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Short communication

Ce–promoted Na_2WO_4/TiO_2 catalysts for the oxidative coupling of methane

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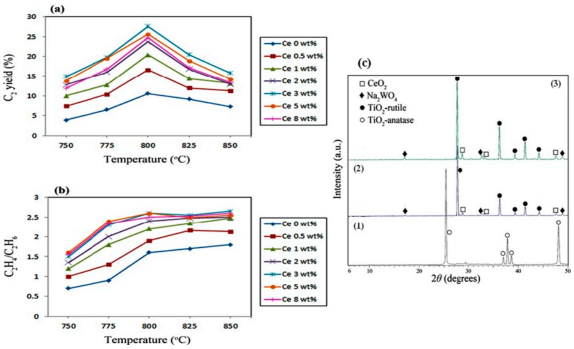
GRAPHICAL ABSTRACT



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ABSTRACT

The catalytic oxidative coupling of methane (OCM) on Ce–promoted Na_2WO_4/TiO_2 catalysts was performed at atmospheric pressure in fixed-bed micro-quartz-tube reactor. The highest methane conversion (50.1%) and C_2 yield (27.6%) were obtained over 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst at 800 °C and the long-term stability test was also described.

Natural gas is composed predominantly of methane (CH_4), which is the simplest hydrocarbon. Oxidative coupling of methane (OCM) is a promising route for producing directly high value-added hydrocarbons (e.g., ethylene and ethane) from natural gas [1]. OCM processes have not been commercialized, mainly due to the limited yield of C_2 hydrocarbons (i.e. ethylene + ethane) [2]. Therefore, the development of efficient catalyst for OCM, which can obtain high yield of C_2 hydrocarbons, is still important challenge. In the past three decades, many catalysts have been reported for the conversion of methane to ethane and ethylene [3–10]. The Mn/Na_2WO_4/SiO_2 catalyst system has attracted great attention as an OCM catalyst for a practical application. Chou et al. [11] studied CeO_2 promoted Na-W-Mn/SiO_2 catalyst in a micro reactor under elevated pressure. They obtained a CH_4 conversion of 47.2% with a C_2-C_4 selectivity of 47.3% at 710 °C and 0.6 MPa. Shahri and Pour [12] investigated the effects of Ce addition on catalytic performance of 2 wt% Mn/5 wt% Na_2WO_4/SiO_2 catalyst for OCM reaction and found that 5 wt% Ce-promoted catalyst showed the highest C_2 yield (21.1%) at 840 °C under atmospheric pressure.

A survey of the literature shows that there are only a few reports for the preparation of OCM catalysts using other support materials than SiO_2 [13–16]. Yildiz et al. [17] reported that TiO_2-rutile exhibited performance similar to SiO_2, with relatively low conversion at high C_2 selectivity.

The materials supported on TiO_2 (rutile or anatase), Fe_2O_3, Fe_3O_4,

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Table 1

Catalytic performance of Ce-Na_2WO_4/TiO_2 catalysts for oxidative coupling of methane.

