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Evaluation of carbon nanotubes produced from toluene steam reforming as catalyst support for selective catalytic reduction of NOx

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Abstract: There is current interest in developing low cost, effective catalysts for the low temperature selective catalytic reduction (SCR) of nitrogen oxides (NOx). In this work, we have applied carbon nanotubes (CNTs), produced as a by-product of hydrogen production from the steam reforming of toluene (as a representative hydrocarbon), as a catalyst support for a V_2O_5-WO_3 catalyst for SCR of NOx. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis showed well dispersed metals on the surface of the CNTs. The V_2O_5-WO_3/CNT catalyst has exhibited NOx reduction efficiency higher than 95% at reaction temperatures between 340 and 400 °C. However, there was a low NOx reduction at SCR reaction temperature of less than 200 °C which is suggested to be due to the lack of Lewis acid sites, as determined from NH_3-TPD (temperature program desorption) analysis. Future work to lower the SCR reaction temperature with high NOx efficiency is suggested.

Key words: SCR, Carbon nanotubes, catalyst, reforming

1. Introduction

Carbon nanotubes (CNTs) are a material that has extraordinary mechanical, thermal and electrical properties. They have been studied for a wide range of applications in areas such as fuel cells [1, 2], composite materials [3, 4], hydrogen storage [5, 6], and nitrogen oxides (NOx) reduction[7-9]. Among these applications, selective catalytic reduction (SCR) of NOx (SCR) with NH_3 is of current interest due to the environmental impact of NOx from industrial processes [10].

Most of the SCR research has focused on developing efficient catalysts [11-13]. V_2O_5-WO_3/TiO_2 is a known catalyst used for the commercial process of SCR in the presence of ammonia between 300 and 400 °C. Currently, research efforts seek to promote V_2O_5-WO_3/TiO_2 [14, 15] catalytic activity in terms of NOx reduction at reaction temperatures lower than 200 °C, where the location of the SCR unit can be after gas cleaning. Therefore, although V_2O_5-WO_3-based catalysts are commercialised, there is interest in the development of novel supports to promote the understanding of the catalyst performance in relation to the SCR process.

We have previously produced multi-walled CNTs with the co-production of hydrogen from catalytic reforming of toluene as a model compound of waste hydrocarbons [16]. Hydrogen produced from steam reforming of waste hydrocarbons has extensive applications e.g. fuel cells [17, 18]. However, evaluation of by-product CNTs is also important to increase the economic feasibility of the steam reforming process. Thus, this work studied the produced CNTs as catalyst support for the SCR application.

2. Experimental

2.1. Catalyst preparation

Multi-walled carbon nanotubes (CNTs) were produced from steam reforming of toluene (model compound of waste hydrocarbons) [16]. CNTs were purified by heating in an atmosphere of air at 500 °C for 1 h, and were further washed with nitric acid solution (2 mol L^{-1}) at 60 °C for 1h. The washed CNTs were filtered and dried at 110 °C for 24h. V_2O_5-WO_3/CNTs catalyst was prepared by impregnation with solutions of NH_4VO_3 and $N_5H_{37}W_6O_{24}\cdot H_2O$ solution to obtain loadings of 2 wt.% V_2O_5 and 6 wt.% WO_3. The precursor of the catalyst was dried at 105 °C for 6 h and calcined at 450 °C for 3h in an atmosphere of N_2.

2.2. SCR reaction system

SCR tests using the V_2O_5-WO_3/CNTs were carried out in a fixed-bed reactor at atmospheric pressure. The schematic diagram was shown in our previous report [19]. Model gases (NO 0.06 Vol.%, NH_3 0.06Vol.% and O_2 3 Vol.% balanced with N_2) were introduced into the reaction system with a total flow rate of 300 ml min^{-1}, where 0.5 g of V_2O_5-WO_3/CNTs catalyst was located. The experimental temperatures investigated were from 180 to 440 °C. The NO concentration was analysed by a Flue Gas Analyzer (KM900; Kane International Ltd.). The NO conversion was calculated as follows:

$$\text{NO} \quad \text{conversion}(\%) = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outler}}}{[\text{NO}]_{\text{inlet}}} \times 100\%$$

Where $[NO]_{inlet}$ is the introduced NO concentration, Vol.%; $[NO]_{outlet}$ is the NO concentration of the exit of the reactor, Vol.%.

