

Synergistic effect of catalyst basicity and reducibility on performance of ternary CeO₂-based catalyst for CO₂ OCM to C₂ hydrocarbons

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Received 16 March 2006; received in revised form 5 June 2006; accepted 7 June 2006
Available online 18 July 2006

Abstract

The present investigation focuses on the synergistic effect of catalyst basicity and reducibility on the catalytic activity of binary and ternary CeO₂-based catalysts in the CO₂ oxidative coupling of methane (CO₂ OCM). Proper amount of medium and strong basic sites together with lower amount of very strong basic sites are identified as pertinent factors in increasing the catalytic performance. The CO₂-TPD and H₂-TPR studies indicate synergistic effect between the catalyst basicity and reducibility for the 12.8CaO–6.4MnO/CeO₂ ternary metal-oxide catalyst in enhancing the CO₂ OCM performance.

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Keywords: CO₂ OCM; CaO–MnO/CeO₂ catalyst; Catalyst basicity; Catalyst reducibility

1. Introduction

In chemical industries, C₂ hydrocarbons (ethylene, ethane, and acetylene) are important basic chemicals in producing higher value-added chemicals. Meanwhile, utilization of both methane and carbon dioxide, known as greenhouse gas contributors, is desirable in our efforts to suppress the trend of global warming. Furthermore, methane and carbon dioxide are components of natural gas which compositions vary with locations. The compositions of natural gas in Natuna's fields are unique with the CO₂/CH₄ ratio being 71/28 making it a highly acidic natural gas. Therefore, the conversions of both gases have significant implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuels industries. The CO₂ OCM offers an alternative route to produce useful chemicals, while utilizing carbon dioxide for environmentally benefit chemical process.

The conversion of methane to C₂ hydrocarbons using carbon dioxide as an oxidant has received considerable attention

[1–4]. Recently, He et al. [5] developed the nano-CeO₂/ZnO catalyst for the CO₂ OCM. In another development, the screening of CeO₂-based catalysts over binary and ternary metal oxides identified the CaO–MnO/CeO₂ as the probable catalyst for the CO₂ OCM process [6] since it displayed notable stability with no obvious coking during 20 h of reaction time on stream. Furthermore, the single- and multi-responses optimizations of CO₂ OCM reported maximum C₂ hydrocarbons selectivity and yield of 76.6% and 3.7%, respectively, over the 12.8% CaO–6.4% MnO/CeO₂ catalyst [7,8]. The optimal CO₂/CH₄ ratio of 2 corresponding to the optimal reactor temperature being 1127 K is relevant for the utilization of Natuna's field natural gas in the CO₂ OCM process [9].

The CO₂ OCM process is a complex heterogeneous–homogeneous process involving [10]:

- oxygen-assisted breakage of a C–H bond in the CH₄ molecule on the solid surface;
- heterogeneous decomposition of CO₂ to CO and oxygen active species;
- homogeneous recombination of CH₃^{*} radicals released from the surface;
- homogeneous oxidative or radical dehydrogenation of C₂H₆ to C₂H₄.

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The correlations among the catalyst basicity, reducibility and catalytic performance could improve the CO₂ OCM process. Earlier studies on O₂ OCM over rare-earth oxides indicated that catalyst basicity is crucial in OCM [11]. Intermediate strength and strong basic sites are critical for high catalytic activity and selectivity in OCM.

In this paper, the synergistic effect of catalyst basicity and reducibility on the catalytic activity in the CO₂ OCM process over binary and ternary CeO₂-based catalysts is addressed using CO₂-TPD and H₂-TPR. The catalytic activities of the ternary metal oxide and the binary and pure metal oxides are compared to study the influence of catalyst basicity and reducibility on the catalytic activity.

2. Experimental

2.1. Catalysts preparation

The ternary CaO–MnO/CeO₂ metal oxide catalyst was prepared by simultaneous incipient wetness impregnation method. Powdered CeO₂ (MERCK) was first immersed into an aqueous mixed solutions of Ca(NO₃)₂·4H₂O (99%, Aldrich) and Mn(NO₃)₂·4H₂O (98.5%, Fluka) for 6 h at ambient temperature and was dried overnight in an oven (Mettler) at 393 K. Next, the powder was calcined at 1123 K in a muffle furnace (Carbolite) for 10 h and then crushed into the desired size (45–60 mesh). The catalyst compositions used in this paper (wt.% CaO and wt.% MnO in the CeO₂-based catalysts) were based on the multi-response optimization results [8].

