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Article

Stabilities of zeolite-supported Ni catalysts for dry reforming of methane

Anis H. FAKEEHA, Wasim U. KHAN, Ahmed S. AL-FATESH, Ahmed E. ABASAEED *

Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

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ABSTRACT

Ni/ γ - Al_2O_3 , Ni/Y-zeolite, and Ni/H-ZSM-5 catalysts were prepared using the incipient wetness impregnation method. Their catalytic performance in dry reforming of methane was studied. The fresh and used catalysts and deposited carbon were characterized using H_2 temperature-programmed reduction, temperature-programmed oxidation, N_2 adsorption-desorption, X-ray diffraction, and thermogravimetric analysis. The H-ZSM-5-supported Ni catalyst proved to be more stable than the other two catalysts, as it had the lowest carbon deposition.

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1. Introduction

Synthesis gas, usually called syngas (CO and H_2), is industrially useful for making various value-added liquid hydrocarbons and oxygenates through the well-known Fischer-Tropsch process [1,2]. Syngas can be produced through the following catalytic processes: partial oxidation, steam reforming, and dry reforming of methane [3,4]. Dry reforming is attracting increasing attention as it consumes two of the most important greenhouse gases (CH_4 and CO_2) to produce syngas [5–7]. The catalyst support plays an important role in coking resistance of metal particles and may even participate in the catalytic activity [8]. Zeolites are attractive supports for CO_2 reforming of CH_4 because they have well-defined structures, high surface areas, high thermal stabilities, and high affinities for CO_2 ; these properties are expected to enhance the catalyst selectivity and stability [9,10]. It is also well known that zeolite supports have the potential to deliver very high metal dispersions and to provide

stable systems. These excellent properties, combined with a low potential for support–metal interactions and superior coking resistance, make zeolites important catalyst supports in the CO_2 reforming of CH_4 .

Ni catalysts are used industrially for both steam reforming and dry reforming reactions because of their fast turnover rates, ready availability, and low costs [11]. A major problem encountered in Ni-based catalysts is carbon deposition on the surface, which leads to deactivation and blockage of reactor tubes. Besides coke formation, sintering of metal particles can also contribute to loss of catalytic activity [12,13]. Materials traditionally used as supports are insulating oxides such as SiO_2 , Al_2O_3 , V_2O_5 , and TiO_2 , and various types of zeolites have also been tested [14,15]. Recently, the activities of different zeolite-supported Ni catalysts for CH_4 reforming with CO_2 have been investigated [4,16]. Among these, MFI- and USY-type zeolites greatly improve the stability and selectivity of the reaction because they have suitable properties (e.g., microporous struc-

* Corresponding author. Tel: +966-1-4676856; Fax: +966-1-4678770; E-mail: abasaheed@ksu.edu.sa

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tures, high surface areas, and high affinities for CO₂ adsorption) for catalyst supports in reforming reactions [17–19].

In this study, the stabilities and catalytic activities of three Ni catalysts, supported on alumina, Y-zeolite, and H-ZSM-5 zeolite, were investigated. Various characterization techniques were used to quantify the carbon deposition.

2. Experimental

2.1. Catalyst preparation

γ -Al₂O₃ (SA-6175) with a Brunauer-Emmett-Teller (BET) area of 230 m²/g, Y-zeolite (CBV500) with a BET area of 750 m²/g, and H-ZSM-5 (CBV2030E) with a BET area of 405 m²/g were used as supports. A series of Ni-based catalysts (the Ni content was fixed at 5 wt%) were prepared on the supports. The catalysts were prepared by the incipient wetness impregnation method using Ni(NO₃)₂·6H₂O as the metal precursor. After impregnation, the catalysts were dried overnight at 120 °C and then calcined at different temperatures, namely 500, 700, and 900 °C, for 3 h.

