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Effect of CO_2 on the structural variation of $Na_2WO_4/Mn/SiO_2$ catalyst for oxidative coupling of methane to ethylene

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ABSTRACT

In this work, the influence of CO_2 on the structural variation and catalytic performance of $Na_2WO_4/Mn/SiO_2$ for oxidative coupling of methane to ethylene was investigated. The catalyst was prepared by impregnation method and characterized by XRD, Raman and XPS techniques. Appropriate amount of CO_2 in the reactant gases enhanced the formation of surface tetrahedral Na_2WO_4 species and promoted the migration of O in MO_x, Na, W from the catalyst bulk to surface, which were favorable for oxidative coupling of methane. When the molar ratio of $CH_4/O_2/CO_2$ was 3/1/2, enriched surface tetrahedral Na_2WO_4 species and high surface concentration of O in MO_x, Na, W were detected, and then high CH_4 conversion of 33.1% and high C_2H_4 selectivity of 56.2% were obtained. With further increase of CO_2 in the reagent gases, the content of active surface tetrahedral Na_2WO_4 species and surface concentration of O in MO_x, Na, W decreased, while that of inactive species ($MnWO_4$ and Mn_2O_3) increased dramatically, leading to low CH_4 conversion and low C_2H_4 selectivity. It could be speculated that Na_2WO_4 crystal was transformed into $MnWO_4$ crystal with excessive CO_2 added under the reaction conditions. Pretreatment of $Na_2WO_4/Mn/SiO_2$ catalyst by moderate amount of CO_2 before OCM also promoted the formation of Na_2WO_4 species.

1. Introduction

Both CH_4 and CO_2 are thought to contribute to greenhouse effect, and their conversion into value-added chemicals is one of the attractive research focuses worldwide [1–6]. As one way to produce valuable chemicals from abundant natural gas resources, oxidative coupling of methane (OCM) has long been widely investigated and is expected to play a major role in the utilization of natural gas [7–12].

Keller et al. [13] published the first report on the production of C_2 hydrocarbons from CH_4 in 1982, and then much more attention has been paid to OCM reaction. In order to find a suitable catalyst, a large number of materials had been tested. Most of the active and selective catalysts for OCM reaction were composed of two or three irreducible oxides, e.g., alkali metal oxides, alkali earth metal oxides, or rare earth metal oxides [14–18]. Fang et al. [19,20] first reported the $Na_2WO_4/Mn/SiO_2$ catalyst for OCM in 1992, 37.7% CH_4 conversion and 66.9% C_2 selectivity were achieved at 800 °C in a microreactor. Then this system has received increasing attention for its excellent catalytic performance [21–24].

A lot of researches concerning the nature of the active phase on Mn-Na_2WO_4/SiO_2 catalyst were published, but an agreement has not yet been reached. The first article about the surface reconstruction of Mn-Na_2WO_4/SiO_2 catalyst was reported by Jiang et al. [25]. A surface cluster compound with a stoichiometry of $Si_3WO_{8.5}$, containing one W=O double bond and three W–O–Si bonds, was proposed. This surface cluster compound formed by the reconstruction of surface tetrahedral WO_4 might constitute to the active phase for OCM on Mn-Na_2WO_4/SiO_2 catalyst. Wu et al. [26] suggested that the shortest W–O bond of the distorted WO_4 tetrahedron might be the active phase for OCM reaction, while the catalyst with W–O octahedral coordinated structure was inactive for effectively converting CH_4 to C_2 hydrocarbons. They proposed that the octahedral structure was changed into a distorted tetrahedron due to the presence of Na^+, and the WO_4 tetrahedron on 5% Na_2WO_4/SiO_2 catalyst distorted to some extent by the interaction of Na_2WO_4 with the silica support. Lunsford et al. [27] studied OCM reaction over $Mn/Na_2WO_4/SiO_2$, $Mn/Na_2WO_4/MgO$ and $NaMnO_4/MgO$ catalysts, and suggested that Na–O–Mn was the active phase. EXAFS and XPS characterizations of $Mn/Na_2WO_4/SiO_2$ catalyst were carried out by Kou et al. [28]. They found that the combination of tetrahedral metallic core of WO_4 and octahedral metallic core of MnO_6 with different oxidation states was responsible for the catalysis in OCM reaction. Ji et al. [29,30] reported that both Na–O–Mn and Na–O–W acted as the active phase, and WO_4 tetrahedron (Na_2WO_4 or $Na_2W_2O_7$) on the catalyst surface appeared to play an essential role