2.3. Catalyst characterization

X-ray diffraction (XRD), D/Max-2500 diffractometer (Rigaku Co., Japan) with monochromatized Cu Kα radiation (λ =1.5405 Å), was used to obtain the crystal structure of the fresh catalyst. Temperature-programmed desorption (TPD) of NH_3 using a thermo-gravimetric analyzer (TGA) (TP5080, XQ-instrument) was used to determine total acidity and acid distribution. The fresh catalysts were also characterized by a scanning electron microscopy (SEM) (FESEM, Zeiss Ultra+) and a transmission electron microscopy (TEM) (Philips CM120).

3. Results and discussion

SEM analysis of the catalyst support, CNTs and V_2O_5-WO_3/CNTs was carried out and are shown in Fig. 1. CNTs with lengths of more than 10 µm were obtained. Metal particles could be observed from the V_2O_5-WO_3/CNTs catalyst (Fig. 1(b)), while the walls of the CNT support (Fig. 1(a)) seemed to be clear of particles. Further analysis using TEM for the fresh V_2O_5-WO_3/CNTs catalyst are shown in Fig. 2. The figure shows that the diameter of the

CNTs used in this work was around 50 nm. In addition, metal particles with size around 8 nm could be observed. Su et al. [9] reported a Mn/CNTs catalyst for SCR experiment; where Mn particles with size around 8 nm were loaded on the CNTs with diameters around 50 nm from the TEM analysis. In addition, similar TEM results were also presented by Huang et al. [20] using V_2O_5/CNTs as SCR catalyst, metal size around 10 nm deposited on CNTs with diameter ranges from 10 to 100 nm.

The XRD analysis, shown in Fig. 3, showed the presence of V_8C_7 and V_2O_3. Tungsten oxides were not identified from the XRD analysis. This might be due to the particle size of tungsten oxides being too small to be detected [21]; also indicating well dispersed WO_3 particles on the catalyst [22].

Fig. 4 shows the result of NH_3-TPD analysis. One main NH_3 adsorption peak was observed at around 180 °C, indicating a majority of weak Brønsted acid sites [23] present on the surface of the catalyst; and Lewis acid sites [23] are suggested to be minor in the catalyst system, as only weak NH_3 desorption was observed at around 550 °C.

SCR results in the presence of the V_2O_5-WO_3/CNTs are shown in Fig. 5. It is shown that NOx reduction efficiency was increased with the increase of reaction temperature from 180 to 360 °C and reduced with the further increase of temperature to 440 °C. For example, 47.5 % NOx reduction was obtained at 360 °C, and higher than 90 % NOx reduction was obtained between 340 to 420 °C. NOx reduction was slightly reduced at the reaction temperature of 440 °C. The high efficiency of NOx reduction around 360 °C seems to be common for the V_2O_5/TiO_2 catalyst [20, 24].

V_2O_5-V_2O_3 based catalyst with CNTs as a support which was produced from the reforming of hydrocarbons (from toluene as a representative model hydrocarbon) has been examined as a SCR catalyst. From the characterization of the catalyst using XRD, SEM and TEM, the V_2O_5-WO_3/CNTs catalyst shows well dispersed metal oxides on the CNTs with CNT diameters around 50 nm and length up to 10 um. The catalyst showed higher (>95% NOx reduction) activity in the temperature range from 340 to 420 °C. The results indicate that the CNTs produced from our previous work [16] are effective for SCR at the middle temperature window (300-400 °C). However, the study shows that the prepared catalyst shows less potential for SCR at temperatures lower than 200 °C.

There are many efforts to reduce the SCR temperature to be lower than 200 °C, as this working temperature could be located downstream of the gas cleaning systems such as sulphur and particulate control. In this work, the low NOx reduction efficiency at temperatures lower than 200 °C in the presence of the V_2O_5-WO_3/CNT catalyst might be due to the lack of Lewis acid sites in the catalyst (as shown by the NH_3-TPD analysis), which has been reported to be responsible for the SCR at lower reaction temperature [20]. As proposed, the Lewis acid sites provide reactions path for NH_3 and NO to generate intermediate NO_2 which will produce N_2 and H_2O [20].

The application of CNTs, as a by-product of hydrogen production from the steam reforming of waste hydrocarbons is important for the commercialisation of steam reforming process. Such cost-effective CNTs production will have advantages for the SCR process, compared with commercial TiO_2 material. In addition, carbon materials can be generated from renewable materials such as biomass-related hydrocarbons [25] or waste materials e.g. plastics [26]. Therefore, exploration of low-cost CNTs for SCR application is meaningful for a sustainable future development. However, further investigation of the by-product CNTs as SCR catalyst support is suggested, especially in low temperature (less than 200 °C) applications.

