Magnesia–carbon nanotubes (MgO–CNTs) nanocomposite: novel support of Ru catalyst for the generation of CO_x-free hydrogen from ammonia

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Magnesia–carbon nanotubes (abbreviated as MgO–CNTs) nanocomposites were prepared by impregnation of CNTs with $Mg(NO_3)_2 \cdot 6H_2O$ in ethanol solution, followed by drying at 353 K and calcination at 873 K, respectively. The nanocomposites are thermally more stable than CNTs in a H_2 flow. The use of the nanocomposites as support yielded more efficient Ru catalysts for the generation of CO_x-free hydrogen from NH_3 decomposition.

KEY WORDS: magnesia–carbon nanotubes nanocomposite; ruthenium catalyst; ammonia decomposition; hydrogen manufacture.

For high energy-conversion efficiency and pollution-free exhaust, the proton exchange membrane fuel cells (PEMFC) have attracted much attention [1–3]. For the commercialization of PEMFC, obstacles related to hydrogen purity and storage has to be overcome [4–8]. On-site generation of H_2 by ammonia decomposition appears to be an attractive route in terms of energy storage and economical benefit [9–13]. Especially, this process produces no CO_x ($x = 1, 2$) that degrades the cell even at extremely low concentration. However, catalytic activities of the catalysts in the literature were low even at 873 K [9–14]. Recently, we found that a Ru catalyst using carbon nanotubes (CNTs) as support is a competitive catalyst for the decomposition reaction [15]. We ascribed the excellent catalytic performance of the Ru/CNTs catalyst to high Ru dispersion, and to high graphitization and purity of the CNTs material. Although the discovery extends the application of CNTs in heterogeneous catalysis, there are disadvantages in the use of CNTs in this reaction, e.g. high cost, methanation, and the presence of electron-withdrawing surface groups (such as —OH and —COOH). In addition, the activity of the Ru/CNTs catalyst is still far from industrial requirement. Much work is still needed to develop a highly efficient and low-cost decomposition catalyst. In a separate study, we discovered that support basicity is a necessity for efficient performance of Ru catalysts in NH_3 decomposition, and MgO is a promising support in terms of TOF [16]. Moreover, unlike alkali or alkaline earth oxides or hydroxides, MgO is very stable and does not react with the Cl ions originated from the $RuCl_3$ precursor [16], and it is easier to remove the Cl inhibitor from the support. In view of the advantages of MgO and CNTs, we prepared the MgO–CNTs nanocomposite and used the material as a support for Ru catalysts. In this letter, we report the performance of this new class of catalysts for NH_3 decomposition.

The MgO–CNTs nanocomposite samples were prepared according to the following steps. An appropriate amount of CNTs, as that described in previous study [15], was added to a solution of ethanol and $Mg(NO_3)_2 \cdot 6H_2O$ (Analytic grade, Aldrich Chemical Company Inc.). After 1 h of stirring, the suspension was dried at 353 K and calcined at 873 K in an Ar flow, respectively. The chemical composition of MgO–CNTs could be adjusted by varying the ratio of $Mg(NO_3)_2 \cdot 6H_2O$ to CNTs. The Ru/MgO–CNTs and the KNO_3–modified Ru/MgO–CNTs catalysts were prepared according to the procedures described in our earlier report [15]. In this paper, the mass (or weight) ratio of MgO–CNTs was bracketed and placed after "CNTs" in sample codes. The Ru loadings of the above-mentioned catalysts were 4.81×10^{-4} mol per g-catalyst (4.85 wt%) and the molar ratio of K–Ru in the KNO_3-modified Ru samples was **2**.

Catalytic testing and product analyses were similar to those described previously [15]. The gas hourly space velocity ($GHSV_{NH3}$) was 60,000 mL/(h · g-cat). Prior to the reaction the catalysts were reduced *in situ* in a

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25%-H_2/Ar flow at 773 K for 2 h, and then flushed with a flow of pure Ar. The reaction temperature was in the range of 623–773 K. We found that NH_3 conversion in a blank reactor or over the individual supports was less than 1.0% at 773 K.

