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CeO_2-Promoted W-Mn/SiO_2 catalysts for conversion of methane to C_3–C_4 hydrocarbons at elevated pressure

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A CeO_2-doped Na-Mn-W/SiO_2 catalyst for oxidative conversion of methane has been studied in a micro-stainless-steel reactor under elevated pressure; a CH_4 conversion of 47.2% with a C_3–C_4 selectivity of 47.3% ($C_2:C_3:C_4 = 1:1:3.3$) was obtained at 983 K with 1.0×10^5 ml g^{-1} h^{-1} GHSV, $CH_4/O_2 = 2.5$ and $P = 0.6$ MPa.

In the last two decades, much attention has been paid to the conversion of methane under oxidative conditions into products with additional value.[1–3] Recently, our work on the 2% Mn_2O_3–5% Na_2WO_4/SiO_2 catalyst showed that this catalyst had excellent activity for oxidative coupling of methane (OCM) under different reaction conditions including under elevated pressures, and was stable for long periods.[3,4] In the OCM over the catalyst, we found that small amounts of C_3 and C_4 hydrocarbons were produced under different conditions, particularly at elevated pressures. On the other hand, Lunsford and coworkers,[5] in particular, reported that C_3 and C_4 hydrocarbons were obtained from methane oxidation through a two-step reaction.

Here, the CeO_2 modified Mn_2O_3–Na_2WO_4/SiO_2 catalyst system was examined and found to have excellent performance in the conversion of methane to C_3–C_4 hydrocarbons under elevated pressure.

The CeO_2 modified 2% Mn_2O_3–5% Na_2WO_4/SiO_2 catalysts were prepared by the wet impregnation method. Silica particles were washed with water several times and dried and used as the stand-by material. The pretreated silica particles (40–60 mesh, surface area = 156 m^2 g^{-1}) were impregnated with aqueous solutions of $Mn(NO_3)_2$ (A.R.), $Na_2WO_4\cdot 2H_2O$ (A.R.) and $Ce(NO)_3\cdot 6H_2O$ in appropriate concentrations at 323 K. The catalysts were dried overnight at 373 K and calcined in air at 1123 K for 8 h (the surface area of the resulting catalyst was 6.8 m^2 g^{-1}). The catalytic runs were carried out in a continuous vertical-flow fixed-bed reactor comprising of a stainless-steel tube (I.D. = 8 mm). 0.4 g catalyst was loaded in the reactor while the remaining space of the reactor was filled with ceramic particles (40 mesh) so as to minimize the contribution due to any gas-phase reactions.

In all experiments, the reactant gases (without diluent) were co-fed into the reactor and their flow-rates were regulated with mass flow controllers. A Ni/Cr–Ni/Al thermocouple was inserted into center of the reactor to monitor the temperature of the catalyst-bed and another thermocouple was positioned at the hottest part of the reactor to manipulate the furnace. The products were analyzed using three on-line gas chromatographs with TCD detectors (two GCs, one with a 5A molecular sieve column, for the separation and analysis of O_2, CH_4, CO and the other with a Poropak Q column for CH_4, CO_2, C_2H_4, C_2H_6) and in the third a GC FID detector with a Al_2O_3 capillary column (40.0 m) was used, with high-purity nitrogen as the carrier gas to separate C_3–C_4 hydrocarbons.

