Carbon nanotubes supported Ni catalyst and the application to steam reforming bio-sourced glycerol

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Abstract: The carbon nanotubes supported Ni based catalysts were prepared by wetness impregnation method, and characterized by XRD, TEM and H_2-chemisorption to study the crystalline phase, morphology and the dispersion of metal active sites. The results showed that the crystallite size increased after reaction, which was also evidenced by TEM. The catalytic results for the glycerol steam reforming showed the effect of dispersion which was determined by chemisorption.

Keywords: Hydrogen product, Carbon nanotubes, Glycerol.

1. Introduction

The combustion of the fossil resources usually accompanies the CO_2 emission, which may have a profound influence on climate change [1]. Hydrogen is considered as an absolute clean energy as water is the unique product during its thermal combustion. However, current hydrogen is mainly from the petroleum refinery, meaning its non-sustainability and the CO_2 emission during the production process [2]. In the context glycerol as a by-product of biodiesel industrial has emerged great interests as an alternative hydrogen source because of its high hydrogen content, nontoxicity and convenience in transportation [3, 4]. The transition metal Ni are most commonly studied due to its high activity in breaking C-C/C-H bonds and low cost [5], which usually suffered from the coke deposition and thus resulting in deactivation. In this work, the NiO was dispersed on carbon nanotubes (CNTs) to improve the catalytic performances as the CNTs possesses excellent properties in electrical conductivity, impressive mechanical and thermal stabilities *etc*.

2. Experimental

The commercial obtained CNTs was firstly functionalized by refluxing it in concentrated HNO_3 and then was used to disperse the NiO through a wetness impregnation process, the samples were denoted as xNi/CNTs where x represented the mass content of NiO. XRD analysis was measured on PANalytical Empyrean diffractometer (CuKα, λ=1.5406 Å). TEM was performed on JEOL JEM-2100F Transmission Electron Microscope. The Micromeritics Autochem II 2920 was employed to run the H_2-chemisorption, the Ni dispersion and the surface area was calculated according to the ref. [6]. The catalytic reaction was carried out in a fixed bed reactor, the liquid feed (10 wt.% glycerol in water) was pumped into the evaporator (250 ^{o}C) by a HPLC pump, and then reacted at 375 ^{o}C after hydrogen pretreatment. The gasous and liquid products were analyzed by an online GC-TCD and an offline GC-FID, respectively.

3. Results and discussion

The crystallite size was estimated by Scherrer’s equation, the results listed in Table 1 showed that all the samples had the similar crystallite size of 12 nm which grew to larger size after reaction, meaning that the sintering of nanoparticle took place under reaction conditions. Although the varied extent just fluctuated in a narrow range from 25.0% to 29.4%, it was interesting to note that the biggest change occurred on the sample with lowest NiO content (3Ni/CNTs). The TEM results (Figure 1) of the selected sample 10Ni/CNTs exhibited the NiO nanoparticles distributed on both the internal and external wall of the nanotubes. By comparing the particle sizes for the calcined and the spent catalyst, it could be clearly found that bigger particles formed after catalytic reaction, which is well agreement with the XRD results.

Table 1 Variation in crystallite size and the catalytic performances at reaction temperature 375 °C

Catalyst	Crystallite size from XRD, nm			Conversion., %	Selectivity, %			
	Calcined NiO	Spent Ni	Δ, %	Glycerol	H_2	CO	CO_2	CH_4
3Ni/CNTs	12.6	16.3	29.4	98	42	41	14	3.2
5Ni/CNTs	10.4	13.0	25.0	100	46	40	15	3.0
10Ni/CNTs	12.1	15.5	28.1	100	54	27	33	0.8
15Ni/CNTs	12.6	15.9	26.2	100	72	22	54	4.2

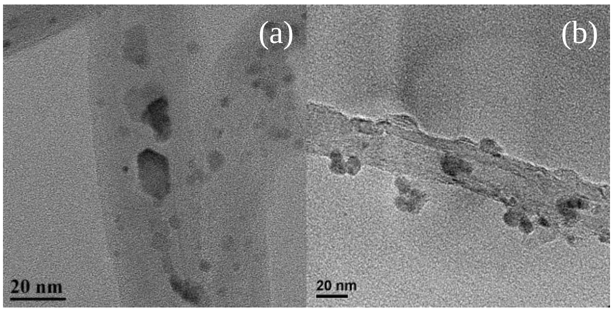

Figure 1. TEM image for calcined (a) and spent (b) 10Ni/CNTs

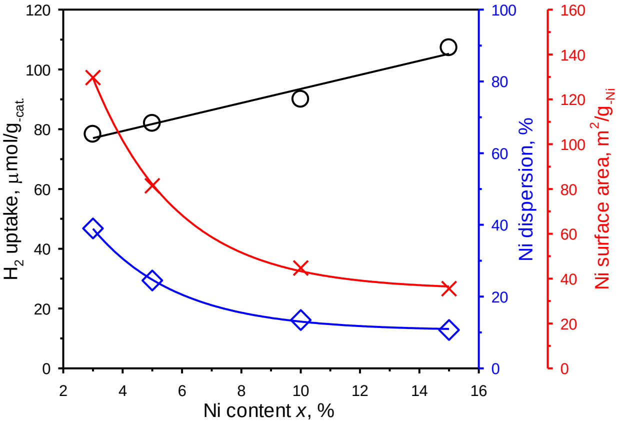

Figure 2. The properties of active Ni sites determined by H_2-chemisorption

The H_2-chemisorption results from Figure 2 showed that the H_2 uptake increased with the increase of loaded NiO, while the Ni dispersion and surface area showed a inverse relation, and decreased gently due to the "confinement effect". All the samples were very active for glycerol steam reforming reaction from Table 1, the reactant could be nearly fully converted, and 15Ni/CNTs had the best selectivity for hydrogen.

4. Conclusions

The nanoparticle with the size of around 12 nm was obtained when NiO was dispersed on CNTs, the sintering can not be avoided during the reaction. The amount of loaded NiO had a complex effect on Ni dispersion, surface area and even the catalytic performances.

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