Powder X-ray diffraction (XRD) experiment was conducted on a Rigaku Automatic Diffractometer (Rigaku D-MAX) with monochromatized CuK_α radiation ($\lambda = 0.15406$ nm) at a setting of 40 KV and 80 mA. HRTEM images were taken on FEI TECNAI Field Emission HRTEM at 300 KV. Temperature-programmed desorption of hydrogen (H_2-TPD) was employed to measure the adsorption capacity of the reduced Ru catalysts. The experiment was carried out in a home-built device using thermal conductivity detector. The temperature-programmed hydrogenation (TPH) analysis was conducted on a MSC-200 quadrupole mass spectrometer from Balzer Company, Ltd.

Shown in figure 1 are the XRD patterns of the Ru catalysts after H_2-reduction. There are characteristic peaks related to CNTs and MgO in all the Ru/MgO–CNTs catalysts. The peak intensity ascribed to CNTs (2θ: 26.02°, 43.96°) decreases while that related to MgO (2θ: 36.9°, 42.9°, 62.3°) increases with an increase in MgO/CNTs ratio. In addition, Ru/CNTs, Ru/MgO–CNTs(1:3), and Ru/MgO–CNTs(1:1) show no clear diffraction signals attributable to Ru particles (2θ: 38.38°, 42.15°, 44.02°), showing that the Ru particles are highly dispersed on these supports. However, when the MgO/CNTs mass ratio is increased to **3** (at 25 wt% CNTs), the supported catalyst exhibits characteristic diffraction lines of Ru crystallites. Much stronger signals related to Ru entities were observed on Ru/MgO catalyst at 0 wt% CNTs, suggesting that excessive MgO shows negative effect on Ru dispersion. TEM results (figure 2) revealed that the size range of MgO is 20–100 nm while that of Ru particles on the nanocomposite MgO–CNTs(1:1) support is 2–7 nm, similar to that of Ru/CNTs (2–6 nm) but smaller than that of Ru/MgO (2–15 nm) [15]. Moreover, the Ru particles on CNTs and MgO show no significant difference in size (figure 2), implying that the nanocomposite is not a simple mixture of CNTs and MgO, but rather a special material composed of strongly interacting CNTs and MgO. Despites a slight decline with increase in MgO/CNTs ratio, the H_2-uptake over Ru/MgO–CNTs(1:1) (48.2 μmol/g), measured as desorbed H_2 in the H_2-TPD experiment, is similar to those observed over Ru/CNTs (49.2 μmol/g) and Ru/MgO-CNTs(1:3) (49.1 μmol/g). Over Ru/MgO–CNTs(3:1) and Ru/MgO, the uptakes were 33.2 μmol/g and 20.6 μmol/g, respectively. The H_2-TPD results are in agreement with those of XRD and TEM. We consider that the high dispersion of Ru is a combined result of the high surface area and the existence of surface functional groups (—OH, —COOH) in CNTs, and the interaction between CNTs and MgO. Those functional groups of the CNTs component (CNTs defects) may act as bridges for chemical interactions between MgO and CNTs.

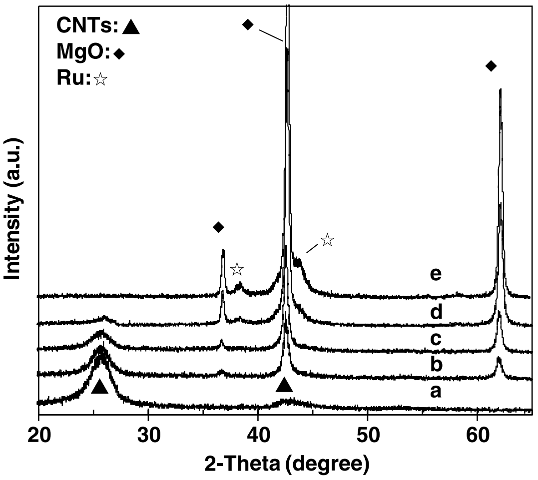

Figure 1. XRD pattern of Ru/MgO–CNTs catalysts with different amounts (wt%) of CNTs in the MgO–CNTs supports: (a) 100%, (b) 75%, (c) 50%, (d) 25%, and (e) 0%. (Ru loading = 4.8%).