Catalyst (Ce wt%)	S_{BET} (m^2/g)	CH_4/O_2	Conversion (%)		Selectivity (%)			Yield (%)	Mole ratio
			CH_4	O_2	C_2	CO	CO_2	C_2	C_2H_4/C_2H_6
Ce (0%)	0.8	2	28.4	91.8	38.2	35.4	26.1	10.8	1.4
		3	25.1	94.3	42.1	34.2	23.3	10.6	1.6
		4	23.2	95.5	40.8	36.2	22.7	9.5	1.5
		5	20.5	97.4	39.5	38.5	21.6	8.1	1.6
Ce (0.5%)	1.3	2	37.7	95.2	44.6	24.6	30.3	16.8	1.8
		3	35.1	96.1	47.4	23.9	28.5	16.6	1.9
		4	31.8	96.9	45.3	27.4	27.1	14.4	2.0
		5	30.3	97.5	44.7	28.7	26.2	13.5	1.9
Ce (1%)	1.4	2	41.2	97.4	48.5	19.5	31.7	20.0	2.0
		3	38.6	98.1	52.9	16.3	30.5	20.4	2.2
		4	34.7	98.9	50.1	20.7	28.8	17.4	2.1
		5	32.5	99.0	49.0	22.4	28.1	15.9	2.2
Ce (2%)	1.7	2	46.8	98.4	51.2	15.1	33.4	24.0	2.2
		3	43.7	98.8	54.3	14.0	31.3	23.7	2.4
		4	42.1	99.0	53.6	16.4	29.5	22.6	2.4
		5	39.9	99.1	52.4	18.0	29.2	20.9	2.5
Ce (3%)	2.2	2	50.1	98.7	52.3	12.8	34.2	26.2	2.4
		3	49.0	99.1	56.4	10.9	32.1	27.6	2.7
		4	44.5	99.5	55.1	13.2	31.4	24.5	2.6
		5	41.1	99.7	54.2	14.6	30.8	22.3	2.6
Ce (5%)	2.1	2	49.8	98.5	51.6	14.4	33.5	25.7	2.4
		3	48.2	98.9	53.2	13.8	32.3	25.6	2.6
		4	44.4	99.3	51.9	16.3	31.1	23.0	2.5
		5	41.5	99.4	50.8	17.5	30.9	21.1	2.6
Ce (8%)	2.1	2	49.5	98.9	49.2	17.1	33.4	24.3	2.4
		3	48.7	99.3	50.7	16.3	32.7	24.7	2.5
		4	44.2	99.1	49.5	18.4	31.3	21.9	2.6
		5	41.3	99.2	48.4	19.8	30.9	20.0	2.6

Operating conditions: $T = 800\,^{\circ}C$, GHSV = 10,000 $ml\cdot g^{-1}\cdot h^{-1}$, 0.2 g catalyst, $P = 1$ atm.

SiC and SiO_2 were either on the reference trajectory or well above, indicating that they could also be suitable support materials. If stability of the catalytic performance is additionally taken into account, then TiO_2-anatase has actually to be excluded.

However, without knowing the exact nature of the active sites it is possible to say, that they are at least as good if not better than that of the reference MnxOy-Na_2WO_4/SiO_2. That could mean that their active sites are either less unselective in parallel or less active for the consecutive combustion of the C_2 products.

Among the remaining materials only SiO_2, SiC, TiO_2-rutile and the Fe_2O_3-based support materials show catalytic performances higher than the reference MnxOy-Na_2WO_4/SiO_2. Considering the C_2 yield, SiO_2 results in the best catalyst, however, the other materials have active sites which are as suitable (SiC, Fe-based) or even more suitable (TiO_2-rutile) for the formation of C_2, but seem to be present in lower numbers.

For MnxOy-Na_2WO_4, a variety of different support materials has been studied. Most of the materials show a catalytic performance inferior to the reference MnxOy-Na_2WO_4/SiO2 and/or deactivate, although MnxOy-Na_2WO_4 without a support material exhibits also significant catalytic activity, questioning suggestions of the active centres like W—O—Si bonds. However, since quartz sand has been used to dilute the catalyst, it cannot be excluded that the active component has smeared over the SiO_2 particles, although it seems unlikely.

La_2O_3 and CaO exhibit a high activity as pure support materials, making them unattractive for fundamental research, since it will be difficult to distinguish the contribution of the support material and the active phase [18].

A surface reconstruction has been assumed with the formation of surface cluster species of tetrahedral WO_4 species, including one W—O bond and three W—O—Si bonds which were suggested as the active site. The tetrahedral WO_4 species were distorted and the distortion was responsible for the activity.

According to the EPR and Raman experiments, a W^{6+}/W^{4+} redox mechanism with W—O—Si bonds was suggested as mechanism [18]. Gas phase O_2 was assumed to be involved in the electron transfer from the W to the vacancy, forming the F-centre. The mobility increase of surface lattice oxygen was suggested as the effect of Mn.

In this paper, a series of Ce/5 wt% Na_2WO_4/TiO_2 catalysts have been prepared by changing the content of cerium and their catalytic performances for OCM were evaluated in a continuous flow reactor. The X wt% Ce/5 wt% Na_2WO_4/TiO_2 (X = 0, 0.5, 1, 1.5, 2, 3, 5, 8) catalysts were prepared by two-step wet impregnation method. First, the TiO_2 support was impregnated with an aqueous solution containing appropriate concentration of $Ce(NO_3)_3{\cdot}6H_2O$ at room temperature and then dried at 110 °C in air for 6 h. After that, obtained material was impregnated with an aqueous solution of $Na_2WO_4{\cdot}2H_2O$ in appropriate concentration at room temperature and then dried at 110 °C overnight. The catalyst samples were then calcined at 900 °C in air for 6 h. Finally, all of catalyst samples were crushed and sieved to 30–40 mesh size. Catalyst without Ce (5 wt% Na_2WO_4/TiO_2) was also prepared using the same procedure described above.

