

## Eco-Friendly Synthesis and Characterization of Ni-Si Nanoparticles Mixed Oxides as Catalyst for Partial Oxidation of Methane

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### Abstract

The nanoparticles of Ni-Si mixed oxides were prepared by co-precipitation method using nickel nitrate;  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and tetraethylorthosilicate (TEOS). The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and hydrogen temperature program reduction ( $\text{H}_2$ -TPR). The results revealed that Ni-Si mixed oxides particles were obtained with average particle size 1-2 nm. The Ni-Si nanoparticles mixed oxides successfully catalyzed the partial oxidation of methane (POM) to hydrogen and carbon monoxide (Syn gas) using a fixed-bed reactor with about 92% activity and high selectivity. No coke formation and deactivation of catalyst were observed during the course of reaction. Particularly significant is the similar reactivity of this catalyst with that of Ni-Ce-Zr mixed oxides.

**Keywords:** Partial oxidation of methane; Nanoparticles; Mixed oxides

### Introduction

The conversion of natural gas into transportable gasoline and diesel fuel is an alternative to the prohibitive transportation costs. The so called gas to liquid technology (GLT) is based on the conversion of natural gas to Syn gas prior to liquid production through Fischer Tropsch synthesis [1]. The great potential of POM in catalytic short contact time reactor has been studied by many scientists [2-4]. Several kinds of catalysts based on the noble metals Ir, Rh, Pt, Ru, and Pd have shown high conversion of methane and high selectivity toward CO and  $\text{H}_2$  [5]. Ru and Rh catalysts have been found to exhibit high activity with good long

term stability against volatilization and resistance to carbon deposition [6,7].

Hayakawa has prepared the  $\text{Ca}_{0.8} \text{Sr}_{0.2} \text{Ti}_{0.8} \text{Ni}_{0.2}$  catalyst for POM [8]. Lago et al. observed that a series of  $\text{LnCoO}_3$  (Ln or La, Pr, Nd, Sm, and Gd) perovskites presented high catalytic activity and selectivity in POM [9].  $\text{LaNiO}_3$ ,  $\text{LaCa}$  (or  $\text{Sr}$ )  $\text{NiO}_3$  and  $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$  ( $x=0.2-1.0$ ) were active for POM and resistant to coke formation [10]. Takehira et al found that Ni supported on perovskites;  $\text{Ni}/\text{ATiO}_3$  (A: Ca, Sr, or Ba) showed high activity and selectivity with very low coke formation [11]. Wang and co-workers showed that  $\text{BaTi}_{0.8}\text{Ni}_{0.2}\text{O}_3$  is a good catalyst for POM [12].

Nickel-based catalysts have attracted much attention

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for POM due to their lower cost and similar activity and selectivity in comparison to those of noble metal catalysts. Recently, Ni/Al<sub>2</sub>O<sub>3</sub> [13, 14], Ni/ La<sub>2</sub>O<sub>3</sub> [13], Ni/MgO [15], Ni/ silica sol [16], Ni / TiO<sub>2</sub> [17], and Ni / ZrO<sub>2</sub> [18] were tested as catalyst for POM.

The main goal of the present investigation is preparation of Ni-Si nanoparticles mixed oxides and its application as catalyst in POM and comparison the results with those obtained with Ni-Ce-Zr mixed oxides.

## Materials and Methods

### Experimental

All solvents and reagents were obtained from Merck Chemical Company. Powder X-ray diffraction (XRD) analysis of the catalyst was carried out using a 3003 PTS Seifert with Cu K<sub>α</sub> radiation ( $\lambda = 1054 \text{ \AA}$ ). FTIR spectra were measured on KBr disks with a Bruker Tensor 27, 2002 spectrometer. The nanoparticles sizes were determined using a XL-30 Philips (1992). The Transmission Electron Microscopy (TEM) was performed on a Philips CM200 FEG. The POM reactions were carried out in a MFC (Brooks Smart mass flow controller). Chemical analyses of the samples were carried out with Perkin Elmer atomic absorption spectrometer.