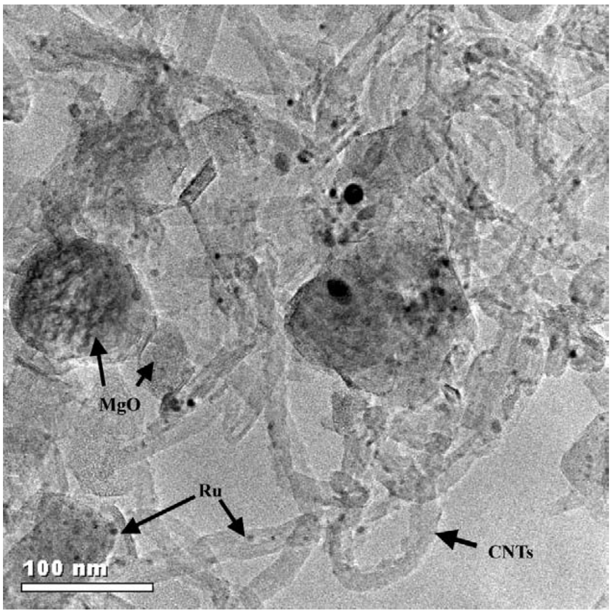

Figure 2. TEM image of Ru/MgO–CNTs(1:1).

In view of the fact that methanation of carbon materials takes place in H_2 flow at high temperatures [17], and would cause sintering of active component, we investigated the thermal stability of MgO–CNTs by comparing the TPH behaviour of MgO–CNTs with that of "pure" CNTs. One can see from figure 3 that for the "pure" CNTs, the onset temperature for the methanation reaction was ca. 700 K; this temperature shifted to ca. 800 K over MgO–CNTs(1:1). Taking the slope of the steep line segment as a representation of the inherent rate of the methanation reaction, we found that the rate of MgO–CNTs(1:1) was just 1/4 that of the "pure" CNTs. The comparison of K–Ru/CNTs and K–Ru/MgO–CNTs(1:1) in terms of either onset methanation

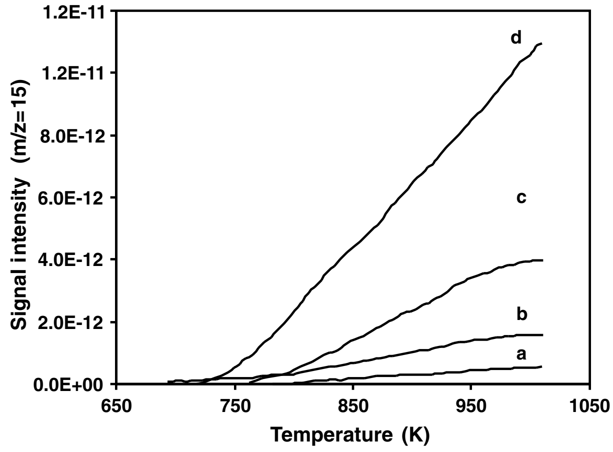

Figure 3. Temperature-programmed hydrogenation (TPH) results of (a) MgO–CNTs(1:1), (b) CNTs, (c) K–Ru/MgO–CNTs(1:1), and (d) K–Ru/CNTs (sample loading = 0.1 g).

temperature or methanation rate reveals that the latter is thermally much more stable than the former. Hence, the introduction of MgO reduces the reactivity of CNTs toward hydrogen, and enhances its thermal stability. We believe that the stabilization of CNTs in the nanocomposites is a consequence of the MgO–CNTs interactions that may happen through reactions between the functional groups of CNTs and MgO.

