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Ni–Mo_2C supported on alumina as a substitute for Ni–Mo reduced catalysts supported on alumina material for dry reforming of methane

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ABSTRACT

In this study, alumina-supported Ni–Mo catalysts were carburized to obtain alumina-supported nickel–molybdenum carbides as potential catalysts for dry reforming of methane. The typical carbide was compared with a low carburized material (in 5% H_2/CH_4) and a reduced Ni–Mo catalyst. It was shown that the passivated alumina-supported Ni–Mo catalysts by carbon lead to higher reactivity, selectivity, and stability for dry methane reforming reaction.

1. Introduction

Dry reforming of methane (DRM) has received considerable attention during the past decades as a promising process for the valorization of CO_2 toward the production of synthesis gas [1–3]. Noble metal catalysts (Ru, Rh, Ir, Pd, and Pt) were found to have high catalytic activity for the DRM reaction, but the large-scale application of these catalysts has been limited by their high cost. Thus, Ni-based catalysts were deeply used because they lead to a comparable catalytic activity with high cost-efficiency, but the deactivation was difficult to avoid because of the carbon deposition and Ni^0 sintering [4–7]. Because Levy et al. reported that carbide tungsten displayed reactivity close to that of platinum for neopentane isomerization [9], there has been a large interest in using carbide catalysts. Molybdenum and tungsten carbides (Mo_2C and WC) have been used as the effective catalysts for DRM, partial oxidation, and steam reforming of methane to produce synthesis gas, because Ni-based catalysts seriously suffered from sintering and coking [4–9]. York et al. found that these early transition metal carbides possessed high catalytic activity for methane reforming reactions. On these catalysts, the carbon deposition is lower than reduced Ni-based catalysts because no deactivation was observed at 8 bar [10]. However, at ambient pressure, deactivation was observed because of the conversion of initial Mo_2C to MoO_2 during the reaction. The catalytic activity of the noble and carbide catalysts for methane reforming has been established as follows: Ru > Rh > Ir ≈ Mo_2C > WC > Pd > Pt. Sehested et al. [11] studied Mo_2C catalyst for the DRM reaction at 8 and 1.6 bar total pressure in different reactors. They found that catalysts deactivated from the top to bottom in the plug flow reactor (8 bar) because of the oxidation of the Mo_2C.

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However, the Mo_2C showed a higher stability at high conversions in the continuously stirred tank reactor (1.6 bar) with no signs of oxidation, but the deactivation was not avoided due to the loss of the surface area of the Mo_2C. Darujati et al. [12] pointed out that both H_2 and CO were found to restrain the oxidation, and this effect could be explained by their influence on the reactions governing carburization and oxidation. The oxidation of the Mo_2C to MoO_2 can be inhibited by feeding CO with the reactants [13]. Although other studies dealt with bulk carbides [14–16] for the DRM reaction, there are only few studies dealing with supported carbides. Brungs et al. [17] found that alumina-supported Mo_2C was stable, and the relative stability of catalysts was as follows: $Mo_2C/Al_2O_3 > Mo_2C/ZrO_2 > Mo_2C/SiO_2 > Mo_2C/TiO_2$. Natio et al. [18] also reported that supported Mo_2C catalysts were stable and durable for the DRM reaction.

Moreover, Ce promotion on molybdenum carbide catalysts led to an improvement in stability of the catalysts [19,20]. Because Mo_2C species are active for the DRM reaction and Ni-based catalyst would suffer from carbon deposition, carburized Ni–Mo/Al_2O_3 catalyst (Ni–Mo_2C/Al_2O_3 catalyst) was studied for the DRM reaction. In the present work, alumina-supported molybdenum carbide (Mo_2C/Al_2O_3) and alumina-supported nickel–molybdenum carbide (Ni–Mo_2C/Al_2O_3) catalysts were studied for the DRM reaction. To investigate the influence of H_2 concentration on the carburization process and on the performance of the catalyst in the DRM reaction, two different mixtures of H_2/CH_4 ($H_2/CH_4/Ar = 4/20/76$ and $H_2/CH_4 = 80/20$) were used to carburize the precursors. It was shown that the Ni–Mo/Al_2O_3 catalyst carburized by 5% H_2 ($H_2/CH_4/Ar = 4/20/76$) showed the higher catalytic activity for the DRM reaction and that the presence of nickel also promoted the carburization process.

