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Oxidative Coupling of Methane Over Na–W–Mn–Zr–S–P/SiO_2 Catalyst: Effect of S, P Addition on the Catalytic Performance

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Abstract The multi-component catalysts we prepared exhibited high performance for the oxidative coupling of methane. The highest activity of catalysts was obtained over the Na–W–Mn–Zr–S–P/SiO_2 at the temperature of 1,023 K, on which the C_2 yield was 23.5% at the methane conversion of 43.8%. XRD and XPS results showed the S, P addition could lead to the increase of lattice oxygen concentration and the formation of phase such as Na_2SO_4, $Na_2Zr(PO_4)_2$ on the catalysts. These phases play great roles in activity of the catalysts system.

Keywords Oxidative coupling of methane · Na–W–Mn–Zr–S–P/SiO_2 · Sulfur · Phosphorus

1 Introduction

Oxidative coupling of methane (OCM) has been gotten much attention since the pioneering work of Keller and Bhasin [1], for which can both utilize the abundant resources of natural gas and produce C_2 hydrocarbons (ethane and ethylene).The key challenge facing the commercialization of OCM is the design of a suitable catalyst capable of high desired products (C_2 hydrocarbons) yield at significant level of methane conversion especially at low reaction temperature.

Numerous catalysts have been investigated in OCM reaction. Among the catalysts tested, some multi-component catalysts, such as $Na_4P_2O_7$–$ZrOCl_2$ [2, 3], Na–Mn–W/SiO_2 [4, 5] and Na–Mn–S/SiO_2 [6] have been found to exhibit promising catalytic performance. In the literature [2], the researchers concluded that sodium was a key element in the catalysts and the active phase for OCM were $NaZr_2(PO_4)_3$ and $Na_2Zr(PO_4)_2$. Ji et al. [4] have reported that sodium and manganese played great roles over the Na–W–Mn/SiO_2 catalyst and the addition of tungsten could enhance the stability of catalyst. The active phase in Na–W–Mn/SiO_2 was identified as Na–O–Mn and Na–O–W species. However, the oxides of transition metals (Mn and Zr) over these multi-component catalysts could increase the concentration of lattice oxygen on the surface of catalyst [7, 8]. Much lattice oxygen over the catalysts arouses the complete oxidation of methane, which leads to a low C_2 hydrocarbon yield. On the other hand, according to the research in methane combustion, the catalyst after the sulfur poisoning caused a rather drastic deactivation [9, 10]. This suggests that the sulfur addition in the catalyst for OCM may promote the C_2 hydrocarbons selectivity. Based on this consideration, we have developed Na–Mn–S/SiO_2 catalyst for OCM reaction [6]. Compared to the Na–Mn–W/SiO_2, the C_2 hydrocarbons selectivity over the Na–Mn–S/SiO_2 catalyst has been improved greatly. Subsequently, a much effective six-component Na–W–Mn–Zr–S–P/SiO_2 was designed by using the artificial neural network (ANN) [11, 12]. Although the ANN technique can provides a convenient predictable method for catalyst design, especially for multi-component one, the disadvantage is that the network is opaque, a ‘black box”. It may give good results, but we cannot follow the “reasoning” behind the model.

Thus, this work aims to further understand the six-component catalysts we have prepared, particularly the effect of S, P addition on the catalytic activity. By using the XRD and XPS, the changes of catalyst structure after S, P addition will be also investigated.

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2 Experimental

2.1 Catalyst Preparation and Catalytic Measurements

The catalysts preparation has been reported elsewhere [11]. Briefly, 5.7 wt%Na-2.4 wt%W-1.5 wt%Mn-3.8 wt%Zr-2.1 wt%S-0.4 wt%P/SiO_2 (Cat1)catalyst was prepared by sol–gel method. A mixed solution comprised of Na_2CO_3, Na_2SO_4, $Na_4P_2O_7$ and Na_2WO_4 was added to silica gel solution to obtain a colloid. The colloid was dried in air at 403 K for 3 h, calcined at 823 K for 3 h and at 1,148 K for 5 h, and crushed to the particle size of 20–40 mesh. Then the obtained sample was impregnated with a mixed solution of $ZrOCl_2$ and $Mn(CH_3COO)_2$, dried in air at 403 K for 3 h, calcined at 823 K for 3 h and at 1,148 K for 5 h, and crushed to the particle size of 20–40 mesh. For comparison, the catalysts of 5.7 wt%Na-2.4 wt%W-1.5 wt%Mn-3.8 wt%Zr-2.1 wt%S/SiO_2 (Cat2), 5.7 wt%Na-2.4 wt%W-1.5 wt%Mn-3.8 wt%Zr-0.4 wt%P/SiO_2 (Cat3) and 5.7 wt%Na-2.4 wt%W-1.5 wt%Mn-3.8 wt%Zr/SiO_2 (Cat4) were also prepared.

