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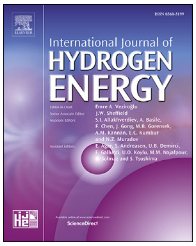

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Effect of Pt doping on activity and stability of $Ni/MgAl_2O_4$ catalyst for steam reforming of methane at ambient and high pressure condition

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ABSTRACT

Effect of addition of Pt noble metal to $Ni/MgAl_2O_4$ catalyst for steam reforming of methane was studied at atmospheric pressure and at high pressure (10 bar). Pt loading of the catalyst was varied from 0.01 wt.% to 1.0 wt.%. Catalyst characterization studies showed that the degree of reduction of the catalyst increased from 44.9% for $Ni/MgAl_2O_4$ to 67.7% for the catalyst doped with 1.0 wt.% Pt, which was attributed to H_2 spill over effect. With increasing Pt loading, the metal dispersion passed through a maxima and the highest dispersion of active metals was obtained with a Pt doping of 0.1 wt.%. Increase in Pt concentration had no effect on the concentration of $NiAl_2O_4$ that had already formed during calcination at 850 °C after nickel impregnation. Addition of Pt significantly increased the catalytic activity of $Ni/MgAl_2O_4$ for the steam reforming of methane at both reactor pressures. Comparison of Pt doped $Ni/MgAl_2O_4$ with $Pt/MgAl_2O_4$ showed that only lower loading of Pt produced a synergetic effect. The highest catalytic activity was obtained with 0.1 wt.% Pt doped $Ni/MgAl_2O_4$. Above this Pt loading the catalytic activity decreased. The highest activity of 0.1 wt.% Pt doped catalyst was credited to an increase in active metal dispersion, while the decrease in catalytic activity on further addition of Pt was attributed to agglomeration of active metals. High pressures decreased the conversion and stability of each Pt doped catalyst. However, at the same operating conditions there was a marginal increase in the catalyst stability due to Pt doping and the decline in catalyst activity with run time was lowest for 0.1 wt.% Pt doped $Ni/MgAl_2O_4$ catalyst.

Introduction

With increasing energy demand and steadily growing population, demand for hydrogen, both as a fuel and as a feedstock for fertilizer production is increasing day by day. To meet the large scale industrial demand, hydrogen is conventionally produced in catalytic packed bed reactors. As the catalyst plays an important role in energy efficiency and economics of the process, a large number of studies have been performed for improving the catalytic activity and stability. Due to its availability and low cost, nickel is widely used as the active

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metal for steam reforming of methane, and magnesium aluminate spinel is the preferred support because of its stability at high temperature [1].

Despite its wide scale use, nickel has a tendency to form carbon over its surface which significantly affects its performance for long period of operation [2]. Since most of the industrial steam reforming plants operate at high pressure (~30 bar) and stability of the catalyst decreases with an increase in pressure, stability of the catalyst at high pressure becomes an important aspect of industrial steam reforming operations [3,4]. Efforts to improve the activity and stability of the catalysts have included different catalyst preparation techniques and doping of the nickel catalyst with other metals. Doping of nickel-based catalyst with noble metals, such as Pt, Rh, Ru or Pd, has drawn significant attention [5,6]. It was found out that addition of noble metal significantly increases the dispersion of nickel metal over the catalyst support and enhances the reducibility of the catalyst. It has also been reported that alloys formed by the noble metal and nickel decreases the formation of unreactive metal complexes, such as $NiAl_2O_4$ and reduces the carbon formation over the catalyst surface [7]. These changes in the physicochemical properties of the catalyst were also significantly affected by the amount of noble metal doping and the preparation method for active metal impregnation.