2. Experimental methods

2.1. Preparation of catalyst

The Mo/Al_2O_3 catalyst was synthesized by an incipient wetness impregnation method. Alumina was impregnated with appropriate amounts of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution corresponding to a nominal Mo loads of 10 wt %. After 2 h of impregnation, the excess solvent (deionized water) was removed by rotary evaporator at 60 °C. Then the obtained sample was dried at 110 °C overnight and calcined in synthetic air at 550 °C for 4 h. With the similar method, alumina was impregnated with appropriate amounts of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Ni(NO_3)_2\cdot 6H_2O$ mixed solution, corresponding to nominal Ni and Mo loadings of 10 wt %, leading to the Ni–Mo/Al_2O_3 catalyst.

Mo/Al_2O_3 and Ni–Mo/Al_2O_3 catalysts were thus carburized by the temperature-programmed process in H_2/CH_4 ($F_{H_2} = 40$ mL/min and $F_{CH_4} = 10$ mL/min) to obtain the Mo_2C/Al_2O_3 and Ni–Mo_2C/Al_2O_3 catalysts, respectively. To investigate the influence of H_2 concentration on the carburization process and on the performance of the catalyst in the DRM reaction, two different mixtures of H_2/CH_4 (5%H_2 and pure H_2) were used to carburize the catalyst precursors.

The first one consisted of used 5%H_2 (argon as balance), and the total ratio was kept 40/10, but the H_2/CH_4 becomes 2/10 because of the use of dilute H_2, that is, $H_2/CH_4/Ar = 4/20/76$. This synthesis has led to a reduced material with a passivation surface of carbon. The second one consisted of a feed with pure hydrogen and pure methane in a ratio of 40/10, that is, $H_2/CH_4 = 80/20$. The 5% H_2/CH_4 carbide Mo/Al_2O_3, 5% H_2/CH_4 carbide Ni–Mo/Al_2O_3, pure H_2/CH_4 carbide Mo/Al_2O_3, and pure H_2/CH_4 carbide Ni–Mo/Al_2O_3 catalysts were named as MC-1, NMC-1, MC-2, and NMC-2, respectively.

For both carburization processes, temperature-programmed process was used as following: temperature was raised from room temperature (around 25 °C) to 300 °C at a rate of 5 °C/min in H_2/CH_4 mixture, then from 300 °C to 700 °C at a rate of 1 °C/min (H_2/CH_4 mixture), after that kept at 700 °C for 2 h (H_2/CH_4 mixture), and then cooled down to room temperature overnight in Ar. After carburization, the catalyst was passivated in a CO_2 atmosphere at room temperature to be characterized or directly tested without passivation or reduction in the DRM reaction.

2.2. Catalytic activity test

DRM activity experiments were carried out over reduced and carbide catalysts. DRM activity experiments of reduced samples were carried out in a tubular quartz reactor at atmospheric pressure using a $CH_4/CO_2/Ar = 1/1/8$ mixture, at temperatures from 850 to 550 °C. Before the catalytic activity test, the catalysts were reduced in situ at 900 °C in 5% H_2–Ar for 1 h. For stability tests, catalysts were reduced at 900 °C for 1 h and then cooled down to 700 °C to carry out the DRM reaction for 300 min.

DRM activity experiments on carburized catalysts were carried out in the similar way. After the carburization, catalysts were directly heated up in Ar to 850 °C to perform the DRM reaction without any prior reduction. For stability tests, the carbide catalysts were directly heated up in Ar to 700 °C to carry out the DRM reaction during 300 min.

For all the catalytic tests, the gas hourly space velocity was kept as 20,000 h^{-1}. The effluent was analyzed in a microgas chromatograph (Varian CPi 4900) online, equipped with COX column. Methane and CO_2 conversions, as well as the H_2/CO ratio, were calculated using the molar composition of both the reactant mixture and the gas exiting the catalytic reactor, determined by gas chromatography.

2.3. Characterization

Nitrogen adsorption isotherms were acquired at −196 °C in an ASAP 2020 device, upon degasification of the materials at 250 °C. The carbide catalysts were analyzed by inductively coupled plasma (ICP, ARCOS) to determine the nominal amounts of Ni and Mo. The Ni and Mo species were extracted by dilute hydrochloric acid, at 80 °C under reflux for 5 h before ICP analysis. The X-ray diffraction (XRD) patterns were obtained using a PANalytical-Empyrean diffractometer, equipped with a Cu Kα (λ =

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