

GLOBAL CO₂ RECYCLING THROUGH METHANATION REACTION USING NEODYMIUM DOPED NICKEL OXIDE CATALYST

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Abstract: Methanation reaction using nickel oxide and neodymium doped nickel oxide-based catalyst was studied. Doping nickel oxide with neodymium results in higher catalytic activity than a pure nickel oxide catalyst with 100% methanation of CO₂ at a low temperature of 350°C. Characterization of the neodymium doped nickel oxide by a XRD, SEM and nitrogen gas adsorption suggested that a small portion of the catalyst showed amorphous properties and that the small sized particles of this catalyst may contribute to the high catalytic activity.

KEYWORDS: CO₂, Methanation, Neodymium, Nickel Oxide, Catalyst

Introduction

Carbon dioxide is a key greenhouse gas and causes 60% of the global warming effect (Turner & O'Connell, 2001). For the past few centuries, carbon dioxide emission has been increasing with economic growth. The principal cause of increased CO₂ emission is the burning of fossil fuels (hydrocarbons). The carbon in the fuel combines with oxygen from the air, producing CO₂. Other sources of carbon dioxide are from animal and human respiration processes and electricity production.

The world is faced with a dilemma because the most abundant and cheapest energy available in most countries are fossil fuels. Combustion of fossil fuels is the main source of CO₂ as it emits tonnes of carbon dioxide every year. In Malaysia alone, a total of 5.13 tonnes of CO₂ are emitted from fuel combustion (Jabatan Alam Sekitar Malaysia, 2000).

Probably the most effective way of reducing atmospheric CO₂ emission is global CO₂ recycling or CO₂ methanation. Methanation is not only capable of preventing global warming but can also supply abundant renewable energy in the form of methane, (CH₄) a major component of natural gas. This is possible as a result of the reaction between carbon dioxide with the feed hydrogen gas to produce methane (CH₄) and water (H₂O), with the presence of a catalyst (Hashimoto *et al.*, 2002). The reaction can be summarized as Equation 1.0.



The use of nickel oxide as a catalyst for methanation is well established. However, studies have shown that nickel oxide is susceptible to coking and deactivates rapidly (Yamasaki *et al.*, 1999). In this paper, the influence of an addition of rare earth elements such as neodymium on the activity and stability of nickel oxide catalysts were investigated with respect to the CO₂/H₂ methanation, aiming to produce catalyst systems with high catalytic activity and low susceptibility towards chemical and physical changes.

Experimental

Catalyst Preparation

The catalysts were prepared by sol-gel method, whereby 5.0 g of the nickel salt, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water and added with calculated amounts of dopant salt of neodymium (III) nitrate hexahydrate, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, according to the ratio 60:40. The samples were then aged at 70°C for 72 hours and calcined at 400°C for 17 hours.

Catalytic Testing

Methanation was done on a flow bed, home-built microreactor of 10 mm inner diameter under atmospheric pressure. The reaction gas mixture of CO_2 and H_2 (1:4 volume ratio) was passed continuously through the catalyst that was filled inside a sample tube and CO_2 peaks from the composition of the gas that flowed through was detected by FTIR. The tabulated data gave percentages of CO_2 methanation within the temperature range studied.

Catalyst Characterization

The prepared catalysts were characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with Cu-K_α radiation, Scanning electron microscopy (SEM), utilized a Philip XL 40 and the Brunauer-Emmet-Teller (BET) method was used to determine the specific surface area.

Results and Discussion

Catalytic Activity

The catalytic activity of the prepared catalyst showed that doping nickel oxide catalyst with neodymium gave better catalytic activity with 100% methanation of CO_2 at 350°C . However, the pure nickel oxide catalyst only managed to achieve 80% methanation of CO_2 at the maximum temperature studied, 500°C due to the coking process and loss of active surface area due to migration and sintering of nickel oxide particles to form larger particles (Rostrup-Nielsen *et al.*, 2007). The presence of a small amount of neodymium as a dopant in the nickel oxide catalyst can stabilize a major component of nickel oxide against degradation of its textural properties upon heat, thereby allowing the catalyst to show good catalytic activity even at higher temperature. In addition, the presence of dopants in the catalyst can enhance the reaction rate of CO_2 methanation reaction (Miller *et al.*, 1997).

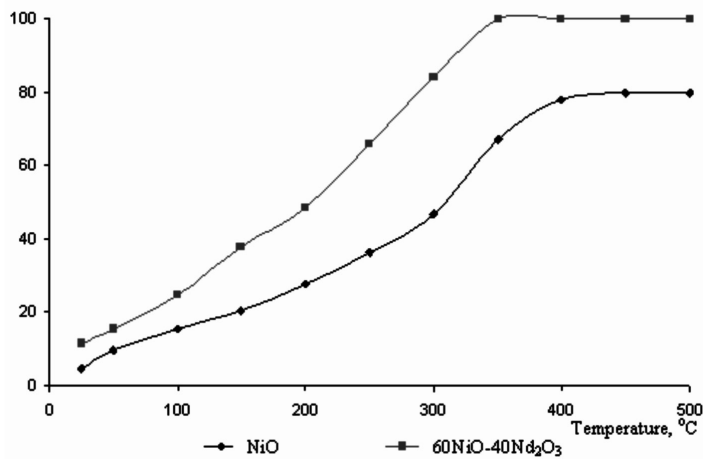


Figure 1: The plot of CO₂/H₂ methanation over undoped NiO and doped 60NiO-40Nd₂O₃ calcined at 400°C for 17 hours.

