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Performance improvement for a fixed bed reactor with layered loading catalysts of different catalytic properties for oxidative coupling of methane

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ARTICLE INFO	A B S T R A C T	
Keywords: Oxidative coupling of methane Mn-Na ₂ WO ₄ /SiO ₂ catalyst Ag and Ce promoted catalysts La-Ce oxide catalyst Layered loading	Layered loading of catalysts with different catalytic properties is studied for oxidative coupling of methane reaction (OCM) in a fixed bed reactor. Layered loading of a more active catalyst Ag-Mn-Na ₂ WO ₄ /SiO ₂ in front of a more selective one Ce-Mn-Na ₂ WO ₄ /SiO ₂ compared to loading Mn-Na ₂ WO ₄ /SiO ₂ catalyst only, lowers reaction temperature and increases selectivity. Such layered loading broadens the temperature range to achieve a high selectivity, which is important for OCM reaction carried out with multi-stage adiabatic fixed bed reactor. Similarly, with a very active La-Ce oxide catalyst loaded in front of a selective catalyst Ce-Mn-Na ₂ WO ₄ /SiO ₂ , the temperature needed to start the reaction is lowered significantly. Therefore, a catalyst bed such as La-Ce oxide can be used as a "pre-heater" for the high temperature OCM reaction to lower the feed temperature. The total CH ₄ utilization can be improved with this loading strategy.	

1. Introduction

As a result of recent shale gas boom, more and more natural gas is being produced. But natural gas generally is used as fuel for electricity generation. There is a strong desire to increase the value of this abundant hydrocarbon resource. Oxidative coupling of methane (OCM) is one of the way to transform methane, the principle component of natural gas, to more valuable products, such as ethylene. Although close to 40 years extensive research and development has been devoted to this technology [1], it has never been commercialized. Efficiency of transformation from methane to ethylene, even when using the best catalyst today, is still low. By using catalysts with different properties, catalyst activity or selectivity can be improved, but it is very challenging to gain activity and selectivity at the same time.

As we know, OCM reaction is a multi-step process, involving consecutive reactions starting from CH_4 activation to form CH_3 radicals, to coupling to form C_2H_6 , to C_2H_6 dehydrogenation or oxidative dehydrogenation to form C_2H_4 [2]. Further oxidation or reforming of the coupling products produces the unwanted CO and CO_2 . For example, when a fixed bed reactor is used for this reaction, there will be a profile of different product species along the reactor [3]. Therefore, it is difficult achieve the best performance by using a single catalyst, because of different properties are needed at the different sections of the bed.

On this basis, one of approaches to improve performance, may be

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use of catalysts with different properties, such as combination of two catalysts, one with high activity and another with high selectivity.

In this work, we studied the OCM reaction with layered loading strategy in a fix bed reactor: loading catalysts with different properties in different sections in the reactor. Two cases are experimentally studied. In the first case, two catalysts with similar catalytic properties are studied with layered loading. In the second case, two catalysts with quite different catalytic properties are studied. Potential benefits for practical applications from layered loading are discussed.

2. Experimental

2.1. Catalyst preparations

Four Mn-Na₂WO₄/SiO₂ based catalysts were studied, all catalyst samples were prepared by using incipient wetness impregnation method [4]. La-Ce oxide catalyst is prepared by drying and calcining the mixture solution of raw material nitrates.

2.1.1. Catalyst 1. Mn-Na₂WO₄/SiO₂ (1.9%Mn-5.0%Na₂WO₄/SiO₂)

18.62 g of Davisil Grade 646 silica gel was used as catalyst support. Before use the silica gel was dried overnight. 1.73 g of $Mn(NO_3)_2$:4H₂O was dissolved in 18.6 ml of DI water. The $Mn(NO_3)_2$:4H₂O solution was added into silica gel dropwise to achieve a uniform distribution of the solution onto the solids. Then the mixture was dried overnight at

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125 °C. 1.13 g of Na₂WO₄·2H₂O was dissolved in 18.6 ml of DI water. The solution obtained was added into the dried Mn containing silica gel dropwise. The mixture was dried at 125 °C again overnight. Then the dried material was calcined at 800 °C for 6 h. The calcined material was ready for performance test.