Table 1 shows BET surface area, CH_4/O_2 mole ratio, catalyst activity, product selectivity, and yield of selective products for all the studied catalyst samples. In order to find the maximum possible yield of C_2 hydrocarbons at 800 °C, the effect of CH_4/O_2 feed ratio was investigated. With increasing CH_4/O_2 ratio from 2 to 5, the methane conversion decreased. It is well known that the most important step in OCM is the activation of methane over the catalyst [19,20]. A higher conversion of methane is obtained with Ce–Na_2WO_4/TiO_2 catalysts in comparison with Na_2WO_4/TiO_2 catalyst, indicating that Ce enhances the activation of methane. It is essential that combinations of Ce and Na_2WO_4 supported on TiO_2 enhance both C_2 selectivity and catalytic activity, which means a considerable synergetic effect of Ce–Na_2WO_4/TiO_2 system. The 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 exhibited the highest C_2 yield because of the combination of methane conversion and C_2 selectivity. Increasing the CH_4/O_2 ratio enhanced C_2 yield passing through a maximum at CH_4/O_2 = 3. Furthermore, the BET surface area increased obviously with the increase in the Ce content from 0.5% to

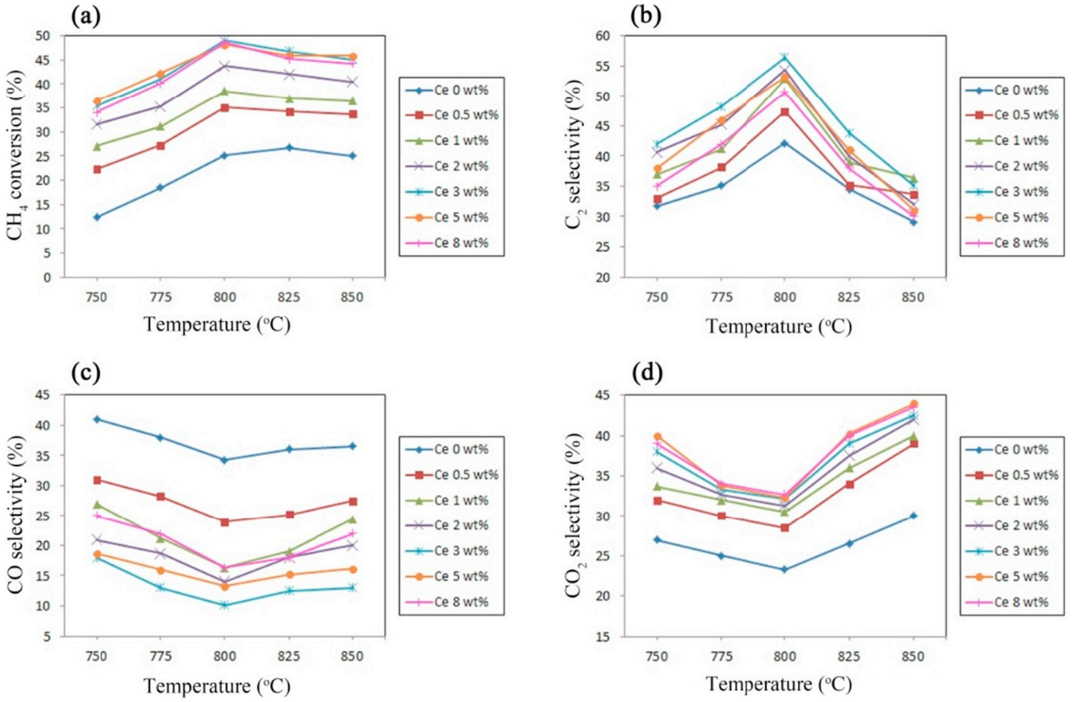

Fig. 1. Catalytic activities of the *X* wt% Ce/5 wt% Na_2WO_4/TiO_2 ($X = 0, 0.25, 0.5, 1, 1.5, 2, 3, 5$) catalysts as related to operation temperatures. GHSV = 10,000 ml·g^{-1}·h^{-1}, 0.2 g catalyst, $P = 1$ atm.