Activity testing was carried out in a fixed-bed reactor under atmospheric pressure. The following reaction conditions were employed: the flow rates of CH_4 (99.99%) and O_2 (99.95%) were 60 and 20 cm^3/min (NTP), respectively (CH_4:O_2 = 3:1) and the catalyst loading was 1.0 g. In all experiments, CH_4 and O_2 were co-fed into reactor and a mass flow controller controlled their flow-rates. The catalyst was located in the hottest part of reactor at the temperature of 1,023 K. The products were analyzed by two on-line TCD-equipped gas chromatographs. One column with organic support 402 separated CH_4, C_2H_4, C_2H_6 and CO_2; another column with molecular sieve 5 Å separated H_2, O_2, CH_4, and CO.

2.2 Catalyst Characterization

The X-ray diffraction (XRD) patterns of the catalysts were obtained with a Rigaku D/max–c diffractometer using a Cu Ka radiation (40 kV, 80 mA). The X-ray photoelectron spectroscopy (XPS) characterization was recorded using a PHI1600 XPS system. A Mg Ka anode was used as the X-ray source. The binding energy of C1 s (284.5 eV) was taken as internal standard for binding energy calibration.

3 Results and Discussion

3.1 Effect of S, P Addition on the Catalyst Activity

Figure 1 compares the catalytic activity of the catalysts we prepared. With the addition of S, P or both on the catalysts, the conversion of reactant and yield of products have been promoted. Over the Cat4 containing no S and P, CH_4 conversion and C_2 yield is only 16.4% and 11.4%. However, in comparison with the activity of 4.6%Na-3.1%W-2%Mn/SiO_2 catalyst [4], on which CH_4 conversion was 12.0% and C_2 yield 7.3%, the performance of catalyst has been enhanced *ca.* 25%. This indicates the Zr addition can improve the catalyst activity. Significantly, the catalysts performance has been further promoted after the S, P addition (Cat1, Cat2 and Cat3) in current work. The maximum CH_4 conversion and C_2 yield is obtained over the Cat 1 containing both S and P, which is 43.8% and 23.5%, respectively. These results indicates the addition of S, P have great influence on the catalytic performance.

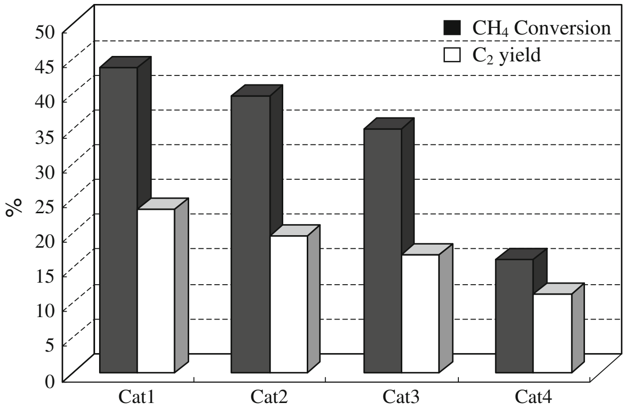

Fig. 1 The activity of the catalysts

3.1.1 *Characterization of Catalysts*

The XRD patterns of Cat1–Cat4 are shown in Fig. 2. The peaks unmarked are ascribed to α-cristobalite. It can be seen that all samples possess the phase of Na_2WO_4, ZrO_2 and α-cristobalite. Ji and his co-workers [4] suggested that Na–O–W species were the most probable active sites of the