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in achieving high CH_4 conversion and high selectivity to C_2 hydrocarbons. Theoretical calculations suggested that the transition state formed via the interaction of WO_4 with CH_4 could be more stable than that of WO_6 with CH_4, demonstrating that WO_4 tetrahedron had suitable geometry and energy matching with CH_4, and this might account for the high OCM activity. However, tetrahedral WO_4 was first formed in the presence of Na and Mn when the W content was low, while the increase of W led to the presence of both tetrahedral WO_4 and octahedral WO_6. In contrast to other researchers, Chua et al. [31] and Mahmoodi et al. [32] found that Mn_2O_3 and α-cristobalite were the predominant species acting as the active phase on the nanocatalyst surface, and Na_2WO_4 and Mn_2O_3 crystalline phases contributed to achieving high selectivity to C_2 products.

In OCM reaction, CO_2 was an undesirable by-product, and it might also have effect on the reaction system. Ross et al. [33] explored the influence of CO_2 on the OCM over the Li/MgO catalyst. They found that CO_2 in the gas phase lowered both the CH_4 conversion and the yield of C_2 products. Suzuki et al. [34] reported that the use of CO_2 as a reactive diluent for OCM increased the C_2 yield and selectivity but lowered CH_4 conversion for some MgO- and Sm_2O_3-based catalysts, whereas for CaO and SrO catalysts, the presence of large amounts of CO_2 was detrimental. The effect of CO_2 on OCM kinetics was also investigated over a Li/Pb/Ca catalyst, and the reduction in CH_4 conversion and increase in C_2 selectivity were observed when CO_2 is added to the feed gas [35]. However, very few studies had been devoted to the influence of CO_2 on the structural nature of $Na_2WO_4/Mn/SiO_2$ catalyst. In this work, the effect of CO_2 addition to OCM reaction system on the structural variation and catalytic performance of $Na_2WO_4/Mn/SiO_2$ catalyst was studied.

2. Experimental

2.1. Catalyst preparation

$Na_2WO_4/Mn/SiO_2$ catalyst was prepared by two-step incipient wetness impregnation method. The silica support (20–40 mesh, $320\ m^2/g$) was impregnated with aqueous solution containing appropriate amounts of $Mn(NO_3)_2$ (purchased from Kelong Company, 50% solution) for 24 h without stirring and then dried at 80 °C in water bath, followed by being dried at 110 °C in air for 4 h, and finally calcined at 800 °C in air for 5 h. The above prepared material was then impregnated with Na_2WO_4 (purchased from Bodi Company, 99.5%) aqueous solution for 24 h without stirring and dried at 80 °C in water bath, then dried at 110 °C in air for 4 h, and finally calcined at 800 °C in air for 5 h to obtain the catalyst.

Pretreatment of $Na_2WO_4/Mn/SiO_2$ catalyst by CO_2 was conducted. The catalyst prepared above was heated from ambient temperature to 800 °C at the rate of 10 °C/min under CO_2 flow (54 mL/min), and the temperature was kept at 800 °C for 10 h to treat the catalyst.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was performed on an X'Pert-Pro MPD diffractometer with a Cu K_α monochromatic X-ray radiation operated at 40 kV and 35 mA. The data was collected over the scattering angle of 2θ from 10° to 80° with a step of 0.03 °/s.

X-ray photoelectron spectroscopy (XPS) analysis was performed on AXIS Ultra DLD (KRATOS) spectrometer, using Al K_α radiation (1486.6 eV) operated at an accelerating power of 150 W, and the binding energy was calibrated with XPS signals of C 1s at 284.6 eV.

Raman spectrum was obtained using a LabRAM HR Raman Spectrometer (HORIBA Jobin Yvon S.A.S.) with a semiconductor laser source and the laser excitation wavelength was 785 nm. The scanning range was set from 200 to 1000 cm^{-1}.

