Oxidative Coupling of Methane over W-Mn/SiO_2 Catalyst[†]

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W-Mn/SiO_2 catalyst has been developed in our laboratory (LICP), which is active, selective and stable for oxidative coupling of methane (OCM) in fixed bed and fluidized bed reactors. The research results have been reproduced at different reaction conditions by two groups of J. H. Lunsford (JH-LL) from Texas A & M University and R. M. Lambert (RMLL) from University of Cambridge respectively. The basic research aspects on this catalyst systems, reaction performances, structure characterization and reaction mechanism were reviewed. A model on two active sites related to $W^{6+/5+}$ and $Mn^{3+/2+}$ has been suggested for activation of methane and oxygen respectively.

Keywords Methane, coupling, oxidation, reaction mechanism

Introduction

Oxidative coupling of methane (OCM) has been an attractive route for direct conversion of natural gas to produce higher hydrocarbons, especially ethylene, since the pioneering work on this subject reported by Keller and Bhasin in 1982.[1] However, identification of high performance catalysts used for such process becomes a great challenge in the field of selective oxidation catalysis. Thousands of catalysts have been tested for OCM reaction, but it is difficult to achieve a sum of CH_4 conversion and C_2 selectivity exceeds 100%.

Currently, basic or rare earth metal oxides with basic metal promoter were used as effective catalysts. The transition metal oxides, which have successfully been applied in industry for selective oxidation of olefins, were considered to be not selective, because they usually favor CO_x formation.[2] Some 30 metal oxides including Mn_2O_3/Mn_3O_4 and WO_3 supported on Al_2O_3 and/or SiO_2 have been screened by earlier workers,[3-5] but only one kind of metal promoted by sodium is used as active site of the catalyst. Nevertheless, the most catalysts used for selective oxidation of hydrocarbons should consist of two active sites of metal for activation of hydrocarbon and molecular oxygen respectively.[6] Therefore, composite transition metal oxides containing Fe-W, Co-W, Ni-W, Zn-W and Mn-W supported on SiO_2 have been studied to catalyze OCM reaction in our laboratory since 1988. It was found that the W-Mn/SiO_2 promoted by sodium has the best performance for OCM reaction under a wide range of operation conditions. In comparison with basic and/or rare earth metal oxides, the W-Mn/SiO_2 catalyst is more active, selective and stable. The best result for OCM reaction reported in 1992 was 37.7% CH_4 conversion at 66.9% C_2 selectivity with 2.6 C_2H_4/C_2H_6 ratio.[7,8] A few years later, Lunsford and coworkers from Texas A & M University reproduced our results, and obtained 20% CH_4 conversion at 81% C_2 selectivity.[9] More recently, Lambert and coworkers from University of Cambridge studied the effect of sodium on selectivity of W-Mn/SiO_2 catalyst and structure of SiO_2 support, as well as obtained 33% CH_4 conversion at 80% C_2 selectivity.[10] In this paper, some basic research aspects on W-Mn/SiO_2 catalyst systems are reviewed. A reaction

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mechanism model involving two transition metal active sites are proposed for explanation of the catalytic behavior of W-Mn/SiO_2 catalyst during OCM reaction.

Reaction performances of catalysts

The reaction performances of W-Mn/SiO_2 catalyst systems were listed in Table 1. It can be seen that sum of CH_4 conversion and C_2 selectivity can exceed 100% at different reaction conditions. In our laboratory, we used much higher space velocity and higher O_2 to CH_4 ratio to obtain higher CH_4 conversion and lower C_2 selectivity. At Lunsford's laboratory by using lower space velocity and lower O_2 to CH_4 ratio without N_2 as diluent gas, 20% CH_4 conversion and 81% C_2 selectivity were obtained. More interesting result has been observed by Lambert and coworkers, CH_4 conversion and C_{2+} selectivity can achieve 33% and 80% respectively at 850℃ and much lower space velocity. In this result, the sum of CH_4 conversion and C_2 selectivity is 113%, which has never been reported in other catalyst systems. This promising result should be very important for OCM process commercial application to produce ethylene from naturalgas economically.