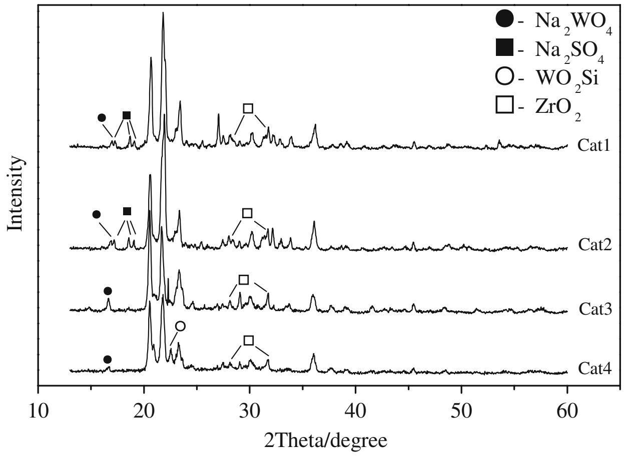

Fig. 2 XRD patterns of the catalysts

Na–W–Mn/SiO_2 catalysts for OCM. In addition, ZrO_2 was reported as an effective crystal phase for activation of methane [13, 14]. This may be one reason why the catalysts we prepared has better activity than that of reported Na–W–Mn/SiO_2 catalysts. Some other peaks are also observed. The peak at 24.8° on the Cat1 XRD spectra is assigned to WO_2Si (silicon tungsten oxide). The formation of WO_2Si is due to the occupation of vacancies in the SiO_2 crystal by W during the catalysts preparation [15]. The peaks correlated with Na_2SO_4 crystal phase are identified on the spectra of Cat1 and Cat2 which are added the S promoter. After the further addition of P (Cat1), this peak becomes much significant. The P promoter can help the formation of Na_2SO_4 phase. However, the phase related with P such as reported $NaZr_2(PO_4)_3$ and $Na_2Zr(PO_4)_2$ is not identified, which may results from the small P loading. Combined with the results of catalyst activity, it is obvious that the existence of Na_2SO_4 crystal phase can enhance the performance of catalyst. Na_2SO_4 is a possible active phase for OCM reaction.

The surface electronic states of the metal in the four catalysts were determined by XPS. Figure 3 shows the Mn 2p XPS spectra of all samples. Similar to the report [16], the binding energy at 641.5 and 654.2 eV should be assigned to the $2p_{3/2}$ and $2p_{1/2}$ feature of the manganese oxides, respectively. But the manganese oxides have not identified by XRD which indicates that Mn species were highly dispersed or in amorphous structure. The Mn oxides can inhibit the deep oxidation of methane and enhance the selectivity of C_2 hydrocarbons [17]. Figure 4 gives the XPS spectra of P2p in the four catalysts. The peaks at 132.7 eV appear on the XPS spectra of Cat1 and Cat 3 indicates the formation of surface phosphate species due to the P addition [18]. These peaks can be assigned to $Na_2Zr(PO_4)_2$ or $NaZr_2(PO_4)_3$, which is responsible for OCM [2].