2.1.2. Catalyst 2. Ag-Mn-Na2WO4/SiO2 (1.0% Ag-1.9%Mn-5.0% Na2WO4/SiO2)

15.75 g of Davisil Grade 646 silica gel was used as catalyst support. Before use the silica gel was dried overnight. 1.48 g of $Mn(NO_3)_2$ ·4H₂O was dissolved in 15.8 ml of DI water. The $Mn(NO_3)_2$ ·4H₂O solution was added into silica gel dropwise to achieve a uniform distribution of the solution onto the solids. Then the mixture was dried overnight at 125 °C. 0.27 g of AgNO₃ was dissolved in 15.8 ml of DI water. The AgNO₃ solution was added into silica gel dropwise to achieve a uniform distribution of the solution of the solution onto the solids. Then the mixture was dried overnight at 125 °C. 0.26 g of Na₂WO₄·2H₂O was dissolved in 18.6 ml of DI water. The solution obtained was added into the dried Mn containing silica gel dropwise. The mixture was dried at 125 °C again overnight. Then the dried material was calcined at 800 °C for 6 h. The calcined material was ready for performance test.

2.1.3. Catalyst 3. Ce-Mn-Na₂WO₄/SiO₂ (5.0%Ce-1.9%Mn-5.0% Na₂WO₄/SiO₂)

17.62 g of Davisil Grade 646 silica gel was used as catalyst support. Before use the silica gel was dried overnight. 1.74 g of $Mn(NO_3)_2$ ·4H₂O was dissolved in 17.6 ml of DI water. The $Mn(NO_3)_2$ ·4H₂O solution was added into silica gel dropwise to achieve a uniform distribution of the solution onto the solids. Then the mixture was dried overnight at 125 °C. 3.10 g of Ce(NO_3)_3·6H_2O was dissolved in 17.6 ml of DI water. The Ce(NO_3)_3 solution was added into silica gel dropwise to achieve a uniform distribution of the solution onto the solution onto the solution onto the solution was added into silica gel dropwise to achieve a uniform distribution of the solution onto the solids. Then the mixture was dried overnight at 125 °C. 1.12 g of Na_2WO₄·2H₂O was dissolved in 17.6 ml of DI water. The solution obtained was added into the dried Mn containing silica gel dropwise. The mixture was dried at 125 °C again overnight. Then the dried material was calcined at 800 °C for 6 h. The calcined material was ready for performance test.

2.1.4. Catalyst 4. Ag-Ce-Mn-Na₂WO₄/SiO₂ (1.0%Ag-5.0%Ce-1.9%Mn-5.0%Na₂WO₄/SiO₂)

17.6 g of Davisil Grade 646 silica gel was used as catalyst support. Before use the silica gel was dried overnight. 1.74 g of $Mn(NO_3)_2$ ·4H₂O was dissolved in 17.6 ml of DI water. The $Mn(NO_3)_2$ ·4H₂O solution was added into silica gel dropwise to achieve a uniform distribution of the solution onto the solids. Then the mixture was dried overnight at 125 °C. 3.10 g of Ce(NO_3)_3·6H_2O and 0.32 g of AgNO_3 was dissolved in 17.6 ml of DI water. This Ce(NO_3)_3 and AgNO_3 solution was added into silica gel dropwise to achieve a uniform distribution of the solids. Then the mixture was dried overnight at 125 °C. 1.12 g of Na_2WO_4·2H_2O was dissolved in 17.6 ml of DI water. The solution onto the solids. Then the dried Mn containing silica gel dropwise. The mixture was dried at 125 °C again overnight. Then the dried material was ready for performance test.

2.1.5. Comparative catalyst. Ag/SiO₂ (3.0%Ag/SiO₂)

This catalyst is prepared for comparison. 3.00 g of Ag (15 nm) in 5% water was added into 3.00 g of silica gel which was calcined at 800 °C. After Ag addition, the mixture is dried overnight at 125 °C.