Catalyst Characterization

The XRD of nickel oxide catalyst showed the presence of highly crystalline cubic NiO. This can be seen in the sharper and narrower peaks. Meanwhile, for neodymium doped nickel oxide catalyst, in addition to broad peaks due to the cubic NiO, the XRD pattern also contained broad peaks due to the cubic Nd₂O₃. The broadening of peaks suggests some degree of amorphous property in the catalyst due to the presence of the neodymium in material and gives better CO₂/H₂ methanation, because of easier adsorption of gasses on the amorphous surface catalyst.

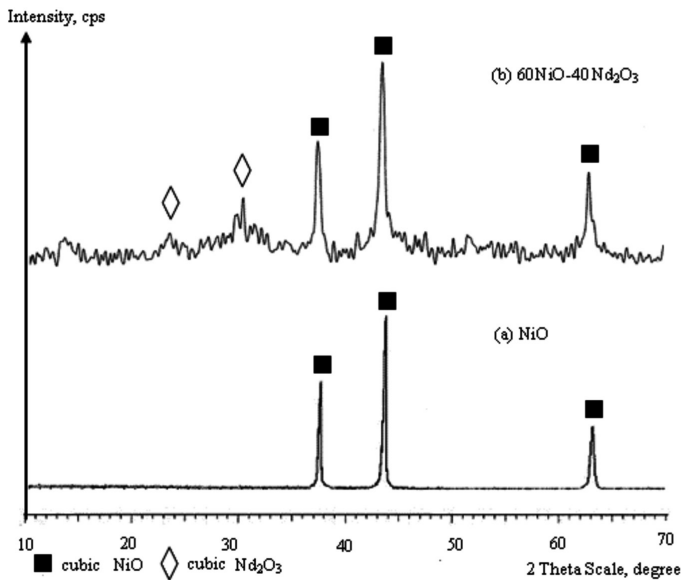


Figure 2: X-ray diffractogram patterns of NiO and 60NiO-40Nd₂O₃ catalysts calcined at 400°C for 17 hours.

Table 1: Average particle size and BET surface area of prepared catalyst.

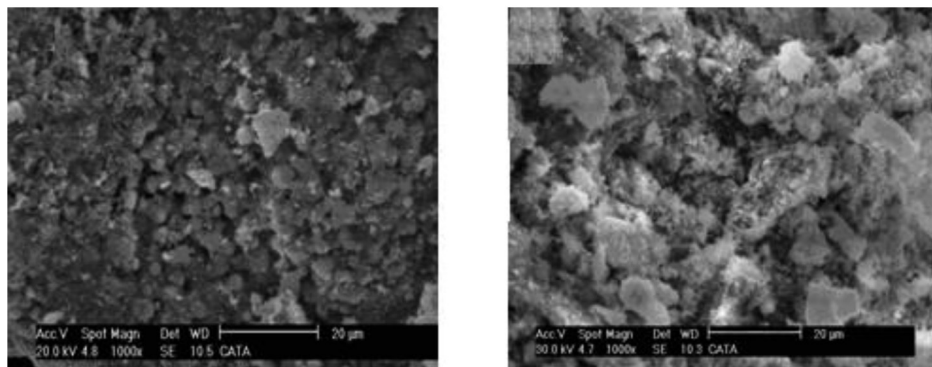
Catalyst	^a Average particle size (μm)	^b BET surface area (m^2/g)
NiO	24.70	5.60
60NiO-40Nd ₂ O ₃	20.62	23.68

a = derived from XRD using Scherrer equation

b = obtain from nitrogen adsorption

The SEM micrograph of NiO showed the formation of bulk NiO, which is less dispersed and distributed non-homogeneously on the surface of the sample (Fig. 3a). The formation of bulk NiO was due to the aggregation process of particles of NiO during calcination and methanation reaction (Mohd Hasmizam, 2005). Upon the addition of neodymium, an irregularity of the particle shape was observed in which smaller particles were dispersed within the matrix of larger particles (Fig. 3b). Apparently the neodymium can retard the aggregation of NiO particles thus leading to higher catalytic activity. Table 1 showed that the BET surface area increases upon the addition of neodymium to the nickel oxide catalyst, indicating that the 60NiO-40Nd₂O₃ has a small particle size compared to the NiO. This result agrees well with the particle size of 60NiO-40Nd₂O₃ derived from XRD using Scherrer equation [Table 1].

In this study, it was found that the surface area of the catalysts is low. This phenomenon is due to the agglomeration process during the calcinations of the catalysts. A probable explanation is that, during the calcination process the primary particles were transformed to secondary particles which gradually eliminated the pores from the catalyst material. In other words, the sintering process took place to form a solid material with a smaller surface area (Mohd Hasmizam, 2005).



(a)

(b)

Figure 3: SEM micrographs of (a) NiO and (b) doped catalyst of 60NiO-40Nd₂O₃ catalyst calcined at 400°C for 17 hours with magnification of 1000X and scale bar 1.7 cm: 20 μm

Conclusion

The neodymium doped nickel oxide catalyst exhibited better catalytic activity than a pure nickel oxide catalyst with 100% methanation at 350°C, due to the presence of the NiO cubic phase and Nd₂O₃ cubic phase structure, which serve as active sites for CO₂/H₂ methanation reaction. The higher BET surface area of 60NiO-40Nd₂O₃ catalyst contributes to the improved performance. Meanwhile the SEM analyses have shown that the 60NiO-40Nd₂O₃ formed homogeneous particles and gave smaller particle size, calculated from Scherrer equation which supports the good performance of the 60NiO-40Nd₂O₃ towards CO₂/H₂ methanation.

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