# Nickel Nanoparticles Supported on Nonreducible Mesoporous Materials: Effects of Framework Types on the Catalytic Decomposition of Methane

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Hydrogen is viewed as a key green energy source by the chemical and petrochemical industries<sup>1</sup> because energic use of hydrogen does not generate greenhouse gas emissions. As a result, many researches have explored methods of generating hydrogen in an economical way.<sup>2,3</sup> Methane is the main constituent of biogas and natural gas, and have the hydrogen/carbon ratio of four, which is higher than that of any other hydrocarbon. Many processes have been devised to extract hydrogen from methane, including steam reforming of methane,<sup>4</sup> catalytic decomposition of methane (CDM),<sup>5</sup> and partial oxidation of methane<sup>6</sup>; however, CDM is considered to have the greatest potential in terms of its low CO<sub>2</sub> emissions.

The CDM has been widely studied for a practical purpose. During this process, coke is formed as a by-product of decomposition, and the cokes can block catalyst surfaces and causes catalyst deactivation.<sup>7,8</sup> Many research studies on active metals,<sup>9–17</sup> supports,<sup>18</sup> and promotors<sup>19</sup> have been performed to achieve high catalyst activity and stability and resistance against deactivation during methane decomposition. These efforts have shown that supported catalysts provide one of the best ways of improving catalytic activity. There are various catalyst supports (metal oxides, zeolites, carbons, silica, and others)<sup>5</sup> and all of these supports increases catalyst activity in one way or another. For example, strong metal-supports interact to enhance the dispersity of active metals and provide resistance to sintering. In turn, the catalytic performance such as activity and stability was enhanced.<sup>20</sup> Furthermore, the reducibility of support can affect catalyst activity.<sup>21</sup> Sometimes, coke formation occurs at acid sites on the support material, and thus, the introduction of basicity to support offers a means of reducing carbon formation.<sup>22</sup> Recent studies have shown that support porosity improves catalyst activity.<sup>23</sup> Porous materials have unique structures with internal pores that provide locations for catalysts. Loading porous material with catalyst enhances catalyst dispersity, and thus, catalyst activity.<sup>24,25</sup> In the present work, we investigated the effects of the

framework types of mesoporous materials on CDM catalytic performance. The supports used in this work were composed of nonreducible oxides (*i.e.*, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) to minimize the effect of support reducibility. Specifically, mesopore walls were composed of crystalline microporous MFI zeolite, amorphous silica, and crystalline  $\gamma$ -alumina. Framework structures were determined by X-ray diffraction (XRD) (Figure S1). The resulting materials are denoted "M-Zeo," "M-SiO<sub>2</sub>," and "M-Al<sub>2</sub>O<sub>3</sub>," respectively, where "M" means mesoporous.

The porosities of individual supports were investigated using N<sub>2</sub> adsorption-desorption isotherms (Figure S2; Table S1). M-Al<sub>2</sub>O<sub>3</sub> had the lowest surface area and pore volume. M-zeo exhibited a higher specific surface area (550 m<sup>2</sup>/g) than M-SiO<sub>2</sub>, but its pore volume was lower, which is attributed to the larger mesopore diameters of M- $SiO_2$  (see Figure S3 for pore size distributions). Note that M-SiO<sub>2</sub> exhibited mesoporosity only, while M-Zeo exhibited a hierarchical structure, in which zeolite micropores and intercrystalline mesopores were highly interconnected.<sup>26</sup> The acidities of M-SiO<sub>2</sub> and M-Zeo samples were characterized by using NH<sub>3</sub>-TPD (Figure S4). M-Zeo exhibited unimodal distribution with maxima at ~310 °C. The NH<sub>3</sub>-desorption peak was shifted to lower temperature (~190 °C) in the case of M-SiO<sub>2</sub>, indicating that M-SiO<sub>2</sub> had a relatively lower acid strength than M-Zeo. For CDM, nickel was selected as the active metal and was loaded on these mesoporous supports using a melting method at  $\sim 15\%$ by weight (see Supporting information for experimental details).