### Preparation Ni-SiO<sub>2</sub>

Ni-SiO<sub>2</sub> was prepared by the co-precipitation method. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (4.3 g in 20 ml water) was slowly added to a solution of TEOS (16.7g, 0.8 mol in 20ml water). After stirring for 30 min at 60-80°C, the pH of the solution was adjusted to 10.5 by addition of KOH (20% W/W) at 80-90°C. The resultant mixture was then refluxed at 80°C for 3 days. The solid was filtered and washed with distilled water until the filtrate solution became neutral. The Ni-SiO<sub>2</sub> solid was dried in an oven at 120°C for 6 h, and then calcined at 800°C for 6 h. The composition of the catalyst was determined as NiO<sub>2</sub>: SiO<sub>2</sub> ; 19.6: 80.4.

### Preparation of Ni-Ce-ZrO<sub>2</sub>

Ni-Ce-ZrO<sub>2</sub> was prepared in a similar procedure [19]. The composition of the catalyst was determined as NiO: CeO<sub>2</sub>:ZrO<sub>2</sub> ; 7.5: 32.3: 60.2.

### Catalytic Reaction

Activity tests were carried out using a fixed-bed quartz tube reactor with inner diameter of 12 mm at

atmospheric pressure. The reactant feed gas comprised a gaseous mixture of CH<sub>4</sub>: O<sub>2</sub>: N<sub>2</sub> equal to 40%: 20%: 40%. The molar ratio of reactant gas stream was 2:1 of CH<sub>4</sub>: O<sub>2</sub> with GHSV<sub>CH<sub>4</sub></sub> = 6000 hr<sup>-1</sup>. The reactions were carried out at 500, 600, 650, 700 and 800°C. Feed gas was passed from up the tubular reactor and pretreatment was performed, and finally was increased to 800°C to reach to the surface catalyst. About 1.5gr of each catalyst was loaded into a quartz tubular reactor. The catalyst of particle size 25-35 mesh was placed in the special part of tube reactor (load of reactor). The loaded reactor was put in a tubular furnace, and the reactant gas stream was circulated of the loaded reactor, and the output Deby of reactor was determined. The product gases were analyzed by on-line gas chromatography (TCD) with HP-PLOT Q and HP-PLOT MOLESIVE column. The reaction was occurred at 800°C for 9h. After being steady of reaction, we can read the output of flow rate with digital flow meter, and the performance of catalyst was investigated in every run of process.

## Results and Discussion

### XRD

The XRD pattern of Ni-SiO<sub>2</sub>, calcined at 800°C presented in Figure 1 showed NiO as rhombohedral phase (card no. 22-1189) on SiO<sub>2</sub> Cristobalite (with card no. 39-1425 as tetrahedral phase). The peaks were relatively broad with low intensities that implied fine particles of nanocatalyst [16,19]. The peak characteristic of the cubic phase for Ni-Ce-ZrO<sub>2</sub> (NCZ) appeared at  $2\theta = 29.01, 48.9^\circ$  and  $58.3^\circ$ , corresponding to JCPD card no. 27-997 [13, 19]

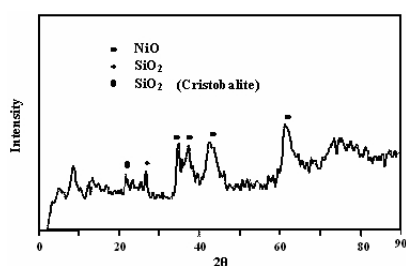
### TEM

Figure 2 displays the TEM images of Ni-Si nanoparticles mixed oxide. It is obvious that Ni-Si sample is in the fine particles with the size of about 1-2 nm.

