Oxidative Coupling of Methane over Na_2WO_4-Mn/SiO_2 Catalyst: Effect of SiO_2 Supports

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Introduction

The oxidative coupling of methane (OCM) has been believed as a potential to produce C2 hydrocarbon from natural gas. A great deal of effort has been devoted to enhancing the methane conversion and C2 hydrocarbon yield in OCM [1]. A large number of catalysts, such as alkali-promoted alkaline earth metal oxides, transition metal oxides and rare earth metal oxides, have been found to show good activity and selectivity in the OCM reaction [2-4]. Among these catalysts, Na_2WO_4-Mn/SiO_2 has been recognized to be an active catalyst for the OCM reaction so far.

The goal of this work is to investigate the effect of silica supports in Na_2WO_4-Mn/silica catalysts on the OCM reaction. For this purpose, we have utilized commercial SiO_2 gel, supercritically-dried SiO_2 aerogel, MCM-41, and MCM-48. Also, fresh and used catalysts have been characterized to determine what makes such catalysts to show different catalytic behavior.

Materials and Methods

Active materials, Na_2WO_4 and Mn, were impregnated on four different silica supports, such as SiO_2 gel (S1), SiO_2 aerogel (S2), MCM-41 (S3), and MCM-48 (S4), by sequential incipient wetness method. The OCM experiments were carried out in a quartz tubular reactor containing 0.2 g of catalyst at the temperature range of 675 to 800°C. The OCM products were analyzed by an on-line gas chromatography equipped with the TCD (molecular sieve 5A, packed column) for H_2, N_2 and O_2 and with the FID (Carboxen 1000, packed column) for CO, CO_2 and hydrocarbons.

Results and Discussion

The OCM activity and product distribution of catalysts prepared in this work were shown in Table 1 and Figure 1. In terms of the CH_4 conversion and C2 yields, Na_2WO_4-Mn/S2 and Na_2WO_4-Mn/S4 showed better performance (CH_4 conversion of 42% and C2 yield of 24% at 675°C) than other two catalysts. Especially, it is worth noting that the catalysts prepared utilizing mesoporous silica materials as a support (initial mesoporosity disappeared after calcination at 800°C) maintained their activity (CH_4 conversion as well as C2 selectivities) at low temperatures of 675-725°C while the activity of SiO_2 gel-supported catalyst dropped considerably from 725 to 650°C. After obtaining the catalytic data reproducibly, we have characterized four different catalysts by BET, SEM-EDX, TEM-EDX, XPS, Raman spectroscopy, etc. Among these data, it was found that big particles (main composition: 55% W) of about 2 μm existed at the support surface of Na_2WO_4-Mn/S1 and, during the OCM reaction, became sintered whereas such particles could not be seen in other catalysts (both fresh and used). Furthermore, more evidences to investigate the effect of SiO_2 support on the OCM activity of Na_2WO_4-Mn/SiO_2 have been revealed, which will be discussed on-site.

Table 1. OCM product distributions obtained over four different catalysts at the maximum CH_4 conversion

Catalyst	Temp. (°C)	Selectivity (%)						
		H_2	CO	CO_2	C_2H_2	C_2H_4	C_2H_6	C_3
Na_2WO_4-Mn/S1	725	1.3	17.1	15.8	0.1	38.3	13.4	4.6
Na_2WO_4-Mn/S2	675	0.6	14.1	17.3	0.2	43.4	14.6	5.9
Na_2WO_4-Mn/S3	675	0.8	16.4	16.1	0.2	40.8	13.4	5.6
Na_2WO_4-Mn/S4	675	0.6	16.7	16.4	0.2	42.5	13.9	5.9

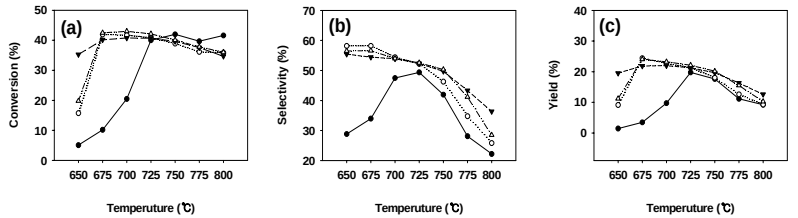

Figure 1. Conversion of CH_4 (a), selectivity (b) and yield (C) of C2 hydrocarbons over Na_2WO_4-Mn/S1 (●), Na_2WO_4-Mn/S2 (○), Na_2WO_4-Mn/S3 (▼), and Na_2WO_4-Mn/S4 (△).

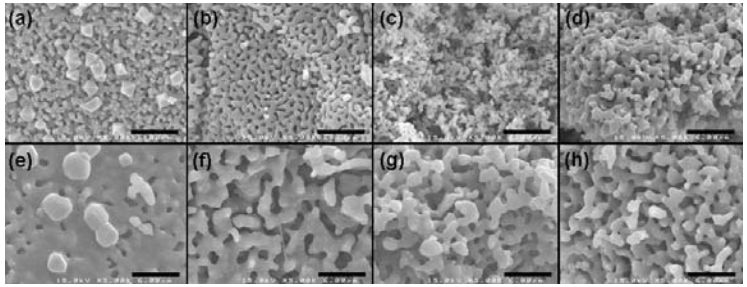

Figure 2. SEM images of four different catalysts which are fresh (a-d) or used (e-h); (a) and (d) Na_2WO_4-Mn/S1, (b) and (f) Na_2WO_4-Mn/S2, (c) and (g) Na_2WO_4-Mn/S3, (d) and (h) Na_2WO_4-Mn/S4 (scale bar: 6 μm).

References

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