle size based on CO chemisorption

Figure 4 depicts the dependence of cobalt particle size determined from CO adsorption measurements on surface area of the carbon used. Referring to Figure 4, it is clear that cobalt particle size decreases with the increase in surface area of AC support used. Although CNTs has a lower surface area compared to AC-2, smaller cobalt particle size was detected on CNTs than that on AC-2.

3.3.2 Relationship Between Structure and Catalytic Activity

In Figure 5, the NH_3 conversion is plotted versus the cobalt particle size. Going from 54.4 nm (Co/AC-3) to about 1.9 nm (Co/AC-1), the NH_3 conversion increases from 7.2% to 33.6%. The increasing catalytic activity of AC supported Co catalysts correlates well with the decreasing Co particle size, which means that these changes are result of the increased number of active centers.

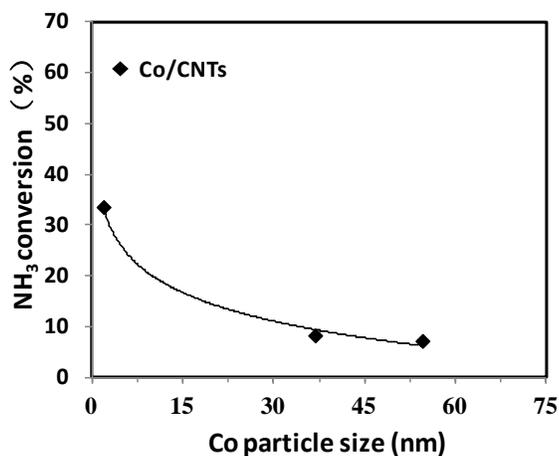


Figure 5: Co particle size effect on catalytic performance for NH_3 decomposition: NH_3 feed, GHSV= 6000 h^{-1} , reaction temperature = 500 $^\circ\text{C}$.

Compared to the AC supported catalysts, Co/CNTs catalyst shows completely different catalytic behavior. Although it has a larger Co particles size than the most active Co/AC-1 catalyst, it exhibits a much higher catalytic activity. The higher activity of the Co/CNTs catalyst may be attributed to the different structure and electronic properties of CNTs. It is established in literature [1,5] that N_2 desorption is the slowest step in the ammonia decomposition reaction. The strong interaction between cobalt and the carbon naotubes support and its electron donation ability seems to facilitate a much faster and easier N_2 desorption and thus a higher catalytic activity [6].

4 CONCLUSIONS

Co/CNTs exhibited much higher catalytic activity in ammonia decomposition than Co supported on AC catalysts. The higher activity of Co/CNTs could be attributed mainly to the electron donation ability of the CNTs support.

Cobalt supported on AC have good activity for ammonia decomposition. The catalytic activity is mainly a function of cobalt particle size supported on AC. Catalysts with smaller Co particle size have higher catalytic activity. Cobalt dispersion is influenced primarily by the surface area of the AC used, where large surface area AC leads to small size of cobalt nanoparticles.

Thus, the future design of highly efficient cobalt catalyst for ammonia decomposition should be focused on decreasing cobalt particles size and combining this effect with the electronic properties of support used.

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