Figure S5 shows XRD patterns for Ni/M-Zeo, Ni/M-SiO<sub>2</sub>, and Ni/M-Al<sub>2</sub>O<sub>3</sub>. These results confirmed the successful loading of metallic nickel after reduction on all supports, as indicated by characteristic nickel peaks at  $44.36^{\circ}$  and  $51.72^{\circ}$ .<sup>27</sup> In the case of Ni/M-Al<sub>2</sub>O<sub>3</sub>, two additional XRD peaks (19.4° and 32.0°) were observed, which were assigned to nickel-aluminate with a spinel structure. This suggested a considerable portion of the Ni reacted

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Figure 1. STEM images and their corresponding EDS elemental mapping images in STEM mode. (a)  $Ni/M-Al_2O_3$ , (b) Ni/M-Zeo, and (c)  $Ni/M-SiO_2$ .

with alumina to form a nickel-alumina compound during the reduction process.<sup>28</sup>

Figure 1 shows representative scanning transmission electron microscopy (STEM) images for Ni/M-Al<sub>2</sub>O<sub>3</sub>, Ni/ M-Zeo, and Ni/M-SiO<sub>2</sub>. Particle size distributions for supported Ni nanoparticles were derived from several TEM images (Figures S6–S9). We considered that 10–20 nm nickel particles appeared to be loaded inside mesopores, whereas larger particles were located on support surfaces in case of all. Ni/M-SiO<sub>2</sub> had the highest loading rate in mesopores. In terms of uniformity, Ni/M-Zeo sample showed a broad distribution of particle diameters for supported Ni. In addition, N<sub>2</sub> isotherms for Ni-supported samples showed a notable decrease in mesopore volume, indicating that a large portion of Ni nanoparticles was located inside mesopores (Figure S10).

Figure 2(a) shows  $CH_4$  conversions as a function of reaction time over Ni/M-Zeo, Ni/M-SiO<sub>2</sub>, and Ni/M-Al<sub>2</sub>O<sub>3</sub>. The initial activity was defined as the  $CH_4$  conversion obtained after reaction for 1 h. Ni/M-SiO<sub>2</sub> exhibited the



**Figure 2.** (a) Conversion of methane as a function of reaction time for Ni/M-SiO<sub>2</sub> (blue), Ni/M-Zeo (black), and Ni/M-Al<sub>2</sub>O<sub>3</sub> (red). (b) Carbon yield of individual supported nickel catalyst. Reaction temperature:  $550^{\circ}$ C, CH<sub>4</sub>/N<sub>2</sub> = 0.5 WHSV: 2.95 h<sup>-1</sup>.

best initial activity (~26.5%), which decreased in the following order: Ni/M-SiO<sub>2</sub> > Ni/M-Zeo > Ni/M-Al<sub>2</sub>O<sub>3</sub>. It would appear that the high dispersity of supported Ni nanoparticles <10 nm is related to catalyst activity. Interestingly, despite well-dispersed nickel in Ni/M-Al<sub>2</sub>O<sub>3</sub>, a considerable amount of this nickel was converted to nickel aluminate, which might reduce the initial activity.<sup>29</sup>

As CDM proceeded,  $CH_4$  conversion was decreased as a function of reaction time for all Ni-supported catalysts, although their deactivation rates differed. In this study, catalytic stability was defined as the time required to achieve 5%  $CH_4$  conversion. The Ni/M-Al<sub>2</sub>O<sub>3</sub> catalyst was most rapidly deactivated to reach the 5%  $CH_4$  conversion within 3 h. Catalyst stability increased in the order of Ni/M-Zeo < Ni/M-SiO<sub>2</sub>. In the case of Ni/M-SiO<sub>2</sub> catalyst, the initial activity was retained for 5 h and then slowly deactivated. Ni/M-SiO<sub>2</sub> reached 5%  $CH_4$  conversion after 20 h of reaction, which was the best result observed.