Shown in figure 4 are the effects of MgO/CNTs ratio on NH_3 conversion and H_2 formation over the Ru/MgO–CNTs and K–Ru/MgO–CNTs catalysts. At 673 K, the NH_3 conversions over Ru/CNTs and Ru/MgO are only 8.8% and 7.3%, respectively, while a maximum conversion of 12.7% appears at the MgO/CNTs ratio of **1**. Since the space velocities of NH_3 used in the catalytic evaluations were identical, the change of H_2 formation rate versus MgO/CNTs ratio followed the same trend of NH_3 conversion. We used KNO_3 to modify the Ru catalysts, and the reaction data are also depicted in figure 4. Obviously, the modification with KNO_3 resulted in significant improvement in catalytic activity, and the trend of activity variation versus MgO/CNTs ratio over K–Ru/MgO–CNTs is similar to that over Ru/MgO–CNTs. Moreover, the modification effect of KNO_3 on the catalytic activity of Ru/MgO–CNTs is similar to that of Ru/CNTs, but much higher than that of Ru/MgO [16]. We hence deduce that the combination of MgO and CNTs leads to an improvement in catalytic activity of Ru and the K-modified Ru catalyst. The results of many research works disclosed that N_2 desorption is the rate-determining step in NH_3 decomposition and is dependent on the employed supports [9,16,18]. Aika *et al.* proposed a mechanism where electrons are transferred from support to Ru, inducing a decrease in the ionization potential of Ru [19]. Thus, we consider that the use of the MgO–CNTs support is beneficial for the combinative desorption of surface nitrogen atoms, a consequence of a change in electronic structure of Ru due to the nanocomposite nature of the support.

Finally, the effects of reaction temperature on the catalyst activity and stability were investigated and the results are shown in figures 5 and 6. At 623 K, NH_3 conversion is 39%, and the H_2 formation rate is 26.1 mmol/(min · g-cat) over the K–Ru/MgO–CNTs(1:1) catalyst, clearly higher than those over K–Ru/CNTs, respectively. Since NH_3 decomposition is endothermic ($\Delta H = 11$ kcal/mol), a raise of reaction temperature would result in NH_3 conversion enhancement [10]. At 723 K, NH_3 was not detected in the effluent, and we observed that the catalytic performances remained unchanged within a reaction period of tens of hours, demonstrating that the catalysts are very stable (figure 6). Although we detected no decrease in activity over both the K–Ru/MgO–CNTs(1:1) and K-Ru/CNTs catalysts within the period of the present investigation (figure 6), we consider that the K-Ru/MgO-CNTs(1:1) catalyst is more stable due to the fact that compared with K-Ru/CNTs, it is less reactive in a H_2 flow (figure 3). On the other hand, MgO by itself is a well-known solid base [20], and support basicity is usually required for enhancing the activity of Ru catalyst for the decomposition/synthesis of NH_3 [9,16,21]. In our earlier work, we showed that due to higher dispersion of Ru metal and higher degree of graphitization of CNTs support, the Ru supported on CNTs exhibited activity higher than that supported on activated carbon for ammonia decomposition [15,16]. We now ascribe the high performance of the K–Ru/MgO–CNTs catalysts to a combined effect of high graphitization and surface area of CNTs, basicity of MgO, and MgO–CNTs interactions. Further studies are needed to disclose the exact nature of the interactions between MgO and CNTs, and the reaction Kinetics of NH_3 decomposition.

