

Role of SnO₂ over Sn-W-Mn/SiO₂ catalysts for oxidative coupling of methane reaction at elevated pressure

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ABSTRACT

The SnO₂-doped W-Mn/SiO₂ catalyst for oxidative coupling of methane (OCM) to high hydrocarbons has been studied in a micro- stainless-steel reactor at elevated pressure. Under 750 °C, 1.0×10⁵ h⁻¹ GHSV and 0.6MPa, 20.3% yield of C₂⁺ hydrocarbons and 29.7% CH₄ conversion with 33.5% selectivity of C₃ ~ C₄ is obtained. The storage-oxygen capability in W-Mn/SiO₂ catalyst is enhanced with adding SnO₂, SnO₂ promotes the migration of Na, W and Mn to the catalyst surface; W⁵⁺ possibly existed over the surface of SnO₂ doped W-Mn/SiO₂ catalyst.

1. INTRODUCTION

In the last two decades, most of the attention on the direct conversion of methane has been devoted to the oxidative coupling reaction (OCM), which involves the catalytic conversion of methane with oxygen to C₂⁺ hydrocarbons and water [1-2]. One of the most effective catalysts for the OCM is W-Mn-/SiO₂ [3], several groups led by Li, Lunsford and Lambert have studied for the OCM over the catalyst on the elementary reaction and role of active composition [4-6]. Most of the researcher's have focused their attention on the OCM at atmospheric pressure, however, the studies on the OCM under elevated pressure are less [7-9]. Recently, we reported that a comparatively high yield of higher hydrocarbons was achieved over SnO₂ promoted W-Mn/SiO₂ catalysts under lower pressure as 0.6MPa in the stainless- steel reactor for oxidative conversion of methane [10, 11]. In this paper, we reported the effects of SnO₂ on crystalline phase; the relation between catalyst structure and catalytic activities was discussed.

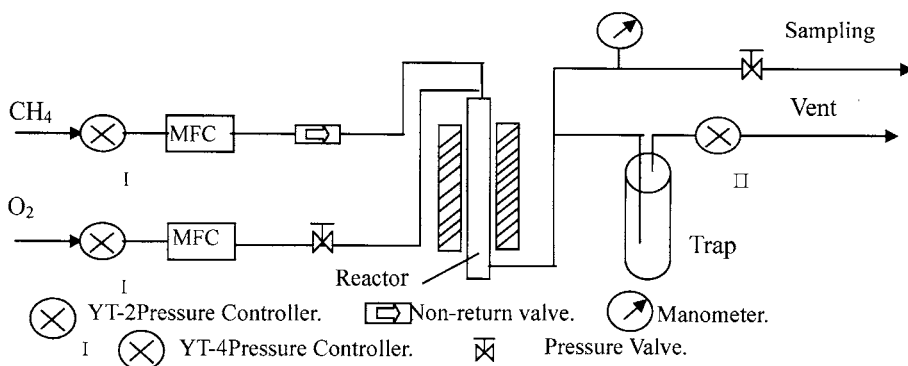


Fig. 1. The schematic diagram of the apparatus on OCM at elevated

2. EXPERIMENTAL

2.1. Catalyst preparation

The SnO_2 modified W-Mn/ SiO_2 catalysts were prepared by the equal-volume impregnation method [6]. Silica particles were washed with water several times and dried. The pretreated silica particles were impregnated with the aqueous solutions of $\text{Mn}(\text{NO}_3)_2$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in appropriate concentrations at 50°C respectively. The impregnated silica particles were evaporated to dryness, and impregnated by the toluene solutions of 5% di-n-butyltin dilaurate at 50°C and dried overnight at 100°C ; the resultant were calcined in air at 850°C for 8 hrs. No carbon deposit was detected over the fresh catalyst surface by XRD.

2.2. Analysis

The major products for oxidative coupling of methane at elevated pressure were detected by two on-line gas chromatographs using TCD with 5A column which separated O_2 , CH_4 , CO and with Poropak Q column which separated CH_4 , CO_2 , C_2H_4 , C_2H_6 , another GS using FID with a Al_2O_3 capillary tube column separated higher hydrocarbons. All data were taken after 30 minutes of reaction.

2.3. Reactor system

In all experiments, the reactant gases, methane and oxygen without diluent, were co-fed into the reactor. The catalytic runs were carried out in a vertical-flow fixed-bed reactor system (In Figure 1) made by a stainless-steel tube (I.D.=8 mm); 0.4 g catalysts were loaded in the reactor, while the remaining space of the reactor was filled with ceramic particles (40 mesh).

2.4. Catalyst characterization

XRD patterns of the catalysts were obtained with a D/MAX-RB diffractometer

using Cu α radiation X-ray at 50 kV and 60 mA. XPS analysis of the catalysts was performed with a VG ESCALAB 210 spectrometer, near-surface compositions were calculated using sensitivity factors, which were provided in the software of the instrument.