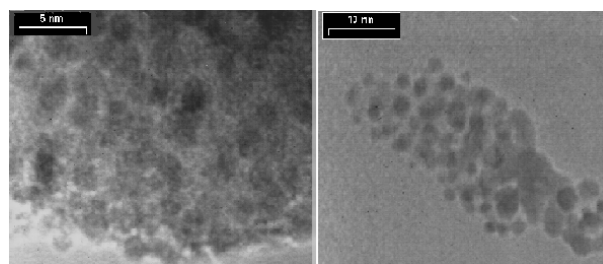
### Reaction Results

#### Effect of Temperature on Catalyst Activity

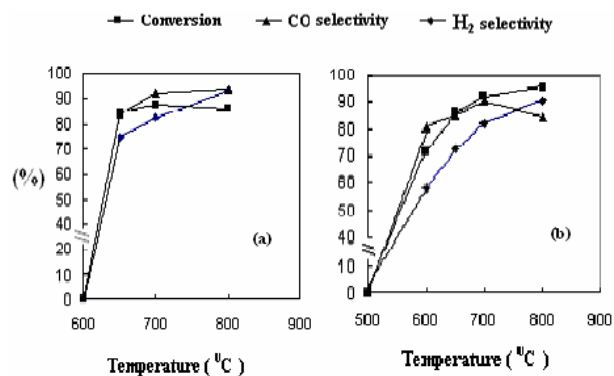
Figure 3 shows the influence of reaction temperature on the activity of Ni-Si nanoparticles mixed oxides catalyst in POM reaction to Syn-gas. The experimental results indicate that methane conversion as well as CO and H<sub>2</sub> selectivities increase with increasing reaction temperature. The results are comparable to those obtained in the presence of Ni- Ce-ZrO<sub>2</sub> as catalyst [18].



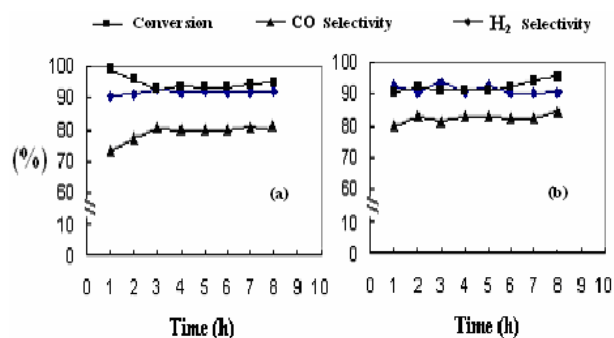
**Figure 1.** XRD pattern of Ni-SiO<sub>2</sub> nanocomposite mixed oxides.



**Figure 2.** TEM of Ni-Si mixed oxides nanoparticles with two different magnifications.



**Figure 3.** Effect of temperature on the catalytic performance of (a) Ni-SiO<sub>2</sub> and (b) Ni-Ce-ZrO<sub>2</sub> nanoparticles mixed oxides on the conversion of methane to Syn. gas.



**Figure 4.** Effect of time on methane conversion to Syn gas over (a) Ni-SiO<sub>2</sub> and (b) Ni-Ce-ZrO<sub>2</sub>.

#### Effect of Time on Catalyst Stability

Stabilities of Ni-SiO<sub>2</sub> and Ni-Ce-ZrO<sub>2</sub> catalysts were investigated during the reaction time. Figure 4 shows the catalytic activity of POM versus reaction time at a CH<sub>4</sub> / O<sub>2</sub> feed molar ratio of 1.73 and at 800°C with GHSV<sub>(CH<sub>4</sub>)</sub> = 6000 hr<sup>-1</sup> over the two catalysts. Evidently, both CH<sub>4</sub> conversion, CO and H<sub>2</sub> selectivities increase with the increasing reaction time during the initial 3h and then remain almost unchanged during 8h life test, which suggests that these catalysts are quite stable at high temperature.