Meanwhile, the binary metal oxide catalysts (CaO/CeO₂ and MnO/CeO₂) were prepared by incipient wetness impregnation method. Initially, the powdered CeO₂ was immersed into Mn(NO₃)₂·4H₂O or Ca(NO₃)₂·4H₂O aqueous solution for 6 h at ambient temperature and then dried overnight in an oven at 393 K. The resulted powder was calcined at 1123 K in a muffle furnace for 10 h.

2.2. Catalyst testing

The catalytic performances of the CO₂ OCM process were tested in a fixed bed quartz reactor at atmospheric pressure and temperature being 1127 K. Before reaction, the catalyst was recalcined at 1127 K in an air flow (100 ml min⁻¹) for 1 h and flushed with high purity nitrogen (100 ml min⁻¹) at 1127 K for another 1 h. Methane and carbon dioxide were fed to the reactor at a total flow rate of 50 ml min⁻¹ and catalyst weight of 1 g (GHSV = 3000 ml g⁻¹ h⁻¹). The reactor temperature was maintained by a tube furnace (Carbolite), while the gas flow rates were measured and controlled by volumetric flow controllers (Alicat Scientific, Inc.). The products and unreacted gases were analyzed by an online gas chromatography (HP AGILENT 6890 series) equipped with a thermal conductivity detector (TCD), Molecular Sieve 5A and Porapak N packed columns.

2.3. Catalyst characterization

The XRD patterns were acquired using a Siemen D5000 with Cu K α radiation with the wavelength of 1.54056 Å at 40 kV

and 30 mA X-ray tube. The 2 θ angle was scanned at a rate of 0.05° s⁻¹ within the range of 5° < 2 θ < 80°. The H₂-TPR characterization was carried out using Micromeritics 2900 TPD/TPR equipped by TCD. About 0.05 g catalyst was purged with Ar (25 cm³ min⁻¹) at 773 K for 1 h before it was cooled to room temperature. A 6% H₂ in Ar (25 cm³ min⁻¹) was then flowed into the system and the sample was heated up to 1223 K from room temperature at a rate of 5 K min⁻¹. The amount of H₂ consumption during the reduction was measured by TCD. The CO₂-TPD was carried out using Micromeritics 2900 TPD/TPR equipped by TCD. The CO₂-TPD technique determines the catalyst surface basicity/base strength. Again, about 0.05 g of catalyst each was initially calcined at 1073 K in a flow of argon (25 cm³ min⁻¹) for 1 h. The chemisorption of CO₂ was carried out at 373 K by flowing CO₂ (25 cm³ min⁻¹) for 1 h. Excess CO₂ was then purged at the temperature of adsorption in a flow of Ar (25 cm³ min⁻¹) for 1 h. The sample was then heated to 1223 K at a linear heating rate of 5 K min⁻¹ in a flow of Ar (25 cm³ min⁻¹). The amount of desorbed CO₂ was detected and determined using TCD.

3. Results and discussion

3.1. Catalyst characterizations

3.1.1. XRD characterization

The X-ray powder diffraction patterns of fresh CeO₂-based catalysts are presented in Fig. 1. The crystalline phases in the catalysts were identified by comparing the diffraction lines of the sample with those from the literatures. A good crystallization is observed on the pure CeO₂, which is demonstrated by sharp and high intensity CeO₂ peaks. The main CeO₂ peak is shown at 2 θ of about 28.61° [12–13]. The diffraction lines observed for pure CeO₂ could be attributed to a typical cubic fluorite struc-