2.2. Catalyst characterization

Phase identification of the prepared catalysts was carried out using X-ray diffraction (XRD), with Cu K α radiation, in the 2 θ range 0°–80° on a Unisantis XMD-300 diffractometer. N₂ adsorption-desorption isotherms were measured to examine the porous properties of each catalyst. The measurements were carried out using a Micromeritics ASAP 2020 instrument. Before the analyses, all the samples were pretreated under vacuum conditions at 200 °C for 12 h. Temperature-programmed reduction (TPR) was carried out using a Chemisorb Micromeritics 2920 instrument to monitor the metal oxide reduction. The sample was first pretreated in a flow of helium at 200 °C and then reduced under a flow (20 ml/min) of a 5.32% H₂/N₂ mixture. The sample was heated from 60 to 900 °C at a heating rate of 10 °C/min. After reaction at 700 °C for 9 h, temperature-programmed oxidation (TPO) was performed to study the reactivity of the carbon species by oxidizing the sample under a flow of air while the temperature was increased from room temperature to 800 °C, linearly with time, at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out to determine the amount of carbon deposited on the catalysts after use in the CO₂ reforming of CH₄. The analyses

were performed using a TGA/differential thermal analysis (EXSTAR SII TG/DTA 7300) instrument; 10 mg of each sample were introduced into a platinum microbalance pan in an air atmosphere, and the heating rate was 10 °C/min.

2.3. Catalytic tests

The CO₂ reforming reaction of CH₄ was carried out in a continuous-flow reactor, at a pressure of 101.3 kPa and different temperatures (500, 600, and 700 °C), with a constant stoichiometric feed mixture of CH₄ and CO₂ (1:1) and a total flow rate of 36 ml/min. Samples of 0.6 g of catalyst were used for each catalytic test. The data were collected every 30 min on stream for 9 h. The reaction products were analyzed using an on-line gas chromatograph (Varian Star 3400 CX). The details of the experimental setup and procedure have been given in previous publications [20,21].

3. Results and discussion

3.1. Catalytic activity

The catalytic performances of 5 wt% Ni/ γ -Al₂O₃, 5 wt% Ni/Y-zeolite (denoted Ni/Y), and 5 wt% Ni/H-ZSM-5 catalysts were investigated at different calcination and reaction temperatures. Table 1 shows the effects of the calcination and reaction temperatures on CH₄ and CO₂ conversions for the Ni/ γ -Al₂O₃, Ni/Y, and Ni/H-ZSM-5 catalysts. It can be seen that the effect of the reaction temperature on the catalytic activity is more pronounced than the effect of the calcination temperature. For all calcination temperatures, an increase in the reaction temperature resulted in higher conversions of CH₄ and CO₂, confirming the endothermicity of the reaction.

It can be seen from Table 1 that the Ni/ γ -Al₂O₃ catalysts at all calcination and reaction temperatures, and the Ni/H-ZSM-5 catalysts at all calcination temperatures and a reaction temperature of 700 °C, showed higher conversions of CO₂ than of CH₄. A similar trend was observed for the Ni/Y catalysts for calcination temperatures of 500 °C (at a reaction temperature of 500 °C), 700 °C (at reaction temperatures of 500 and 600 °C), and 900 °C (at a reaction temperature of 500 °C). A CO₂ conversion greater than that of CH₄ is the result of the reverse water shift reaction, which consumes the formed H₂, resulting in an H₂/CO ratio less than one. For the Ni/H-ZSM-5 catalysts, for all calcination temperatures and reaction temperatures of 500 and 600

Table 1

Activity tests for Ni/ γ -Al₂O₃, Ni/Y, and Ni/H-ZSM-5 catalysts with different calcination temperatures.

Calcination temperature (°C)	Reaction temperature (°C)	Conversion of CH ₄ (%)			Conversion of CO ₂ (%)			H ₂ /CO		
		Ni/ γ -Al ₂ O ₃	Ni/Y	Ni/H-ZSM-5	Ni/ γ -Al ₂ O ₃	Ni/Y	Ni/H-ZSM-5	Ni/ γ -Al ₂ O ₃	Ni/Y	Ni/H-ZSM-5
500	500	18.1	16.3	24.9	18.7	18.0	19.3	0.60	0.74	1.26
	600	46.7	59.7	63.7	51.1	50.4	45.2	0.81	1.20	1.31
	700	80.1	70.8	78.2	82.9	67.4	86.3	0.96	0.97	0.97
700	500	10.2	14.9	21.9	16.6	15.8	18.1	0.40	0.66	1.29
	600	42.0	37.6	58.1	49.3	41.7	36.2	0.68	1.20	1.38
	700	79.8	65.2	77.5	81.5	64.4	83.2	0.94	0.97	0.98
900	500	10.8	13.8	24.1	17.6	14.7	18.2	0.46	0.98	1.42
	600	42.1	45.0	61.5	49.8	31.9	37.4	0.71	1.10	1.49
	700	81.6	70.7	79.1	84.6	66.4	81.7	0.95	0.96	0.97