5. Conclusions

Carbon nanotubes (CNTs) prepared as a by-product from the steam reforming of toluene (a model compound of waste hydrocarbons) was used as a catalyst support for V_2O_5-WO_3 for an investigation of selective catalytic reduction (SCR) of NOx. The V_2O_5-WO_3/CNTs, with well dispersed metal particles, showed high NO reduction (>90 %) at reaction temperatures between 340 and 420 °C. However, further investigation of the CNTs as catalyst support is suggested for the determination of SCR for NOx at lower reaction temperatures of <200 °C.

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Figure Captions:

Fig. 1 SEM analysis of (a) CNTs and (b) V_2O_5-WO_3/CNTs (b)

Fig. 2 TEM result of the fresh V_2O_5-WO_3/CNTs catalyst

Fig. 3 XRD analysis of the fresh V_2O_5-WO_3/CNTs catalyst; ▽ : C ● : V_8C_7

Fig. 4 NH_3-TPD analysis of the fresh V_2O_5-WO_3/CNT catalyst

Fig. 5 NOx reduction efficiency at temperature in the presence of the V_2O_5-WO_3/CNT catalyst

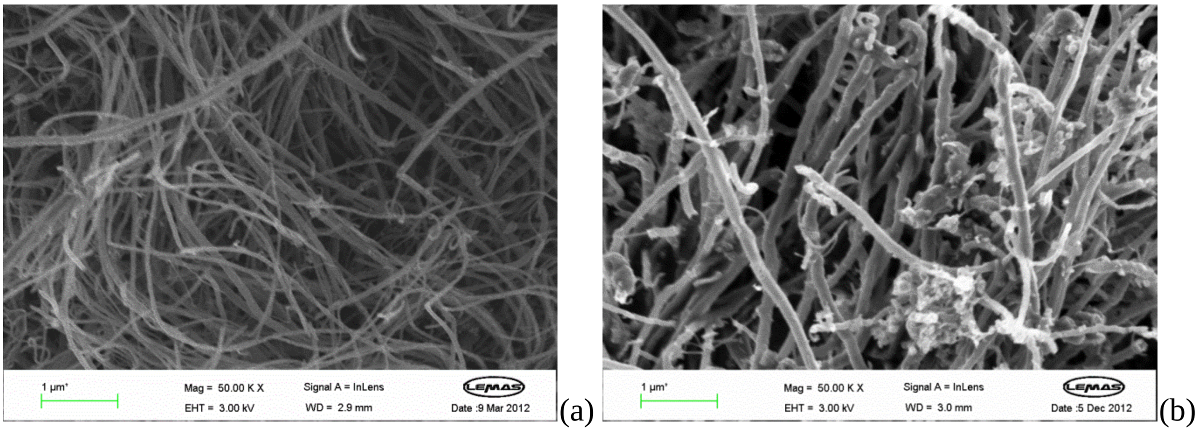

Fig. 1 SEM analysis of (a) CNTs and (b) V_2O_5-WO_3/CNTs (b)