3% because some cerium can inhibit the agglomeration of Na_2WO_4/TiO_2 catalyst particles. However, the surface area decreased as the Ce content decreased from 3% to 0%. The 3% Ce catalyst, which has the largest surface area, showed the best OCM activity, indicating that BET surface area is one of the most important factors responsible for the different catalytic behaviors of the Ce–Na_2WO_4/TiO_2 catalysts with different Ce contents.

The effect of temperature on methane conversion and products selectivity are shown in Fig. 1(a–d). The conversion of methane dramatically increased with temperature, especially in the range of 750–800 °C (Fig. 1(a)). For 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst, CH_4 conversion increased with temperature and passed through a

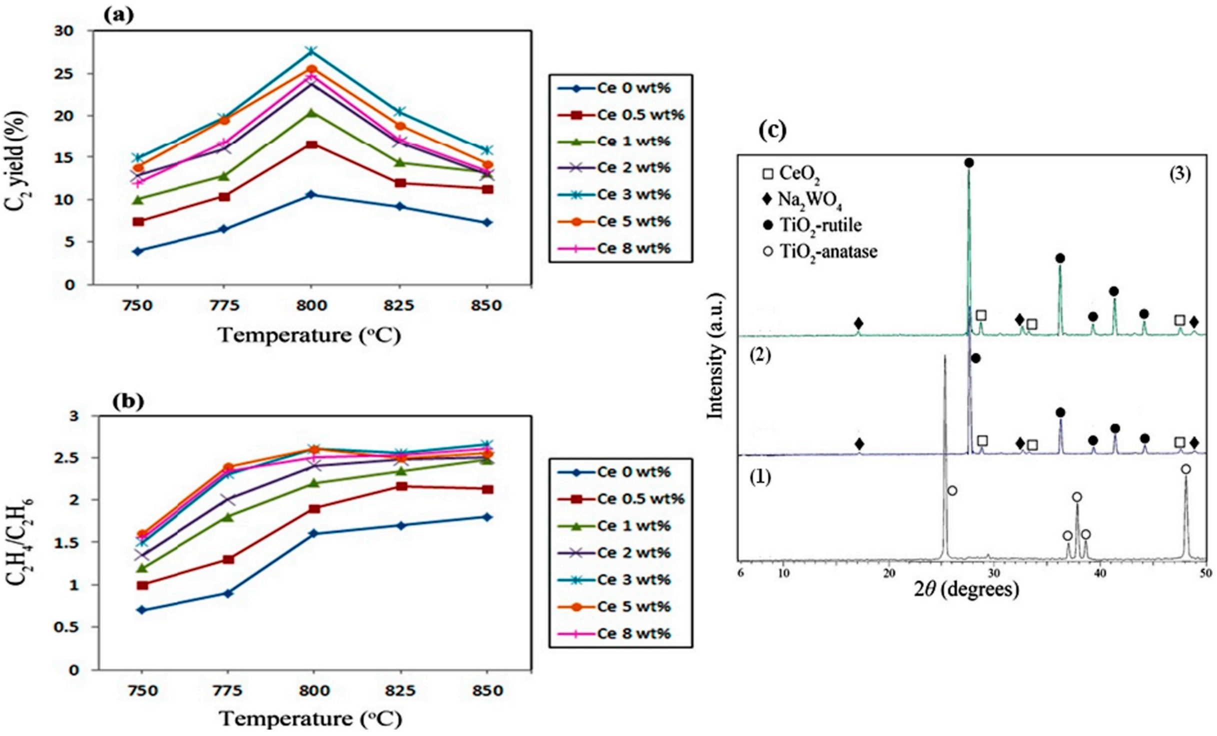

Fig. 2. Yield of C_2 hydrocarbons and C_2H_4/C_2H_6 ratio of the *X* wt% Ce/5 wt% Na_2WO_4/TiO_2 ($X = 0, 0.25, 0.5, 1, 1.5, 2, 3, 5$) catalysts as related to operation temperatures (a,b). GHSV = 10,000 ml·g^{-1}·h^{-1}, 0.2 g catalyst, $P = 1$ atm. XRD patterns of the 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst: (1) before calcination, (2) after calcination, and (3) after OCM activity testing for 6 h (c).