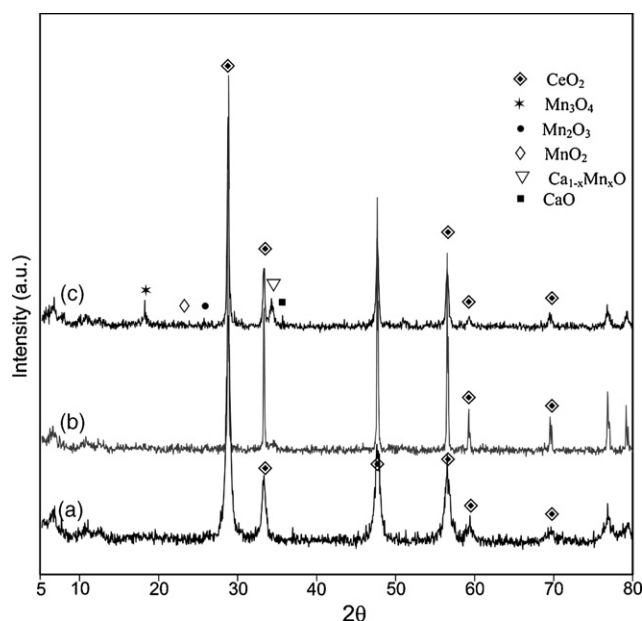


Fig. 1. X-ray diffraction patterns of fresh CeO₂-based catalysts. (a) CeO₂; (b) 12.8CaO/CeO₂; (c) 12.8CaO–6.4MnO/CeO₂.

ture of CeO_2 . The solid solution of CaO and MnO , denoted as $\text{Ca}_{1-x}\text{Mn}_x\text{O}$, is identified at about 33.5° [3]. The disappearance and/or very slight CaO diffraction lines of CaO/CeO_2 and $\text{CaO-MnO}/\text{CeO}_2$ catalysts is attributed to the formation of the solid solution, since CaO can partially dissolve in CeO_2 and/or manganese oxide, or assigned to high dispersion of CaO on the catalyst surface. It was also observed that no shift was detected in the diffraction lines of all catalysts compared to the pure CeO_2 suggesting that Mn^{3+} and Ca^{2+} may not be substituted to Ce^{4+} in the CeO_2 lattice. The weak diffraction lines exhibited by CaO and MnO_x crystallite implies that the Ca and Mn species are either highly dispersed on the CeO_2 surface or may be formed as $\text{Ca}_{1-x}\text{Mn}_x\text{O}$ solid solution. The result is corroborated with the previous study using Raman spectroscopy [6]. Based on the intensity of diffraction lines, it is evident that the MnO_x crystalline phase of the fresh catalyst consists of mainly Mn_3O_4 and solid solution of $\text{Ca}_{1-x}\text{Mn}_x\text{O}$, but less MnO_2 and Mn_2O_3 .

3.1.2. Surface basicity/base strength distributions of catalysts by CO_2 -TPD

The basicity properties of the catalysts were measured by TPD with CO_2 as the probe molecule. Although CO_2 appears to be the proper probe molecule because of its acidic nature, the CO_2 -TPD profile in the literatures varies depending on the adsorption condition of CO_2 . Only a broad desorption peak appeared if too much CO_2 is adsorbed. The CO_2 -TPD peaks representing the base strength distribution of different CeO_2 -based catalysts are presented in Fig. 2. The numbers of weak, medium, strong and very strong catalyst basic sites are estimated from the area under their TPD curves for the temperature range of 373–523, 523–673, 673–923, and >923 K. Distributions of the number of basic sites for the binary and ternary CeO_2 -based catalysts are listed in Table 1. The temperature ranges chosen for the weak, medium, strong and very strong basic sites are such that the CO_2 -TPD peaks are observed in these temperature ranges for most catalysts [11,14]. The strengths of the basic sites are expressed in the temperature range wherein the CO_2 chemisorbed on the basic sites is desorbed. As a matter of fact, the adsorbate adsorbed on weaker sites is desorbed at lower temperatures and that adsorbed on stronger sites is desorbed at higher temperature. As shown in Table 1, all the values for the basic sites appear to be higher than those usually reported in the literature [11]. The discrepancy may be due to the differences in the conditions used for CO_2 adsorption. In our case, the CO_2 adsorption was carried out at 373 K using pure CO_2 . The chemisorption of CO_2 is stronger