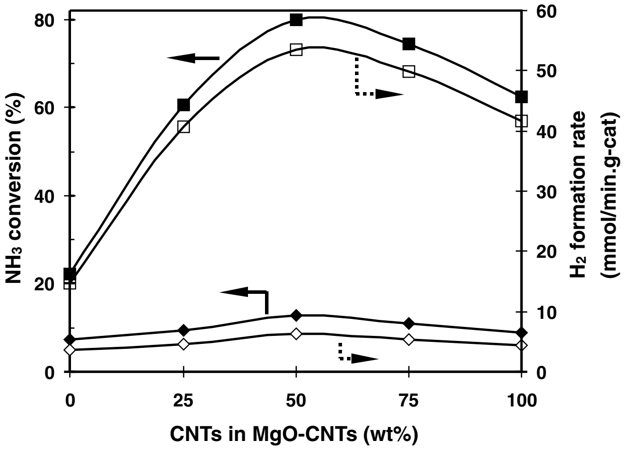

Figure 4. Effect of CNTs percentage (wt%) on NH_3 conversion (solid symbols) and H_2 formation rate (hollow symbols) over Ru/MgO–CNTs (◆,◇) and the K–Ru/MgO–CNTs (■,□) catalysts [Reaction temperature: 673 K, $GHSV_{NH_3} = 60{,}000$ mL/(h · g-cat)].

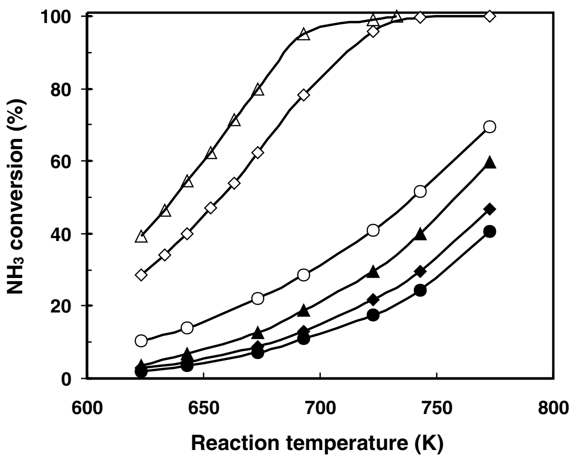

Figure 5. NH_3 conversion versus reaction temperature over Ru/CNTs (◆), K–Ru/CNTs (◇), Ru/MgO–CNTs(1:1) (▲), K–Ru/MgO–CNTs (1:1) (△), Ru/MgO (●), K–Ru/MgO (○) catalysts [$GHSV_{NH_3} = 60{,}000$ mL/(h · g-cat)].

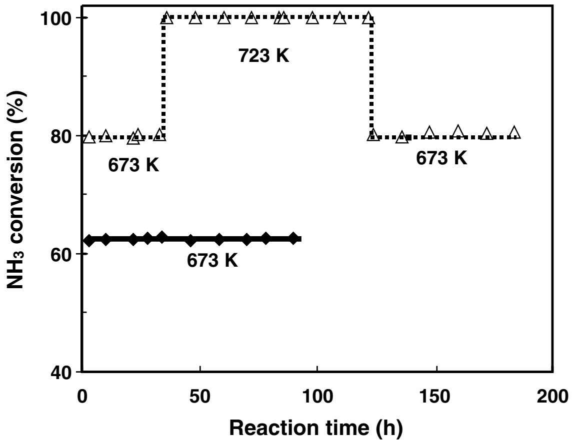

Figure 6. Catalytic stability of K–Ru/MgO–CNTs(1:1) (△) and K–Ru/CNTs (◆) [$GHSV_{NH_3} = 60{,}000$ mL/(h · g-cat)].

In conclusion, the present data show that impregnation of CNTs with $Mg(NO_3)_2 \cdot 6H_2O$ in ethanol solution followed by calcination resulted in the formation of MgO–CNTs nanocomposites. The nanocomposite is thermally more stable and less reactive toward hydrogen than "pure" CNTs. The Ru catalyst supported by the nanocomposite exhibits higher dispersion, and higher catalytic activity for NH_3 decomposition as compared to that of Ru supported by MgO; a maximum activity appears when the MgO/CNTs weight ratio is 1. The high activity is ascribed to a combined result of the high graphitization and surface area of CNTs, basicity of MgO, and interaction between CNTs and MgO. The results of this study not only reveal a novel support for the development of highly efficient catalyst for on-site generation of hydrogen from ammonia, but may also open a new route for CNTs utilization.

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