We examined the effects of several reaction conditions, such as temperature, pressure, GHSV and ratio of methane to oxygen on selectivity to C_3–C_4 hydrocarbons and conversion of methane. Based on the investigated effects of the operation conditions, all experiments were chosen under mild temperatures and high GHSVs. The results obtained over the CeO_2 doped Mn-W/SiO_2 catalyst at 983 K and 0.6 MPa with a range of GHSVs are presented in Table 1, where data were taken after 30 min of reaction. In the reaction of CeO_2 modified 2% Mn_2O_3–5% Na_2WO_4/SiO_2 catalysts for oxidative conversion of methane, it was found that a 16.5% yield of C_3–C_4 hydrocarbon with a 37.2% of CH_4 conversion could be obtained at a CH_4/O_2 ratio of 4 and 1.0×10^5 ml g^{-1} h^{-1} GHSV (run 6 in Table 1). Table 1 illustrates that CH_4 conversion and selectivity of C_3–C_4 hydrocarbons increases, with an increase of GHSV from 0.4×10^5 to 1.0×10^5 ml g^{-1} h^{-1}, however, when the GHSV was increased from 1.0×10^5 to 2.0×10^5 ml g^{-1} h^{-1}, CH_4 conversion and selectivity of C_4 hydrocarbon decreased, but C_3 selectivity still increased. Table 1 also shows that in terms of the conversion of methane to C_3–C_4 hydrocarbons the CeO_2 doped Mn-W/SiO_2 catalyst (Mn_2O_3–Na_2WO_4/SiO_2 with added CeO_2) have excellent catalytic activity. However, in other catalyst formulations, such as CeO_2 doped Mn/SiO_2, Na_2WO_4/SiO_2, Mn/SnO_2 and Na_2WO_4/CeO_2, only small amounts of C_3–C_4 were observed, which indicates a synergistic interaction Ce, Mn and W over the CeO_2 doped Mn-W/SiO_2 catalyst.

Fig. 1 shows the effects of CH_4/O_2 on CH_4 conversion and C_3–C_4 selectivities. With a decrease of CH_4/O_2, CH_4 conversion, C_3–C_4 yield and C_3–C_4 selectivities increase, whereas

Table 1 Performances of CeO_2–Mn_2O_2–Na_2WO_4/SiO_2 and other catalysts for the oxidative conversion of methane at elevated pressures[a]

			Selectivity (%)							
Cat.	10^{-5} GHSV/ml g^{-1} h^{-1}	Conv. (%)	C_2	$C_2^=/C_2^-$	C_3	$C_3^=/C_3^-$	C_4	$C_4^=/C_4^-$	CO_2	CO
A[b]	1.0	18.5	60.4	1.57	0	—	5.0	0	20.6	14.0
B[c]	1.0	23.3	62.2	1.85	2.6	0.23	0	—	21.4	15.2
C	1.0	32.1	34.2	1.40	4.5	0.41	19.5	4.11	20.5	21.3
D	0.4	22.4	49.6	1.14	11.1	0.13	3.4	0.28	20.6	15.3
D	0.5	20.3	32.3	2.09	13.0	0.14	16.0	6.45	19.4	19.1
D	1.0	37.2	29.4	2.18	16.4	0.18	28.0	5.20	10.6	15.6
D	1.5	30.7	30.8	2.61	19.2	0.10	8.2	4.94	13.6	28.2
D	2.0	30.0	27.2	3.15	23.3	0.10	7.3	0.82	17.0	25.2

[a] *Reaction conditions*: $CH_4/O_2 = 4$, $P = 0.6$ MPa, $T = 983$ K. [b] SiO_2 non-treated. [c] SiO_2 treated by washing with water, A = 2% Mn_2O_3–5% Na_2WO_4/SiO_2, B = 2% Mn_2O_3–5% Na_2WO_4/SiO_2-treated, C = 5% CeO_2–2% Mn_2O_3–2.5% $Na_4P_2O_7/SiO_2$, D = 5% CeO_2–2% Mn_2–5% Na_2WO_4/SiO_2.

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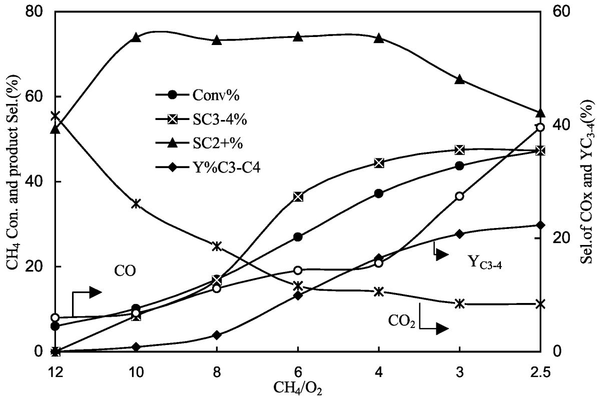

Fig. 1 Effect of CH_4/O_2 on the conversion of methane over 5% CeO_2–Na_2WO_4–Mn_2O_3/SiO_2: T = 983 K, GHSV = 1.0 × 10^5 ml g^{-1} h^{-1}, P = 0.6 MPa.