Table 2Coke deposition on, and surface areas of, Ni/ γ -Al₂O₃, Ni/Y, and Ni/H-ZSM-5 catalysts.

Catalyst	Calcination temperature (°C)	Conversion (%)				DF ^a (%)	Coke ^b (wt%)	A _{BET} /(m ² /g)	
		Initial		Final (after 9 h)				Before reaction	After reaction
		CH ₄	CO ₂	CH ₄	CO ₂				
Ni/γ-Al ₂ O ₃	500	80.1	82.9	78.1	76.2	2.5	8.0	208.7	170.7
	700	79.8	81.5	77.4	75.4	3.0	9.8	189.9	161.8
	900	81.6	84.6	79.7	78.7	2.3	7.8	146.2	138.0
Ni/Y	500	70.8	67.4	65.8	66.3	7.1	13.5	572.3	497.1
	700	65.2	64.4	61.8	63.4	5.2	13.1	572.7	488.4
	900	70.7	66.4	67.8	65.3	4.1	9.4	562.5	525.9
Ni/H-ZSM-5	500	78.2	86.3	76.8	85.3	1.8	3.3	334.3	317.4
	700	77.5	83.2	75.9	79.4	2.1	6.8	327.1	305.6
	900	79.1	81.7	76.8	78.2	2.9	7.7	270.4	259.3

Reaction temperature 700 °C. ^aDF = ((Initial conversion – Final conversion)/Initial conversion) × 100%. ^bDetermined by TGA.

°C, and for the Ni/Y catalysts, for all calcination temperatures and a reaction temperature of 600 °C, the higher CH₄ conversion compared to CO₂ conversion could be attributed to thermal cracking of CH₄, leading to coke formation and, consequently, an H₂/CO ratio greater than one [21].

The data in Table 1 also shows the effect of calcination temperature on catalytic activity. It can be seen that for the Ni/ γ -Al₂O₃, Ni/Y, and Ni/H-ZSM-5 catalysts, at low reaction temperatures (500–600 °C), the catalytic activity is higher for a calcination temperature of 500 °C, whereas at a higher reaction temperature (700 °C), a calcination temperature of 900 °C leads to high activity. These differences could plausibly be attributed to phase formation in the catalysts.

3.2. Catalytic stability

Time-on-stream conversions, amounts of coke deposited, and the surface areas of the fresh and spent catalysts are presented in Table 2. It can be seen that both CH₄ and CO₂ conversions decreased over a time period of 9 h. The main reason for this deactivation of the catalysts was carbon deposition.

Based on thermodynamics, at a high reaction temperature (>650 °C) coke is expected to be formed mainly via CH₄ decomposition (reaction (1) below). TGA was used to estimate the amounts of carbon deposited. It is clear from Table 2 that the average amount of carbon deposited on Ni/H-ZSM-5 (5.9 wt%) was much less than the amounts deposited on Ni/ γ -Al₂O₃ (8.5 wt%) and Ni/Y (12.0 wt%). This proves the higher stability of the Ni/H-ZSM-5 catalyst and lower carbon deposition on its surface; the stabilities of the catalysts are in the order Ni/H-ZSM-5 > Ni/ γ -Al₂O₃ > Ni/Y.

3.3. Catalyst characterization

Figure 1 shows the XRD patterns for fresh Ni/Y and Ni/H-ZSM-5 catalysts calcined at different temperatures. It can be seen that Ni/Y and Ni/H-ZSM-5 passivated catalysts calcined at 500, 700, and 900 °C showed the diffraction peaks of NiO(111), NiO(200), and NiO(220) at $2\theta = 37.2^\circ$, 44° , and 62.5° (JCPDS 04-850), respectively.