Table 1 Reaction performances of W-Mn/SiO_2 catalyst at different pressure

	LICP	JHLL	RMLL
Reaction performances at normal pressure	800℃, 1600 mL/min·g $CH_4:O_2:N_2 = 3:1:2.5$ $C_{CH_4} = 37.7\%$, $S_{C_{2+}} = 66.9\%$	800℃, 115 mL/min·mL $CH_4:O_2 = 7.4:1$ $C_{CH_4} = 20\%$, $S_{C_{2+}} \geqslant 80\%$	850℃, 45 mL/min·mL $CH_4:O_2 = 4.5:1$ $C_{CH_4} = 33\%$, $S_{C_{2+}} = 80\%$
Reaction performances at higher pressure	800℃, 0.5 Mpa, 36000 h^{-1} $CH_4:O_2 = 4:1$, 220 h, $C_{CH_4} = 26.0\%$, $S_{C_{2+}} = 68.5\%$	800℃, 0.5 Mpa, 33000 h^{-1} $CH_4:O_2 = 10$, 60 h $C_{CH_4} = 13$—14%, $S_{C_{2+}} = 80\%$	
Stability testing	1000 h	30—60 h	
Active oxygen species	Surface lattice oxygen	Lattice oxygen is not involved in reaction at cofeeding mode	
Reaction mechanism	Redox mechanism	Surface active species are unstable without gas phase oxygen	
References	7, 8, 11, 12	2, 9	10

The stability of W-Mn/SiO_2 catalyst is particularly good for OCM reaction in different type of reactors. It has been tested on stream for 1000—500 h with a micro quartz reactor, a 30 mL of fixed bed quartz reactor[11] and a 200 mL of fluidized bed stainless steel reactor[12] in our laboratory, and no significant decrease of activity and selectivity was observed.

Other excellent performances of W-Mn/SiO_2 catalyst are that the C_2H_4/C_2H_6 ratio is higher and CO_2 formation is lower than other catalyst systems during OCM reaction. Moreover, the W-Mn/SiO_2 catalyst can be operated at elevated pressure, the CH_4 conversion and C_2 selectivity decreased slightly with increasing total pressure and space velocity simultaneously. After long term OCM reaction CO_2 formation is decreased while CO formation increased. The W-Mn/SiO_2 catalyst is also active and selective for partial oxidation of methane to synthesis gas and is a good catalyst for oxidative dehydrogenation of ethane to ethylene.[13]

Catalyst structure characterization

The surface and bulk structure as well as nature of active site of W-Mn/SiO_2 catalyst have been investigated by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), laser raman spectroscopy (LRS), O_2 temperature program desorption (TPD) and CH_4 pulse reaction. The results were summarized in Table 2 and Figs. 1—5.

The optimum chemical composition of the catalyst is 1.9 wt% Mn-5 wt% Na_2WO_4/SiO_2 with Na : W : Mn atom ratio of 2:1:2. Enrichment of Na and W on catalyst surface was found by XPS. The extent of such enrichment depends on catalyst composition and preparation method, and normally Na:W:Mn atom ratio is 3:1:0.6 on catalyst surface. The surface enrichment of Na and W in W-Mn/SiO_2 catalyst is considerable.

Table 2 Characterization of W-Mn/SiO_2 catalyst

	LICP	JHLL
Optimum chemical composition	1.9% Mn 5%Na_2WO_4/SiO_2 Mn:Na:W = 2:2:1 (bulk) 0.6:3:1 (surface)	2% Mn 5% Na_2WO_4/SiO_2 Mn:Na:W = 2:2:1 (bulk) 0.6:3:1 (surface)
Bulk phase structure	Mn_2O_3, Na_2WO_4 α-cristobalite	Mn_2O_3, Na_2WO_4 $MnWO_4$, α-cristobalite α-tridymite
Active components and Function	Mn: catalytic activity for O_2 activation Na_2WO_4: selectivity	Mn: catalytic activity Na: selectivity W: stability
Surface active species	WO_4 tetrahedron W-O-Si	Na-O-Mn
References	7,8,14,15,16	9