Mukainakano and co-workers [8]investigated the effect of sequential and co-impregnation method for the preparation of Pd doped Ni/Al_2O_3 catalyst for oxidative reforming of methane. The performance of sequentially impregnated catalyst was found to be better than the co-impregnated catalyst. They observed that sequential impregnation resulted in surface segregation of Pd particles, which in turn reduced the hot spot formation over the catalyst bed. As a consequence, better reducibility of the catalyst was reported. Similar results were reported for Pt doped Ni/Al_2O_3 catalyst due to the higher surface concentration of Pt particles, the catalyst prepared by sequential impregnation gave a better performance in comparison to catalyst prepared by co-impregnation method [9]. Doping of noble metal can also contribute to the self-activation properties of the catalyst, i.e. no separate activation of the doped catalyst was required [10]. Miyata et al. [6] investigated the effect of self-activation properties of Pt, Rh and Pd doped Ni/Mg(Al)O catalyst for SRM process. It was found that, in contrast to the noble metal doped catalysts, Ni/Mg(Al)O catalyst did not produce any product without activation of the catalyst. Furthermore, the activity of Rh and Pt catalyst was higher than Pd doped catalyst. In their work Iglesia and co-workers have found that Pt on various oxides showed the highest turnover rates (C–H bond activation) in comparison to other noble metals, such as Ir, Rh and Ru [11]. Furthermore, Pt possessed a higher ability of self activation than Rh and Ru noble metal for frequent startup and shutdown operations [12]. In their work, Parizotto and coworkers found that Pt sites induced the activation of methane, which was required for the initial dissociation of methane. This initial dissociation of methane is helpful in the reduction of NiO present over the catalyst surface [13]. It was also observed that the recent cost of Pt metal is lower than Rh metal [14]. These results suggest that Pt is a suitable metal that can be used to enhance the activity of supported Ni catalysts for the steam reforming of methane.

All the published studies on Pt doped nickel catalyst were carried out at atmospheric pressure, while the industrial SRM operations are performed at high pressure conditions. Recently, we have shown that the reactor pressure has an effect on the activity and stability of $Ni/MgAl_2O_4$ catalyst [4]. Furthermore, most of the above studies were carried out with Al_2O_3 as the support and information from catalyst characterization was limited. Thus, catalyst characterization and testing at high pressure conditions is required to effectively compare catalysts. This work focuses on the study of promotional effect of Pt for $Ni/MgAl_2O_4$ catalyst. Specifically, the effect of doping 15 wt.% $Ni/MgAl_2O_4$ with 0–1.0 wt.% Pt on the activity, selectivity and stability of the catalyst both at atmospheric and high pressure (10 bar) reactor pressure has been investigated. The catalysts were characterized with the help of XRD, TEM, TPR, H_2 chemisorption and UV–vis analysis to provide suitable structure-reactivity information.

Experimental

Catalyst preparation

To study the effect of doping 15 wt.% $Ni/MgAl_2O_4$ with Pt, the doped catalyst was prepared by the sequential impregnation method. The Pt loading was varied from 0.01 to 1.0 wt.%. To form the $MgAl_2O_4$ spinel support, aluminum magnesium hydroxy carbonate powder, $Mg_{2x}Al_2(OH)_{4x+4}CO_3 \cdot nH_2O$, (MG30, Sasol, Germany), was calcined at 900 °C for 4 h. The aluminum magnesium hydroxy carbonate powder contained approximately 30 wt.% MgO and 70 wt.% Al_2O_3.

For catalyst preparation, first a large batch of the 15 wt.%.$Ni/MgAl_2O_4$ was prepared by wet impregnation method. In this preparation method, the required amount of $Ni(NO_3)_2 \cdot 6H_2O$ (Loba Chemicals, India), was used as the active metal precursor salt. The precursor salt was dissolved in excess amount of water (five times of the total pore volume). Magnesium aluminate spinel powder was added to the aqueous solution of the precursor salt and stirred for 30 min. Drying of the catalyst was first done in a rotary vacuum evaporator at 90 °C, and then followed by drying in an oven at 120 °C for 3 h. The dried powder was then calcined at 850 °C for 3 h. This catalyst was denoted as 0Pt15Ni. For doping Pt on the prepared $Ni/MgAl_2O_4$ catalyst, the incipient impregnation method was used. The required amount of $H_2PtCl_6 \cdot 6H_2O$ was dissolved in a calculated amount of water and added dropwise to $Ni/MgAl_2O_4$ and the mixture was continuously stirred during addition. This Pt doped catalyst was first dried in an oven at 120 °C and then calcined at 600 °C for 3 h. In all calcination steps the temperature ramp rate of was 2 °C/min. Catalyst doped with Pt were denoted as xPt15Ni, where x is the wt.% of Pt in the catalyst. For comparative purposes 0.1 wt.% $Pt/MgAl_2O_4$ and 1.0 wt.% $Pt/MgAl_2O_4$ catalysts were prepared using incipient impregnation method. After Pt impregnation the catalyst were dried in an oven at 120 °C for 3 h and then calcined at 600 °C for 3 h. The 0.1 wt.% $Pt/MgAl_2O_4$ and 1.0 wt.% $Pt/MgAl_2O_4$ catalysts were referred to as 0.1Pt0Ni and 1.0Pt0Ni, respectively.

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