The formation rate percentage of CO, H<sub>2</sub>, carbon balance and H<sub>2</sub> / CO ratio of the prepared catalysts are presented in Table 1. Based on the obtained results (Figures 3 and 4), it was found that the catalytic activity of Ni-Si nanoparticles mixed oxides is comparable with Ni-Ce-ZrO<sub>2</sub> in POM catalytic activity.

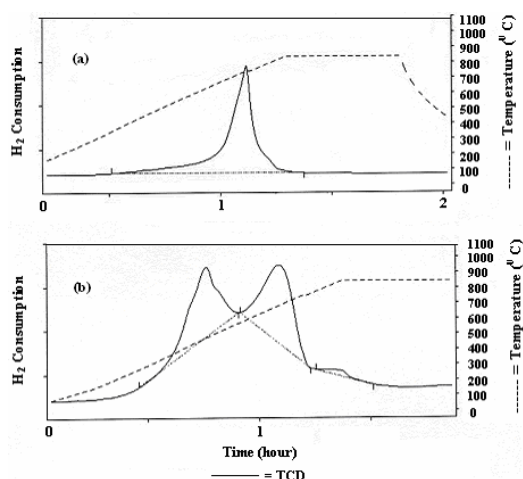
#### Temperature Programmed Reduction (TPR)

H<sub>2</sub>-TPR experiments were carried out using a TPR analyzer (TPD/TPR 2900, Micromeritics). The samples were pretreated in He atmosphere at 200°C for 30 min prior to running the TPR experiment and then cooled

down to room temperature in He atmosphere. The reduced gas contained 5.1% of H<sub>2</sub> in Ar. The sample temperature was raised at a constant rate of 10°C min<sup>-1</sup> from room temperature to 850°C. The amount of H<sub>2</sub> consumption as a function of temperature was determined from a TCD signal.

The H<sub>2</sub>-TPR profiles of Ni-CeO<sub>2</sub>-ZrO<sub>2</sub> (Fig. 5b) shows three broad peaks at 477, 687 and 811°C which are due to the reduction of NiO, ZrO<sub>2</sub> and CeO respectively [21]. The H<sub>2</sub>-TPR of Ni-SiO<sub>2</sub> mixed oxides (Fig. 5a) shows only a relatively single sharp peak at the 742°C. As has been reported previously, the reduction of bulk NiO happens at about 300-400°C [17]. Moreover, reduction of NiO attached to the silica and SiO<sub>2</sub> occurs at 400-500°C and 700°C respectively. Therefore, the reduction temperature of our system at 742°C indicates that NiO is very well dispersed within SiO<sub>2</sub> lattices [16].

In summary the nanoparticles of Ni-SiO<sub>2</sub> show a high catalytic activity for partial oxidation of methane at the temperature range of 500-800°C for 8 hours. Deposition of coke on the catalyst surface as well as deactivation of catalyst was not observed during the



**Figure 5.** Temperature program reduction (TPR) profile of (a) Ni-SiO<sub>2</sub> and (b) Ni-Ce-ZrO<sub>2</sub> mixed oxides.

**Table 1.** Comparison of catalytic activity of two catalysts

Catalysts	CO (ml/min) %	H <sub>2</sub> (ml/min) %	Carbon balance	H <sub>2</sub> /CO
Ni-SiO <sub>2</sub>	37	63	4.3	1.73
Ni-Ce-ZrO <sub>2</sub>	36	64	4.3	1.8

course of reaction. Such excellent catalytic characteristics are based on the physical construction and strong metal-support interaction produce by co-precipitation method. A sharp reduction of Ni-SiO<sub>2</sub> catalyst observed in H<sub>2</sub>-TPR at 734°C is due to the well dispersed Ni in silicate support. In addition, the catalytic activity to that of Ni-SiO<sub>2</sub> is similar to Ni-Ce-ZrO<sub>2</sub>. As such, it is merit to be considered as a good, cheap and eco-friendly candidate catalyst for mass production of Syn gas.

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