2.1.6. Catalyst 5. La-Ce oxide catalyst

La-Ce oxide catalyst with La/Ce = 10 was used in this study. It was prepared using the method described in [5]. 24.06 g of La(NO₃)₃·6H₂O was dissolved in 40 ml of DI water to yield a La(NO₃)₃ aqueous solution. 2.39 g of Ce(NO₃)₃·6H₂O was dissolved in 10 ml of Di water to yield a Ce(NO₃)₃ aqueous solution. These two aqueous solutions

were mixed and then heated at 85 °C for 2 h under agitation. The obtained mixture was then dried overnight at 125 °C to yield a dried powder, which was then calcined at 625 °C for 5 h to yield the catalyst.

2.2. Catalyst testing

Experiments were carried out in quartz tube fixed bed reactor of 4 mm inner diameter. Gases are fed to the reactor by the use of mass flow controllers. The reactor is heated by using conventional clamshell furnace. The furnace has three heating zones. During reaction, the top and bottom zones are set at 300 °C. Then middle zone is set at the reaction temperature. Due to the small inner diameter reactor used, there is no thermocouple inside the reactor, the temperature reported is the middle zone furnace set point temperature. We measured the temperature inside the reactor before reaction in nitrogen feed, the temperature inside is 50 °C higher than the furnace temperature.

The necessary reaction temperature was settled by using the constant-temperature furnace set up described above which was varied from experiment to experiment, similar method was used in [6].

The catalyst bed is located in the center of the middle zone furnace. On the top and bottom of the catalyst bed, quartz chips are loaded to reduce the empty volume. On the both ends of the quartz chip sections, quartz wools are used to hold the catalyst bed and quartz chips to the targeted position.

Catalyst performance test was carried out under atmosphere pressure. The reaction products were analyzed by using online Gas Chromatography (Agilent 6890). Two columns are used to separate the products. Molecular sieve 13X column is used for permanent gases analysis, CO, CO₂, O₂ and Ne. They are detected with TCD detector. HP-Q-Plot column is used for hydrocarbon products analysis. Products observed are C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄'s and C₅'s. These products are detected with FID detector. C₂₊ selectivity reported below is the total selectivity to the hydrocarbons from C₂ to C₅.

Catalyst loading strategy and different testing conditions used are described below.

2.2.1. Testing of $Mn-Na_2WO_4/SiO_2$ and promoted $Mn-Na_2WO_4/SiO_2$ catalysts

The first condition was used for testing $Mn-Na_2WO_4/SiO_2$ and promoted $Mn-Na_2WO_4/SiO_2$ catalysts with 100 mg catalyst loading. For layered loading studies, two catalysts were loaded in layers, one (with 50 mg) was loaded in the front section of the bed and the other (with 50 mg) loaded on the back. The flow rates of gases used for this condition are shown in Table 1, with Ne as the internal standard. The methane to oxygen ratio is 7.4 under this condition. By varying the reaction temperature, performances under different temperatures are obtained.

2.2.2. Testing of La-Ce oxide and Ce-Mn-Na₂WO₄/SiO₂ based catalysts

The second testing condition was applied for testing La-Ce oxide and Ce-Mn-Na₂WO₄/SiO₂ system. For testing La-Ce oxide catalyst alone, 20 mg of catalyst was loaded. For layered loading, different amounts of La-Ce oxide were loaded in front of the bed with 240 mg of Ce-Mn-Na₂WO₄/SiO₂ on the back. Ce-Mn-Na₂WO₄/SiO₂ alone with 240 mg loading was also tested for comparison. The flow rates of gases at methane to oxygen ratio of 4.0 with Ne as the internal standard are

Table 1 Flow rates of feed with $CH_4:O_2 = 7.4$.

Gas component	Feed rate
Oxygen Methane Neon	3.9 sccm 28.9 sccm 0.5 sccm
Total flow	33.3 sccm

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