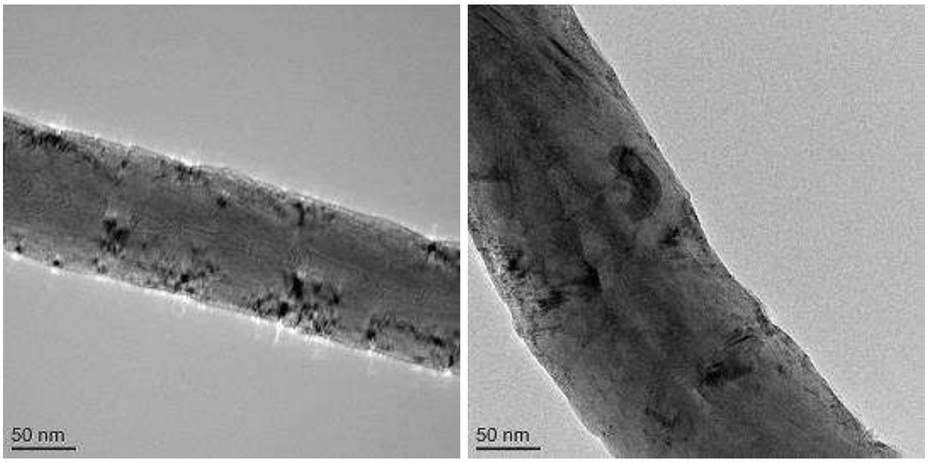

Fig. 2 TEM result of the fresh V_2O_5-WO_3/CNT catalyst

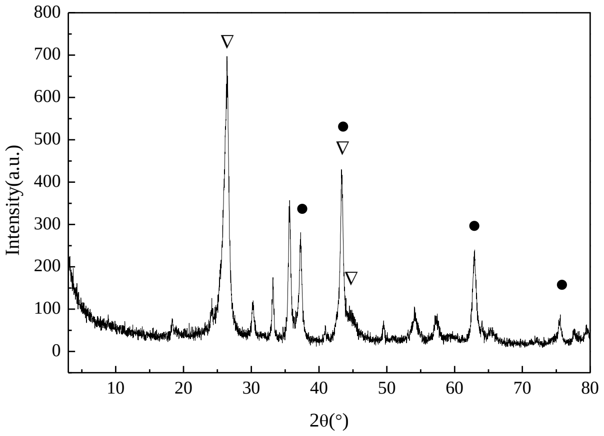

Fig. 3 XRD analysis of the fresh V_2O_5-WO_3/CNTs catalyst; ▽ : C ● : V_8C_7

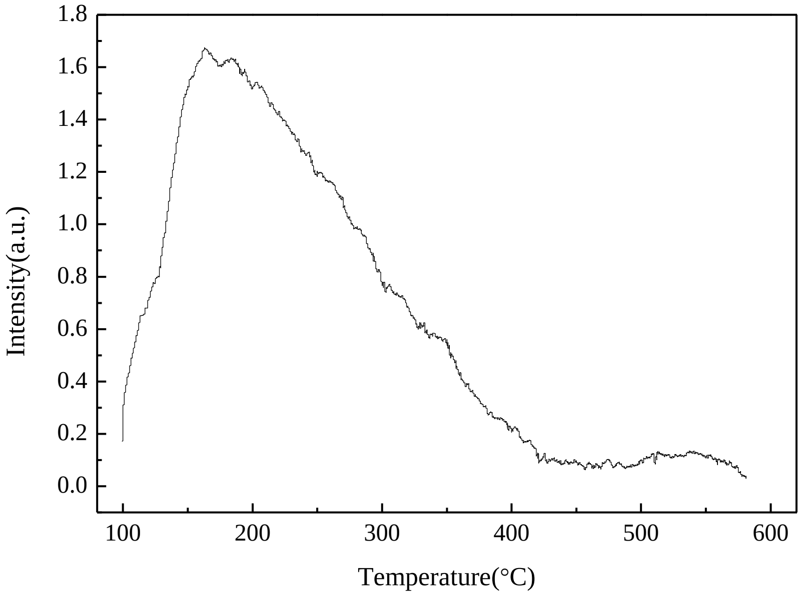

Fig. 4 NH_3-TPD analysis of the fresh V_2O_5-WO_3/CNT catalyst

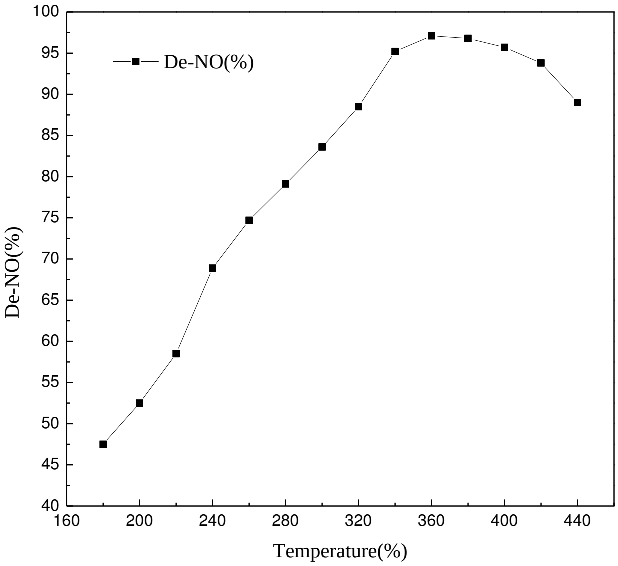

Fig. 5. NOx reduction efficiency in relation to temperature in the presence of the V_2O_5-WO_3/CNT catalyst