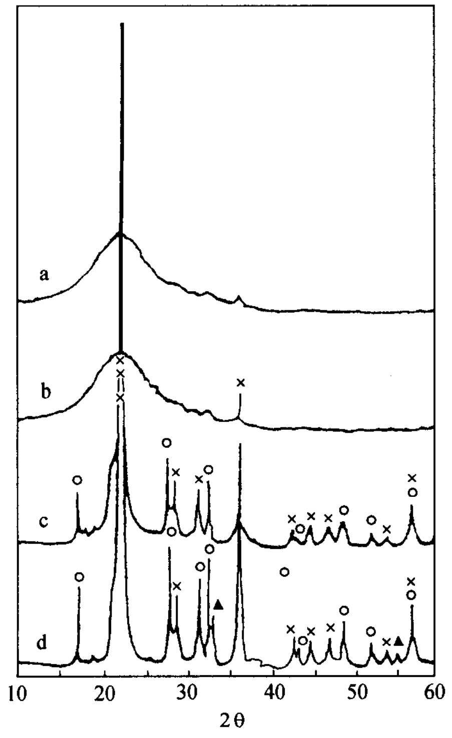

Fig. 1 XRD patterns of W-Mn/SiO_2 catalyst (a) SiO_2, (b) 1.9 wt% Mn/SiO_2, (c) 5 wt% Na_2WO_4/SiO_2, (d) 1.9 wt% Mn 5 wt% Na_2WO_4/SiO_4, × a-Cristobalite. ○ Na_2WO_4, ▲ Mn_2O_3 (Ref. 8).

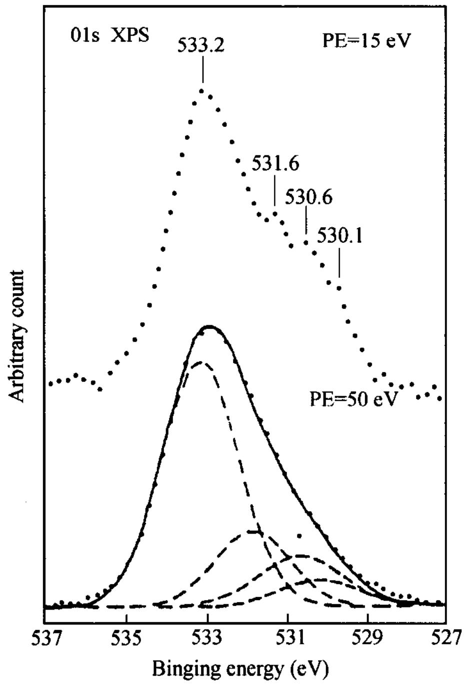

Fig. 2 XPS spectra of W-Mn/SiO_2 catalyst (Ref. 14).

The bulk catalyst is composed of Mn_2O_3, Na_2WO_4 and α-cristobalite phases found by XRD. Active species on the surface observed by XPS, W = O (E_b = 530.3 eV) and W-O-Si (E_b = 531.6 eV) were proposed as the active site related to methane activation[14]. O_2 TPD results of the catalysts with different active components revealed that Mn_2O_3 is responsible for O_2 transfer from gas phase to catalyst surface. The strong interaction between Na_2WO_4 and SiO_2 support results in W-O-Si species formed, SiO_2 structure changed from amorphous to α-cristobalite at lower temperature and the surface area decreased significantly. Further studies carried out by using LRS proved that low coordinated WO_4 tetrahedron is probably an active site for CH_4 activation.[15] Information obtained by using ESR, XPS and CH_4 pulse reaction without gas phase O_2 proved that W^{6+} and

