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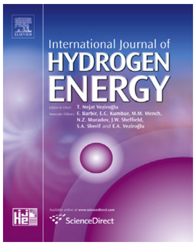

CO_2 reforming of methane to syngas over highly-stable Ni/SBA-15 catalysts prepared by P123-assisted method

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ABSTRACT

Ni/SBA15-P123 (1/X) catalysts were prepared via a simple and novel P123 (PEG-PPG-PEG triblock copolymer)-assisted wet impregnation method, in which 1/X indicates the molar ratio of P123 to Ni. Various techniques including N_2 physisorption, ICP, XRD, TEM, XPS, TGA-DSC and Raman were employed to characterize the physicochemical properties of the catalysts. The catalytic performances of Ni/SBA15-P123 (1/X) catalysts in carbon dioxide reforming of methane to syngas were evaluated with a vertical fixed-bed quartz tube reactor. XRD and TEM characterization results of as-prepared samples revealed that the Ni dispersions of Ni/SBA15-P123 (1/X) catalysts were dramatically improved with n_{P123}/n_{Ni} ratios in the range of 1/500- 1/50. Significant improvement of the catalytic performances for the above optimum catalysts can be clearly explicated by comparing with those catalysts prepared with no P123, insufficient P123 (1/X = 1/750) or superabundant P123 (1/X = 1/5). That is, Ni/SBA15-P123 (1/500), Ni/SBA15-P123 (1/100) and Ni/SBA15-P123 (1/50) catalysts exhibited better stability, higher activity and less carbon deposition during the 50 h CRM reaction.

Introduction

With diminishing availability of oil resource and growing concerns upon pollution from coal resource, rational development of clean and cheap resources captures much attention in recent researches. Methane, as one of the most crucial fossil energies, possesses better application prospect than oil and coal according to the BP's energy outlook [1]. Specifically, the exploitation and utilization of shale gas will have tremendous influence on the current energy structure [2]. Among a number of conversion routes [3], carbon dioxide reforming of methane (CRM) could convert two greenhouse gases into syngas for ultimate conversion to desired fuels and chemicals, as firstly reported by Fischer and Tropsch [4]. Various Ni-based catalysts have been investigated for the CRM process in consideration of the reasonable cost and high activity [5–7]. However, these studies have also indicated that the sintering of Ni active sites and carbon deposition would lead to catalyst deactivation.

Researchers have proposed a multitude of methods to improve the performances of Ni-based catalysts, among

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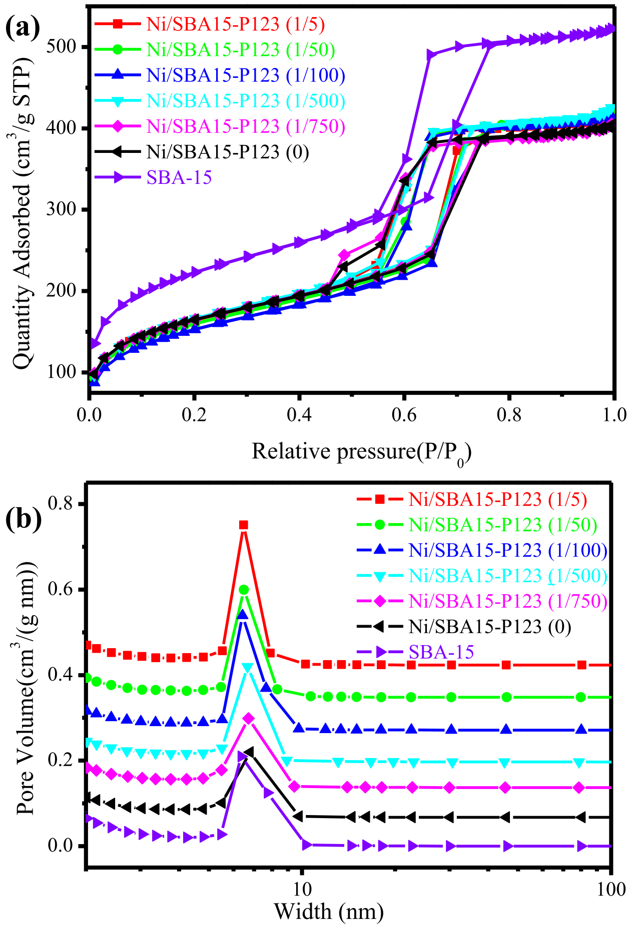