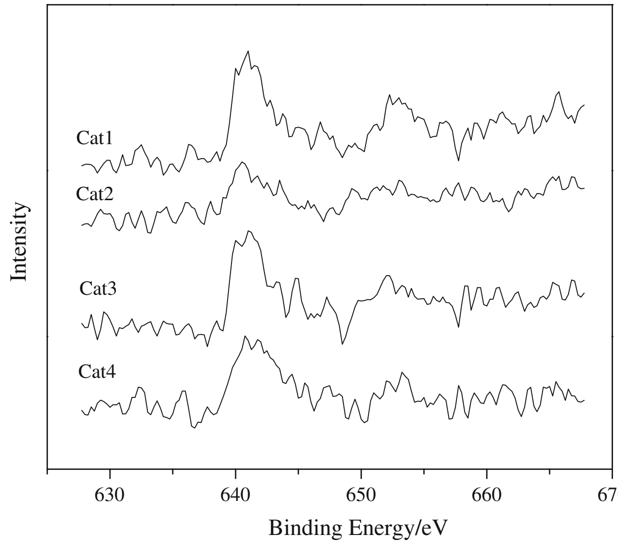

Fig. 3 Mn2p XPS spectra of the catalysts

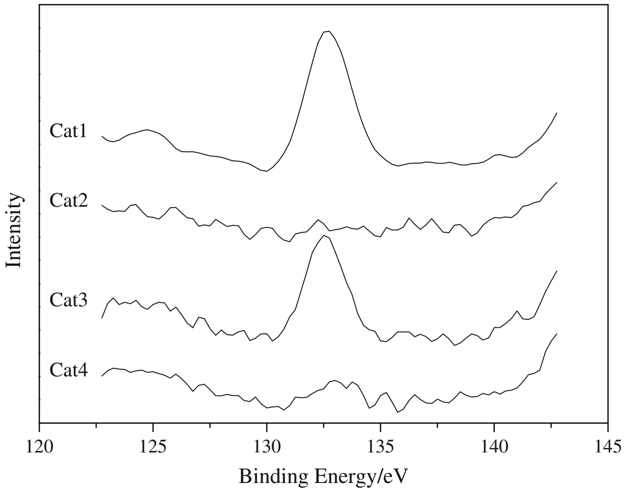

Fig. 4 P2p XPS spectra of the catalysts

The deconvoluted O1 s XPS spectra of the catalysts are presented in Fig. 5. One peak with binding energy of *ca.* 530.2 eV corresponds to O atom in metal oxides (MO_x). Another peak with binding energy of *ca.* 532.0 eV corresponds to O atom in SiO_2 [4]. Figure 6 depicts the O atomic percentage in MO_x and SiO_2 on the Cat1–Cat4 calculated from O1 s spectra. It is found that the atomic percentage of total surface oxygen on various catalysts is similar (about 68%). However, the atomic percentage of oxygen in MO_x and SiO_2 varies notably. The order of the oxygen concentration in MO_x is Cat1 > Cat2 > Cat3 >

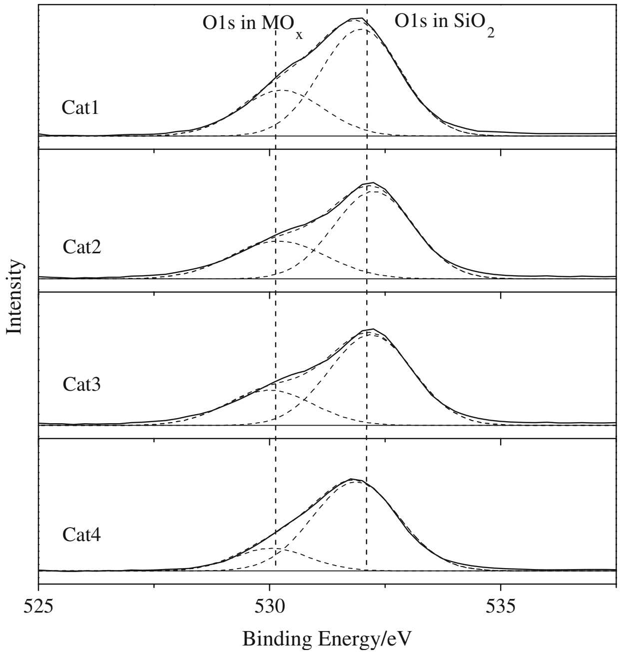

Fig. 5 The deconvoluted O1 s XPS spectra of the catalysts

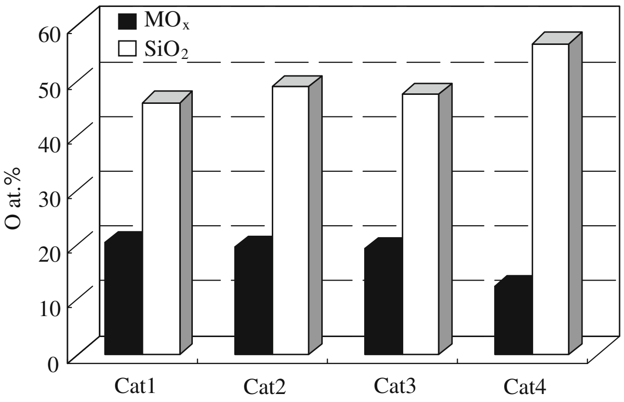

Fig. 6 The O atomic percentage in metal oxides (MO_x) and SiO_2 on the catalysts

Cat4. This suggests that the S, P addition make the O concentration in the MO_x richer. More lattice oxygen is in favor of the activation of methane. This could explain why the order of methane conversion on the catalysts has the same tendency as that of the lattice oxygen.

Based on the above results, it can be seen that S, P addition can enhance methane conversion and C_2 yield. One reason is the increase of lattice oxygen concentration and the formation of ZrO_2 phase which are responsible for the methane activation. Another should be ascribed to the Na_2SO_4, $Na_2Zr(PO_4)_2$ and manganese oxides identified on the prepared catalysts in this work, which may account for C_2 formation.

4 Conclusions

Oxidative coupling of methane has been investigated on multi-component Na–W–Mn–Zr–S–P/SiO_2 catalyst. Compared with the reported results, the methane conversion and C_2 yield on the catalyst have been greatly improved. XRD and XPS characterization illustrate the S, P addition can increase the concentration of lattice oxygen which is in favor of methane activation. In addition, some phases like Na_2SO_4 and $Na_2Zr(PO_4)_2$ are identified on the catalysts we prepared. The catalyst which possesses these phases has the highest activity at the temperature of 1,023 K in this study. It is reasonable to conclude that the phases of Na_2SO_4 and $Na_2Zr(PO_4)_2$ are also active for OCM reaction. Further studies will be performed to confirm how these phases function in the reaction.

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