It is well known that methane decomposes to carbon and hydrogen, and thus, carbon yield also provides a measure of catalyst performance (*i.e.*, hydrogen productivity). Carbon yield can be calculated using Eq. (1), as previously described.<sup>24,30</sup>

Carbon yield = 
$$\frac{\text{Weight of formed coke}}{\text{Weight of Ni in catalyst}}$$
 (1)

The weight of coke formed can be calculated using thermogravimetric analysis (TGA) results. Figure S11 shows TGA results for reacted-Ni/M-SiO<sub>2</sub>, reacted-Ni/M-Zeo, and reacted-Ni/M-Al<sub>2</sub>O<sub>3</sub>. All samples experienced an abrupt mass loss from 400°C to 600°C, which was attributed to the decomposition of the cokes produced in air. Therefore, mass losses in the range of 400–600°C are associated with the weight of coke formed during CDM reaction. The carbon yield was determined using Eq. (1); and results are summarized in Figure 2(b). As was expected, Ni/M-SiO<sub>2</sub> provided the highest carbon yield, which suggests high initial activity and catalyst stability.

TEM and Raman spectroscopy were used to determine the characteristics of the coke formed on the catalyst. For

three catalysts, the coke was formed as carbon nanotube (CNT). TEM shows most of the formed CNTs in Ni/M-SiO<sub>2</sub> and Ni/M-Zeo had around 10–20 nm, though exceptionally some of them were ~50 nm in Ni/M-SiO<sub>2</sub> (Figures S12–S14). Figure S15 shows g-band (~1580 cm<sup>-1</sup>) and d-band (~1350 cm<sup>-1</sup>) peaks were detected in Ni/M-SiO<sub>2</sub> and Ni/M-Zeo, whereas a low intensity g-band and d-band peak was observed in Ni/M-Al<sub>2</sub>O<sub>3</sub> due to the small amount of coke produced.<sup>31</sup> We also confirmed the presence of CNTs by XRD, as it produces a characteristic peak at ~26° (Figure S16).<sup>32</sup>

There are two main causes of supported Ni catalyst deactivation during CDM reactions, that is, metal sintering and coke formation. To determine the cause of deactivation, we first investigated changes in Ni particle size distribution after CDM. Figure S17 shows nickel particle sizes were not changed, which indicates deactivation was not caused by sintering during the reaction. In addition, when the N<sub>2</sub> adsorption behaviors of the spent catalysts were almost restored after air regeneration, indicating that textural properties might not be changed during the CDM reactions. Therefore, we believe the deactivation was primarily due to coke formation, as has been previously reported.<sup>8,23</sup> The catalytic activity of the spent Ni/M-SiO<sub>2</sub> catalyst can be restored by coke removal through air calcination (Figure S18).

As regards catalyst stability, we observed deactivation was slower for higher pore volumes. According to XRD and TEM measurements, the cokes formed may be multi-walled CNTs.<sup>30</sup> Thus, it seems that higher mesopore volumes might increase the amount of CNTs formed, which might enhance catalyst stability of supported Ni catalysts during CDM. To support the effect mesopore volume, Ni supported on bulk MFI was prepared and compared the CDM performance with Ni/M-Zeo (Figure S19). Deactivation rate is faster for Ni/bulk-MFI, as compared to Ni-M-Zeo.

We also found that total carbon production when nonreducible mesoporous supports were used was strongly related to pore volume. Higher pore volumes might provide more space for the formation of multi-layered CNTs, which means coke capacity is closely connected to catalytic ability. Accordingly, for a high quantity of H<sub>2</sub> generation, higher pore volume should be considered a driver of catalyst activity and stability during CDM.

In conclusion, the catalytic performance of Ni supported materials in CDM reaction is highly related to the amount of mesopore volume of supports. This might be attributed to that higher pore volumes might provide more space for the multi-layered CNTs (*i.e.*, cokes), which means coke capacity is closely connected to catalytic ability.

#### Experimental

Mesoporous silica and  $\gamma$ -alumina were purchased from Sigma-Aldrich (St. Louis, MO, USA). Mesoporous MFI zeolites are synthesized in the laboratory according to the

previous paper.<sup>26</sup> Nickel nanoparticles were supported on the support using the melting method. CDM reaction was performed in a fixed-bed reactor system using quartz reactor (see detailed description in Supporting Information).

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**Supporting Information.** Additional supporting information may be found online in the Supporting Information section at the end of the article.

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