Fig. 1 – Textural properties of fresh Ni/SBA15-P123 (1/X) catalysts. (a) N_2 adsorption–desorption isotherms, (b) pore size distributions.

which the dispersion of active sites has been mostly focused on [8–15]. Iglesia et al. demonstrated that the forward rates of CH_4 reactions just depended on the dispersion and identity of metal clusters, and carbon formation rates increased with the increasing Ni crystalline diameter after rigorously excluded transport and thermodynamic artifacts [5]. Meanwhile, Jun et al. reported that Ni–Ce–ZrO_2 catalyst showed much higher activity and stability than Ni–ZrO_2 catalyst due to the enhanced oxygen transfer ability and better dispersion of metallic Ni particles [8,9]. The addition of a small amount of promoters such as K [10] or Na [11], and introducing trace amounts of noble metals such as Pt [12] or Ru [13], could also alter the arrangement of Ni on the supports and accelerate the gasification of deposited coke, thereby reducing the influence of carbon deposition on the catalyst activity. Moreover, Tian et al. observed that the 10% Ni/$(Sm_2O_3)_{0.77}(La_2O_3)_{0.23}$ catalyst prepared by sol–gel method, which existed strong interaction between nickel and Sm_2O_3–La_2O_3 support, displayed higher catalytic performance and stability than the catalyst prepared by impregnation method [14]. Kawi et al. also investigated the influences of catalyst preparation methods on the interaction between metals and supports in the more recent study [15].

Except the methods mentioned above, selecting ethanol as solvent other than water [16], altering gas flow rate and gas composition during calcination process [17] and adding some modifying agents during the impregnation process [18–23] all could affect the particle sizes of the catalysts. Zhang's group prepared a highly dispersed Co_3O_4/SiO_2 catalyst via surface modification of silica support by ethylene glycol (EG) [18]. Afterward, Wang et al. applied the support surface modification method to promote the Ni dispersion in Ni/MCM-41 catalysts via EG Ref. [19]. Similarly, a well-dispersed CeNi/SBA-15 catalyst via a CTAB-assisted iso-volumetric impregnation method was achieved by Gong et al. [20]. Kawi's group invented an *in situ* self-assembled core–shell precursor route to produce ultrasmall nanoparticles on silica via addition of oleic acid (OA) [15] and fatty acids (FAs) [21]. Our group previously employed a β-cyclodextrin (β-CD) modified impregnation method to obtain a highly dispersed Ni/SBA-15 catalyst [22,23].

P123 is a sort of nonionic surfactant and has been widely used as a template to synthesize mesoporous materials [24,25]. In the present work, we chose P123 as a modifying agent to assist the preparation of Ni/SBA-15 catalysts.

Table 1 – Physicochemical properties of fresh Ni/SBA15-P123 (1/X) catalysts.

Sample	Ni content (wt %)[a]	Textural properties			d_{XRD}[c]	
		S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	D_{BJH} (nm)[b]	d_{NiO} (nm)[d]	d_{Ni} (nm)[e]
SBA-15	n.a.	790	0.65	5.7	n.a.	n.a.
Ni/SBA15-P123 (0)	4.78	586	0.52	5.6	13.0	14.3
Ni/SBA15-P123(1/750)	4.84	586	0.52	5.6	9.3	11.1
Ni/SBA15-P123(1/500)	4.23	593	0.56	5.7	n.d.	3.7
Ni/SBA15-P123(1/100)	4.58	549	0.56	5.8	n.d.	3.4
Ni/SBA15-P123(1/50)	4.34	573	0.56	5.7	n.d.	3.1
Ni/SBA15-P123(1/5)	4.24	588	0.54	5.6	n.d.	3.9
Ni/SBA15-P123(1/100)-Uncal	n.a.	436	0.50	5.8	n.a.	n.a.
Ni/SBA15-P123(1/5)-Uncal	n.a.	2	0	n.d.	n.a.	n.a.

n.a. = not applicable, n.d. = not determined.

[a] The actual content measured by ICP-AES.

[b] The pore-size distribution determined from N_2 physisorption by the BJH method.

[c] Crystal sizes calculated by Scherrer equation from XRD profiles.

[d] The NiO crystal sizes of as-prepared catalysts.

[e] The Ni crystal sizes of reduced catalysts.

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