Temperature programmed desorption (TPD) of O_2 was carried out in Y-type quartz reactor with 0.1g catalysts using AM-100 catalyst character system. The fresh catalysts was treated in O_2 (30 ml min^{-1}) at 800°C for 30 min, followed by decreased to room temperature with O_2 (30 ml min^{-1}) flow, then sequentially flushed by He (50 ml min^{-1}). Each run was conducted between room temperature and 850°C at a heating rate of $30^\circ\text{C min}^{-1}$ by He at a flow rate of 50 ml min^{-1} .

3. RESULTS AND DISCUSSION

The significant reaction on the SnO_2 modified W-Mn/ SiO_2 catalysts for OCM was found, 20.3% yield of C_2^+ hydrocarbon and 29.7% CH_4 conversion with 33.5% selectivity of $\text{C}_3 \sim \text{C}_4$ could be obtained at a CH_4/O_2 ratio of 4 and $1.0 \times 10^5 \text{ h}^{-1}$ GHSV (Fig.2); through investigation of reaction conditions, the 2.5-4.0 of CH_4/O_2 , $1.0\text{-}1.5 \times 10^5 \text{ h}^{-1}$ of GHSV and $720\text{-}780^\circ\text{C}$ as the optimal operated condition was established. As SnO_2 addition in W-Mn/ SiO_2 catalyst, CH_4 conversion and selectivity of C_2^+ were enhanced obviously. But $\text{SnO}_2\text{-Na-Mn/SiO}_2$ catalyst exhibits lower C_2^+ selectivity; addition of Na_2WO_4 , the C_2^+ selectivity increases markedly because Na_2WO_4 is responsible for selectivity of higher hydrocarbons [1]. Thus a kind of synergistic reaction occurs positively among Sn, Mn and W over the SnO_2 -promoted W-Mn/ SiO_2 catalysts.

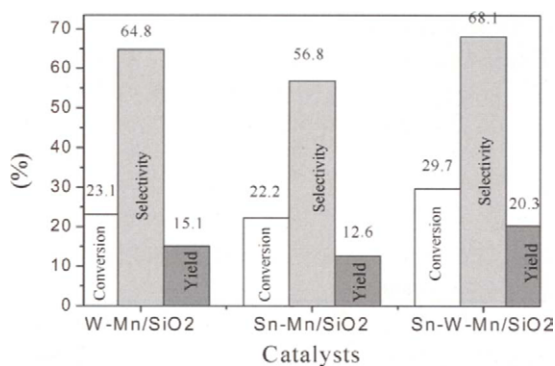


Fig. 2. Performance of SnO_2 promoted W-Mn/ SiO_2 catalysts for the oxidative coupling of methane without diluent at elevated pressure under $P=0.6\text{ MPa}$, $\text{CH}_4/\text{O}_2=4$, $T=750^\circ\text{C}$, $\text{GHSV}=1.0 \times 10^5 \text{ h}^{-1}$.

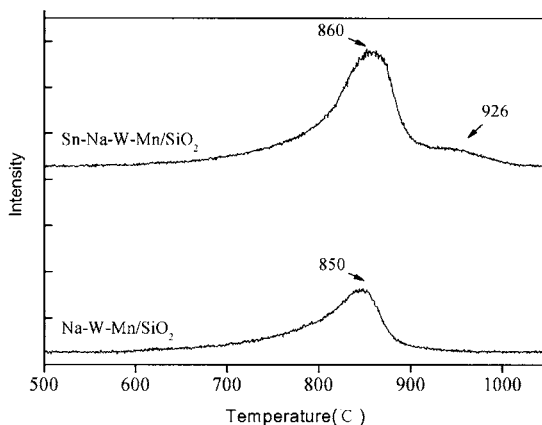


Fig. 3. Comparison between the O₂-TPD results of 8.0%SnO₂/W-Mn/SiO₂ and W-Mn/SiO₂ catalysts.

The comparison between the O₂-TPD results of 8.0%SnO₂/W-Mn/SiO₂ and W-Mn/SiO₂ catalysts were shown in Fig. 3. As may be seen, the oxygen storage capability in W-Mn/SiO₂ catalyst was enhanced with addition of SnO₂ so as to 1.5 times than that of W-Mn/SiO₂ catalyst. So the surface lattice oxygen in SnO₂ doped W-Mn/SiO₂ catalyst was responsible for methane activation, catalytic activity for OCM over Sn-W-Mn/SiO₂ catalyst (Fig.2) is increased the contribution due to enhancing oxygen storage capability.

Near-surface concentration and related binding energy of SnO₂/W-Mn/SiO₂ and W-Mn/SiO₂ catalysts are shown in Table 1. As can be seen, the near-surface concentration of Na and Mn are 5.8% and 1.3% over W-Mn/SiO₂ catalyst, after adding SnO₂ in W-Mn/SiO₂, the near-surface concentration of Na and Mn are increased to 8.2% and 3.1% respectively. So adding SnO₂ promotes obviously that the migration of Na and Mn to the catalyst surface due to the interaction between SnO₂ and SiO₂; the migration of Mn and Na to the near surface resulted in a marked shift to higher molecular weight products.