Table 1
The influence of $CH_4/O_2/CO_2$ mole ratio on catalytic performance.

$CH_4/O_2/CO_2$	Conversion (%)		Selectivity (%)				
	CH_4	CO_2	H_2	CO_2	CO[d]	C_2H_4	C_2H_6
3/1/0[a]	28.7	–	5.6	14.3	18.7	50.0	17.0
3/1/0[b]	29.4	–	6.2	13.4	16.8	52.4	17.4
3/1/1[a]	31.2	−43.2[c]	1.9	7.6	20.6	54.0	17.8
3/1/2[a]	33.1	−14.0[c]	2.6	4.1	21.0	56.2	18.7
3/1/2.5[a]	27.1	−9.6[c]	2.7	10.0	26.5	45.9	17.6
3/1/2.8[a]	14.7	−1.6[c]	3.3	3.1	70.4	15.0	11.5
3/1/3[a]	12.7	2.0	3.1	–	92.6	2.2	5.2
3/1/4[a]	11.3	1.7	2.9	–	98.8	0.6	0.6

Reaction conditions: $T = 800$ °C, total flow rate = 120 mL/min, 0.25 g $Na_2WO_4/Mn/SiO_2$ catalyst

[a] Catalyst without pretreatment;
[b] Catalyst pretreated by CO_2;
[c] Minus sign showed that CO_2 was generated other than being converted;
[d] The amount of CO produced from the carbon atom in CH_4, not from CO_2

2.3. Activity test

The catalytic activity test was carried out in a fixed-bed continuous flow micro-quartz-tube reactor (70 cm length, 8 mm i.d.) under ambient atmospheric pressure. 0.25 g catalyst was loaded in the middle of the reactor. A thermocouple centered at the catalyst bed was bound to the outer wall of the reactor to control the reaction temperature. The catalyst was heated from ambient temperature to reaction temperature (800 °C) at the rate of 10 °C/min under argon flow (99.99%, 30 mL/min). Then the reactants, CH_4 (99.95%) and O_2 (99.95%) were co-fed into the reactor ($CH_4/O_2 = 3/1$). The effect of CO_2 addition on the reaction system was studied by keeping the total GHSV of CH_4, O_2 and CO_2 (or Ar) constant, and changing the amount of CO_2 (or Ar) added. Mass flow controllers (D07-11A/ZM made by Beijing Sevenstar Electronics Co. Ltd.) were used to control the flow rate of reactant gases. A cold trap and a desiccator were used at the reactor outlet to remove the water from the effluent. Then the effluent after removal of water was analyzed by an on-line gas chromatograph (Fu Li 9750 GC) with a plot-C2000 capillary column for separating the products, and a TCD to determine the amount of each component. The data discussed in this paper were obtained at TOS (time on stream) = 10 h. Experimental data were repeatable and the deviation was about ±0.2%. In all experiments, the amount of deposited carbon was below 7 $mg/(g_{cat})$, which was negligible.

2.4. Transient experiment

The reaction equipment in transient experiment was the same as that used in activity test. 0.25 g catalyst was loaded in the middle of the reactor. The catalyst was heated from ambient temperature to reaction temperature (800 °C) at the rate of 10 °C/min under argon flow (99.99%, 30 mL/min). Then the reactants and diluent gas, CH_4, O_2 and Ar were co-fed into the reactor ($CH_4/O_2/Ar = 3/1/2$). When OCM reaction was carried out for about 1 h, Ar was immediately switched to CO_2 ($CH_4/O_2/CO_2 = 3/1/2$). The effluent was analyzed by on-line multichannel HP R-20QIC mass spectrometry.

3. Results and discussion

3.1. Activity results

The catalytic activity data at TOS = 10 h in both the absence and presence of CO_2 were listed in Table 1. CH_4 conversion of 28.7% and C_2H_4 selectivity of 50.0% were obtained without dilution of reagent gases ($CH_4/O_2/CO_2 = 3/1/0$). On the other hand, with the introduction of CO_2, from the $CH_4/O_2/CO_2$ molar ratio of 3/1/0 to 3/1/2, the conversion of CH_4 increased gradually, from 28.7% to 33.1%, while