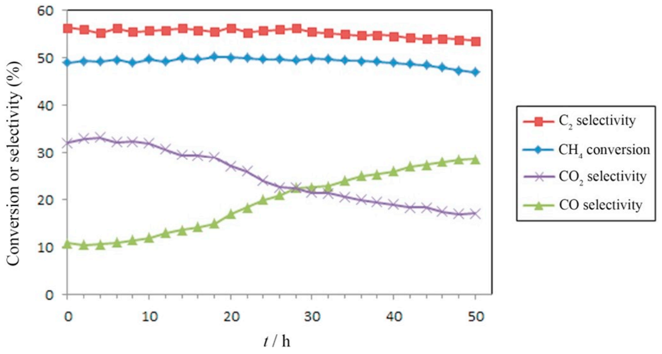

Fig. 3. Stability test over the 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst at GHSV = 10,000 ml·g^{-1}·h^{-1}, CH_4/O_2 = 3 and T = 800 °C.

maximum at 800 °C. As seen in Fig. 1(b), the best C_2 selectivity for each catalyst obtained at 800 °C. For undesirable products, CO selectivity decreased with increasing the operating temperature, which attained a minimum at 800 °C, and then increased with a further rise of the operating temperature (Fig. 1(c)). Moreover, CO_2 selectivity increased slightly with Ce addition (Fig. 1(d)).

The variation of the yield of C_2 hydrocarbons and C_2H_4/C_2H_6 ratio with the temperature is presented in Fig. 2(a) and (b). The C_2 hydrocarbons yield increased with the increase of temperature and passed through a maximum value at 800 °C and then decreased gradually (Fig. 2(a)). The 3 wt% Ce catalyst showed the highest C_2H_4/C_2H_6 ratio at 800 °C (Fig. 2(b)). Although the 5–8 wt% Ce catalysts exhibited the high methane conversion, they exhibited a low C_2 yield, indicating that they converted methane to fully oxidized CO and CO_2. Fig. 2(c) shows the XRD patterns of the 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst before calcination, after calcination, and after OCM activity testing for 6 h. Only the peaks of anatase phase TiO_2 (2θ = 25.39, 37.04, 37.88, 38.65 and 48.13) can be observed in the diffraction pattern of the catalyst before calcination (Fig. 2(c)(1)).

After calcination at 900 °C, all the characteristic XRD peaks of anatase disappeared, while those of rutile appeared at 2θ = 27.52, 36.16, 39.27, 41.33 and 44.13 (Fig. 2(c)(2)). This indicated that anatase completely transformed to rutile phase during calcination. Beside the XRD peaks of rutile TiO_2, the peaks correlated with Na_2WO_4 (2θ = 16.89, 32.54 and 48.87) and CeO_2 (2θ = 28.63, 33.16 and 47.54) can be identified in the XRD pattern of the fresh catalyst. The used catalyst, which tested in OCM reaction for 6 h, did not show significant differences in the XRD patterns compared to the fresh catalyst (Fig. 2(c)(3)) though. The result suggests that there was a strong interaction between cerium (Ce), sodium (Na) and tungsten (W) with the TiO_2 support.

As it is well-known, the long-term stability of a catalyst is an important factor for its potential application in industry. Fig. 3 shows the results of stability test for the 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst. It can be seen that CH_4 conversion remained at about 49% even after 50 h on stream. It was interesting that C_2 selectivity maintained at about 56%. CO selectivity increased with time on stream, while the opposite trend was found for CO_2 selectivity. In other words, the total amount of CO and CO_2 remained almost constant. Furthermore, the surface area of the fresh catalyst slightly decreased from 2.1 to 1.7 m^2/g after 50 h.

In summary, it has been demonstrated that Ce–Na_2WO_4/TiO_2 is a very promising catalyst for the oxidative coupling of methane. Combination of Ce and Na_2WO_4 in the catalyst showed the essential synergetic effect in the OCM activity and C_2 selectivity. The 3 wt% Ce/5 wt% Na_2WO_4/TiO_2 catalyst showed the best performance and was rather stable up to 50 h at 800 °C, and the highest C_2 selectivity and yield were 56.4% and 27.6%, respectively.

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