Table 1

Near-surface concentration (atom%) and related binding energy of 8%SnO₂/W-Mn/SiO₂ and W-Mn/SiO₂ catalysts.

Cat.	Na _{1s}		Mn _{2p}		W _{4f}		O _{1s} (SiO ₂)		O _{1s} (MO _x)	
	BE	In*	BE	In	BE	In	BE	In	BE	In
Na-W-Mn	1071.8	5.8	641.4	1.3	35.1	2.4	532.5	51.4	530.1	16.1
Sn-Na-W-Mn	1072.0	8.2	641.1	3.1	35.3	2.3	532.7	46.0	530.2	19.2

*In= Near-surface concentration (atom%).

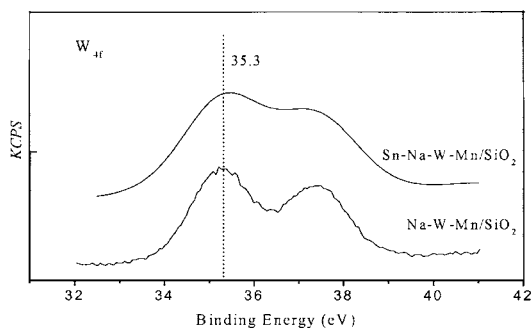


Fig. 4. XPS spectra in W_{4f} region of $SnO_2/W-Mn/SiO_2$ and $W-Mn/SiO_2$ catalysts.

When adding SnO_2 in $W-Mn/SiO_2$, the peaks of $W_{4f_{7/2}}$ and $W_{4f_{5/2}}$ had overlapped (Fig. 4); W^{5+} possibly existed over the surface of SnO_2 -doped $W-Mn/SiO_2$ catalyst. The structural, catalytic performance and spectroscopic results indicated that SnO_2 played a dual role as chemical promoter, it was that promoted Mn and Na_2WO_4 migrate to near surface. A kind of transmittal mode about molecular oxygen was existed possibly between W and Mn or among W, Mn and Sn; the transmittal mode is due to existence of metal oxide being changeable valence in a series of W-Mn catalysts. The mechanism for OCM over SnO_2 doped $W-Mn/SiO_2$ catalysts should be described about equal to which of $W-Mn/SiO_2$ catalyst by using the Redeal-Redox mechanism [1].

The fresh SnO_2-W-Mn/SiO_2 catalyst and the catalysts after reaction at 0.6MPa and 3.5MPa were subjected to XRD measurement (Fig.5). The crystalline phase of the fresh catalyst is SnO_2 , Mn_2O_3 , Na_2WO_4 and α -cristobalite. $Na_2W_2O_7$ and tridymite are detected after reaction 8.0 hrs at 0.6MPa and do not change during further pressure and longer reaction time. It shows that the catalyst is steadier under high pressure.

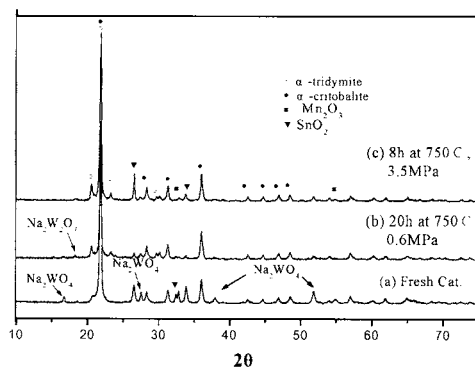


Fig. 5. XRD patterns of used and fresh 8% $SnO_2/W-Mn/SiO_2$.

4. CONCLUSION

A CH₄ conversion of 29.7% with C₂₊ selectivity of 68% is obtained in a micro-stainless-steel reactor at elevated pressure. Lower temperature and lower CH₄/O₂ were more suitable for oxidative coupling of methane to C₂₊ formation over the SnO₂-doped W-Mn/SiO₂ catalysts. This reaction is especially sensitive to operating conditions, particularly CH₄/O₂ ratio and total pressure. Adding SnO₂ promotes the migration of Na and Mn to the catalyst surface, it is due to the interaction between SnO₂ and SiO₂; the migration of Mn and Na to the near surface resulted in a marked shift to higher molecular weight products; and the oxygen storage capability in W-Mn/SiO₂ catalyst was enhanced with addition of SnO₂. So the surface lattice oxygen in SnO₂ doped W-Mn/SiO₂ catalyst was responsible for methane activation, catalytic activity for OCM over Sn-W-Mn/SiO₂ catalyst is increased the contribution due to enhancing oxygen storage capability. When adding SnO₂, the peaks of W4f_{7/2} and W4f_{5/2} had overlapped; W⁵⁺ possibly existed over the surface of SnO₂ doped W-Mn/SiO₂ catalyst.

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