



Ni-modified Mo₂C catalysts for methane dry reforming

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ABSTRACT

Dry reforming of methane with CO₂ (DRM) was studied over Ni–Mo₂C catalysts with Ni/Mo molar ratios of 1/3, 1/2, and 1/1 (denoted as Ni–Mo₂C (1/3), Ni–Mo₂C (1/2), and Ni–Mo₂C (1/1), respectively) aiming to investigate the catalytic roles of Ni and the carbide. The results of XRD and XPS characterizations indicated that the carbonization process was promoted by the presence of Ni. The CH₄-TPR and CO₂-TPO over the fresh samples proved that CH₄ dissociation was greatly enhanced by Ni. The Ni–Mo₂C (1/2) catalyst showed the best catalytic activity and stability for CH₄/CO₂ (1/1) dry reforming. Above 80% of CH₄ and CO₂ conversions were maintained at 800 °C during a test run of 20 h at W/F = 0.3 g s cm^{−3}. Characterizations of the spent samples revealed that the deactivation of Ni–Mo₂C (1/1) was due to coke formation whereas that of Ni–Mo₂C (1/3) was due to bulk oxidation of Mo₂C into MoO₃. Only at a Ni/Mo molar ratio of 1/2, a catalytic oxidation–reduction cycle could be established. It was suggested that Ni–Mo₂C was a typical bi-functional catalyst. In CH₄/CO₂ dry reforming, the dissociation of CH₄ was catalyzed by Ni, while the activation of CO₂ took place on Mo₂C. By regulating the molar ratio of Ni and Mo₂C, a catalytic redox cycle could be established.

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1. Introduction

Catalytic dry reforming of methane with CO₂ (DRM) has become an interesting alternative for syngas production due to the fact that the greenhouse gases CO₂ and CH₄ can be utilized through the reaction. The DRM process produces syngas with a H₂/CO ratio of 1 that is suitable for Fischer–Tropsch (F–T) and methanol synthesis [1–3]. The DRM reaction has been performed over a wide range of catalysts, including noble as well as non-noble metals [4,5]. Among them, the nickel-based catalysts are preferred due to the inherent availability and low cost of nickel. However, the major drawback is coking, in particular when the reaction was conducted over nickel-based catalysts [6–9]. It is hence highly desirable to develop a new catalyst that is inexpensive, active and stable for the DRM reaction.

In recent years, transition metal carbides have attracted much attention, owing to the fact that the metal carbides show catalytic properties similar to those of noble metals in a variety of

reactions such as methane reforming, hydrogenation reaction and hydrocarbon isomerization [10–12]. Previous studies indicated that unsupported β-Mo₂C was catalytically active for the DRM process, showing high thermal stability and good resistance toward coking [13,14]. According to Claridge et al., stable activity (72 h) at 850 °C could be achieved in CH₄/CO₂ reforming over β-Mo₂C at high pressure (8 bar) [15]. Cubic α-MoC_{1–x} was also tested for DRM, although the conversion levels over α-MoC_{1–x} were higher than those over β-Mo₂C, the α-MoC_{1–x} phase was transformed to β-Mo₂C phase during the reaction [16]. On the other hand, bimetallic carbides were used as catalysts for DRM [17–19]. Stable catalytic activity (80 h) was observed by Shao et al. over bimetallic Co–W carbides at 850 °C and 3.4 bar [17]. Despite the positive results and high thermal stability of these low-cost materials, the carbide catalysts deactivated rapidly due to oxidation by CO₂ at atmospheric pressure as pointed out by Thomson [14].

In our previous studies, we demonstrated that the Ni modified Mo₂C catalyst performed well in CH₄/CO₂ reforming [20,21]. The advantage of Ni–Mo₂C over hexagonal Mo₂C or other traditional carbide catalysts is its stable performance at atmospheric pressure. Herein, we report the results of our recent study on the catalytic performance of Ni–Mo₂C, with attention given to the synergistic effect of Ni and Mo₂C. The different catalytic behaviors of Ni–Mo₂C catalysts with different Ni/Mo ratios allowed us to discriminate the catalytic roles of Ni and carbide for DRM.

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