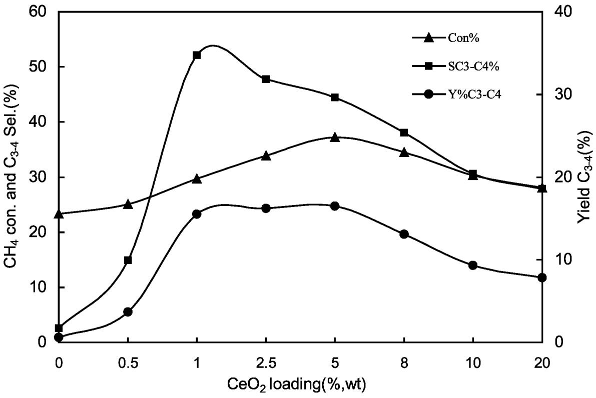

Fig. 2 Effect of CeO_2 loading on the conversion of methane over CeO_2–Na_2WO_4–Mn_2O_3/SiO_2: T = 983 K, GHSV = 1.0 × 10^5 ml g^{-1} h^{-1}, CH_4/O_2 = 4, P = 0.6 MPa.

CO_2 selectivity decreases significantly and CO selectivity increases sharply, but the total CO_x selectivity decreases slightly. This implies, at least partly, that the origin of CO_x is mainly from the oxidation of CH_4 at this rather high temperature (983 K), pressure and GHSV over CeO_2 modified Mn_2O_3–Na_2WO_4/SiO_2 catalyst. An increase in oxygen pressure results in a marked shift to higher molecular weight products. A 22.3% yield of C_3–C_4 with 47.2% of CH_4 conversion and 47.3% of C_3–C_4 selectivity was obtained at CH_4/O_2 = 2.5. Additionally, it is found that higher temperatures do not favor the formation of C_3–C_4 hydrocarbons.

The addition of CeO_2 to the Mn-W/SiO_2 catalysts on the conversion of methane to C_3–C_4 hydrocarbons at elevated pressures led to significant effects. Fig. 2 shows the effects of CeO_2 loading on CH_4 conversion and C_3–C_4 selectivities for the reaction. With CeO_2 loading increased from 0 to 5%, CH_4 conversion and C_3–C_4 yield increases. Further CeO_2 loading from 5 to 20% led to a slight decrease in CH_4 conversion and C_3–C_4 yield. The performances of catalyst depend on the loading of CeO_2 and the most suitable amount of CeO_2 is 1–5%. We found that other metal oxide doped 2% Mn_2O_3–5% Na_2WO_4/SiO_2 catalysts also exhibit good conversions of methane to C_3–C_4 hydrocarbons, for example, on a 8% SnO_2 promoted Na-Mn-W/SiO_2 catalyst, a CH_4 conversion of 29.7% with a C_3–C_4 selectivity of 42.0% was attained at a pressure of 0.6 MPa and 1013 K.

By investigating all these results, it is concluded that the CeO_2 promoted Na-Mn-W/SiO_2 catalysts not only exhibit excellent performance for conversion of methane to C_3–C_4 hydrocarbons at elevated pressure but also show excellent behavior for the oxidative coupling of methane: at 1.5 × 10^5 ml g^{-1} h^{-1} GHSV and 993 K with a CH_4/O_2 ratio of 6, a 23.0% CH_4 conversion with 84.7% C_{2+} selectivity was achieved. On the basis of the above results, we propose that high GHSV, low CH_4/O_2 ratio, low temperature and elevated pressure favor the output of C_3–C_4 hydrocarbons. We consider that C_3 or C_4 hydrocarbons are formed by oxidative dehydrogenation and oxidative re-coupling of C_2H_4 and/or C_2H_6 (containing CH_4) in the gas phase and the partial pressure of oxygen in the gas phase plays an important role in the implementation of the reaction.[6]

Further experiments are currently being carried out in our laboratory to confirm these deductions through catalyst characterization and to explain the nature of the CeO_2 promoted Mn-W/SiO_2 catalysts under elevated pressure.

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