Figure 2 shows the elemental analyses of the spent catalysts determined using energy-dispersive spectroscopy (EDS). The

Fig. 1. XRD patterns of fresh Ni/Y and Ni/H-ZSM-5 catalysts with different calcination temperatures.

Fig. 2. EDS of carbon deposited on used Ni/ γ -Al₂O₃, Ni/Y and Ni/H-ZSM-5 catalysts.

Fig. 3. TPO results for Ni/γ-Al₂O₃, Ni/Y, and Ni/H-ZSM-5 catalysts at different calcination temperatures.

figure shows carbon formation on the catalyst surfaces (with Ni/H-ZSM-5 having the lowest amount). This deposition of carbon is in agreement with the TGA results listed in Table 2.

TPO is a useful technique for investigating carbon deposition in more detail. TPO provides important information regarding accumulated carbon species, and their structures, amounts, and compositions. It is widely recognized that amorphous carbon species can be combusted at lower temperatures than crystalline species, i.e., the oxidation temperature increases with increasing degree of crystallinity. Figure 3 displays the signals of generated CO₂ for the three catalysts as a function of temperature. The spent catalysts calcined at 900 °C showed a significant CO₂ release peak at 450–620 °C, which can be related to combustion of different crystalline forms of carbon, e.g., carbon nanofibers and carbon nanotubes. Generally speaking, the most probable reactions leading to carbon formation during reforming processes are those shown in Equations (1)–(4):

Reactions (2), (3), and (4) are favored at low temperatures (<575 °C); CH₄ decomposition (reaction (1)) takes place at higher temperatures, and is therefore the prime cause of carbon formation [22].

Figure 4 presents the TPR results for fresh and used Ni/γ-Al₂O₃, Ni/Y, and Ni/H-ZSM-5 catalysts. The fresh Ni/γ-Al₂O₃ catalysts calcined at 500 and 900 °C showed three

Fig. 4. TPR results for Ni/γ-Al₂O₃, Ni/Y, and Ni/H-ZSM-5 at different calcination temperatures.

peaks in the temperature range 420–800 °C, and the fresh Ni/Y catalysts calcined at 500, 700, and 900 °C showed three peaks in the temperature range 500–800 °C. The fresh Ni/H-ZSM-5 catalyst calcined at 500 °C showed two peaks, at 350 and 470 °C, and a shoulder at 575 °C. The low-temperature peaks can be assigned to NiO reduction as a result of very low metal–support interactions, and the high-temperature peak is assigned to reduction of NiO particles with high interaction with the support. The peak for the fresh Ni/γ-Al₂O₃ catalyst calcined at 900 °C at around 800 °C is attributed to reduction of spinel NiAl₂O₄. For the fresh Ni/Y catalyst calcined at 900 °C, the peak at 750 °C can be attributed to the reduction of Ni²⁺ hexagonal prisms, and for the fresh Ni/H-ZSM-5 catalyst calcined at 900 °C, the peak at around 600 °C can be related to NiO particles of a different size. In contrast, the Ni/γ-Al₂O₃, Ni/Y, and Ni/H-ZSM-5 spent catalysts showed only one peak, in the temperature range 300–600 °C, which can be attributed to a methanation reaction, i.e. the reaction of H₂ with carbon deposited on the catalyst surface (reverse of reaction (1) above).

4. Conclusions

CO₂ reforming of CH₄ is efficiently catalyzed by supported Ni catalysts. The activity towards CH₄ conversion was found to depend on the nature of the support material. H₂/CO ratios close to unity and lower carbon deposition leading to high stability were obtained for Ni/H-ZSM-5 catalysts. These findings were confirmed using XRD, EDS, TPO, and TPR techniques.

Graphical Abstract

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Anis H. FAKEEHA, Wasim U. KHAN, Ahmed S. AL-FATESH,
Ahmed E. ABASAEED*
King Saud University, Saudi Arabia

In dry reforming of methane, the Ni catalyst supported on H-ZSM-5 zeolite was found to be more stable than those supported on alumina or Y-zeolite.

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