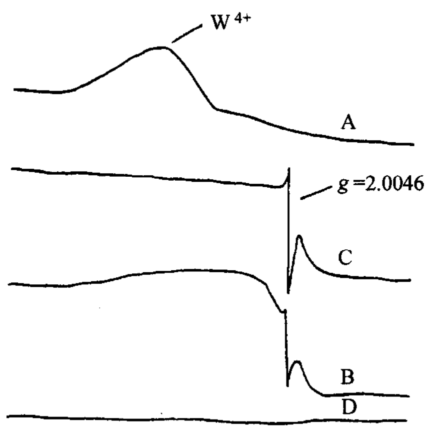

Fig. 3 ESR spectra of W-Mn/SiO_2 catalyst pretreated with methane at 1073 K (A) and then oxygen admission at 253 K (B), 298 K (C) and 353 K (D) (Ref. 16).

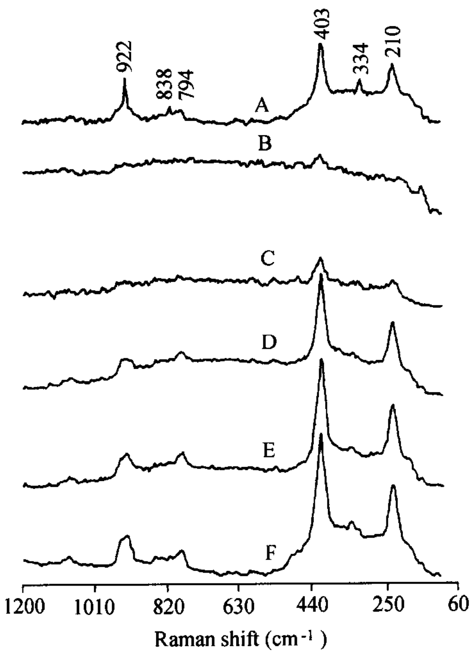

Fig. 4 Raman spectra of W-Mn/SiO_2 catalyst without pretreatment (A), pretreated with methane at 1073 K (B) and then oxygen admission at room temperature (C), 353 K (D), 523 K (D), 523K (E), and 1073 K (F) (Ref. 16).

Mn^{3+} could be reduced to W^{5+} and Mn^{2+} respectively.[16] The ESR signal of W^{5+} can only be observed in Na_2WO_4/SiO_2 without Mn catalyst sample. A shake up peak of Mn^{2+} species was identified by XPS analysis of used catalyst.

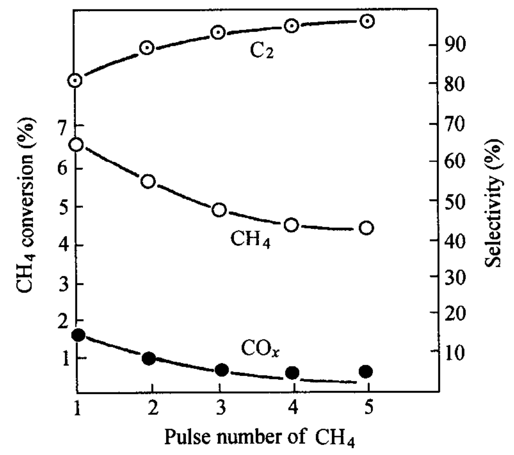

Fig. 5 Result of methane pulse reaction over W-Mn/SiO_2 catalyst (Ref. 16).

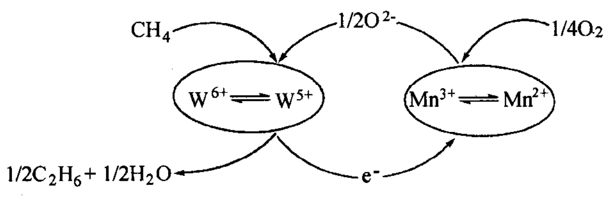

Fig. 6 Two metal active sites model for OCM reaction on W-Mn/SiO_2 catalyst.

Lunsford and coworkers believed that Na-O-Mn is the active site, in which Mn is an active component, Na provides selectivity, and W is required to stabilize catalyst. Lambert and coworkers emphasized the function of Na, which is a chemical and structure promoter for α-cristobalite surface formation and stabilizing key surface active species W. They suggested that WO_4 tetrahedron is an active site for OCM reaction.

Reaction mechanism

An accepted mechanism for OCM reaction is that an active oxygen species abstracts a hydrogen atom from CH_4 molecule to form methyl radical on catalyst surface at high temperature. The methyl radical coupling occurs at the gas phase to form ethane, ethane dehydrogenates with or without oxygen to produce ethylene at the gas phase or on the surface. The CO and CO_2 can be generated from ethane and ethylene or from methane directly. The methyl radical residence on catalyst surface is in favor of CO and CO_2 formation. Generally a good catalyst for OCM reaction has to use a strong basic metal as promoter to enhance C_2 selectivity. The argument is a route of C—H bond breakage: Lunsford and other researchers proposed a homolytic mechanism, whereas Sokolovskii *et al*. raised a heterolytic possibility. There is no enough evidence to identify which is acceptable.

Based on catalyst characterization information obtained above, in the case of W-Mn/SiO_2 catalyst we proposed a two metal active sites model for OCM reaction:

Surface reaction

$$CH_4 + W^{6+} + 1/2O_S^{2-} \rightarrow CH_3 \cdot W^{6+} + H^+ \cdot 1/2O_S^{2-} \tag{1}$$

$$CH_3 \cdot W^{6+} \rightarrow CH_3 \cdot + W^{5+} \tag{2}$$

$$H^+ \cdot 1/2O_S^{2-} \rightarrow 1/2H_2O \tag{3}$$

$$W^{5+} - e \rightarrow W^{6+} \tag{4}$$

$$Mn^{3+} + e \rightarrow Mn^{2+} \tag{5}$$

$$1/4O_2 + Mn^{2+} \rightarrow 1/2O_S^{2-} + Mn^{3+} \tag{6}$$

Gas phase coupling reaction

$$CH_3 \cdot \rightarrow 1/2C_2H_6 \tag{7}$$

Gas phase or surface(oxidative) dehydrogenation

$$1/2C_2H_6 \rightarrow 1/2C_2H_4 + H_2(O) \tag{8}$$

In this model it is believed that active oxygen species is surface lattice oxygen O_S^{2-}, and the redox mechanism involving two metal sites, $W^{6+/5+}$ and $Mn^{3+/2+}$, could be used to explain CH_4 and O_2 activation. The CH_4 is activated by O_S^{2-} to generate $CH_3^{\cdot}$ radical on $W^{6+/5+}$ site, and electron transfer from $W^{6+/5+}$ site to $Mn^{3+/2+}$ site which is responsible for molecular oxygen activation to form surface lattice oxygen O_S^{2-} as an active oxygen species for CH_4 activation. Lunsford and coworkers argued that without gas phase oxygen the active oxygen species is not stable. The bulk lattice oxygen is not involved in OCM reaction at cofeeding mode.

This model is not typical Mars and van Krevelen redox mechanism, because active component concentration of the catalyst is quite low, and most of the active lattice oxygen distributed on the surface. Enhancing W and Mn concentration should be in favor of bulk lattice oxygen utilization as active species for CH_4 activation.

Summary

W-Mn/SiO_2 is an active, selective and stable catalyst for OCM reaction. It can be used in fluidized bed reactor and operated at elevated pressure. The catalyst structure and nature of active sites have been characterized by means of XRD, XPS, ESR, LRS *etc*.. WO_4 tetrahedron and Mn_2O_3 were proposed as active sites for CH_4 and O_2 activation respectively, and surface lattice oxygen O_S^{2-} as active species. Redox mechanism and two metal active sites model have been suggested for OCM reaction on W-Mn/SiO_2 catalyst.

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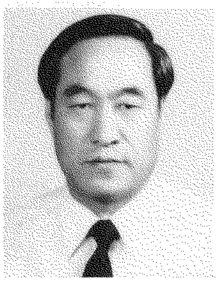

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