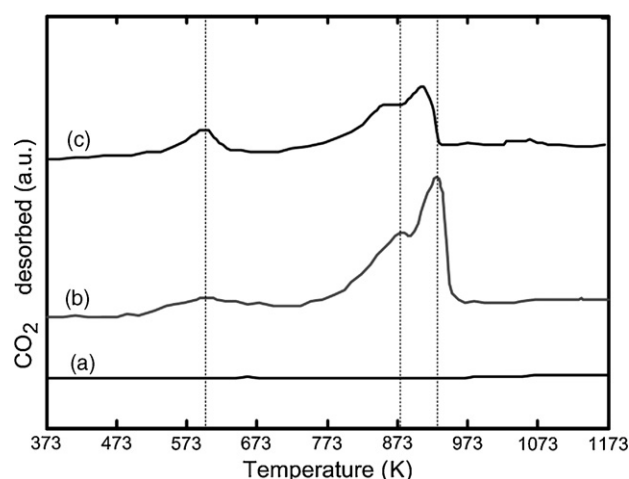


Fig. 2. CO_2 -TPD spectra of different fresh catalysts. (a) CeO_2 ; (b) $12.8\text{CaO}/\text{CeO}_2$; (c) $12.8\text{CaO}-6.4\text{MnO}/\text{CeO}_2$.

in our case, which may be attributed to the increase of CO_2 chemisorption with temperature and the use of pure CO_2 . The total CO_2 desorbed for the binary and ternary CeO_2 -based catalysts (CaO/CeO_2 and $\text{CaO-MnO}/\text{CeO}_2$, respectively) are in the range of $400\text{--}700 \mu\text{mol g}^{-1}$. Meanwhile, based on the result of Kuš et al. [15] the total CO_2 desorbed on other metal oxides, such as La_2O_3 , Sm_2O_3 , and $\text{La}_2\text{O}_3\text{-Nd}_2\text{O}_3$, were in the range of $40\text{--}50 \mu\text{mol g}^{-1}$ which is adsorbed at 330 K. However, the positions of the desorbed CO_2 temperature peak are in accordance with the results reported by other researchers [12,15–16].

As revealed in Fig. 2 and Table 1, the difference in the distribution of basic sites for each catalyst indicates that the basicity and base strength distributions are influenced by CaO in the CeO_2 -based catalysts and also by the addition of MnO_x . According to Fig. 2(b) and (c), the deposition of CaO and CaO-MnO on the CeO_2 -based catalysts results in the creation of a large number of medium, strong and very strong basic sites at the expense of the weak basic sites as compared to the pure CeO_2 catalyst. In the ternary metal oxides (Fig. 2(c)), the distribution of basic sites is influenced by the presence of calcium and manganese oxides. Impregnation of calcium and manganese nitrate solutions to the CeO_2 catalyst leads to higher distribution of medium and strong basic sites and lower number of very strong basic sites. In fact, the pure CeO_2 catalyst shows no basic sites as evident by the horizontal lines with no peaks in Fig. 2(a). It is apparent that the CeO_2 is an acidic catalyst as in agreement with the result of Choudhary et al. [11]. The effect of CaO doping on the CeO_2 catalyst leads to adsorption of CO_2 as demonstrated in

Table 1

Number of basic sites of different basicity strengths determined by CO_2 -TPD expressed in micromoles CO_2 desorbed per gram catalyst

Catalyst	Basic sites ($\mu\text{mol g}^{-1}$)				
	Weak (373–523 K)	Medium (523–673 K)	Strong (673–923 K)	Very strong (>923 K)	Total
CeO_2	0	0	0	0	0
$12.8\text{CaO}/\text{CeO}_2^{\text{a}}$	7.0	77.2	385.7	226.6	696.5
$12.8\text{CaO}-6.4\text{MnO}/\text{CeO}_2^{\text{b}}$	12.6	62.0	223.2	106.0	403.8

^a Binary metal oxides catalyst prepared by impregnation method.

^b Ternary metal oxides catalyst prepared by simultaneous impregnation method.

the CO₂-TPD peak at 933 and 893 K for very strong and strong basic (Fig. 2(b)) sites, respectively. Medium catalyst basic sites are also observed slightly at 598 K desorption peak. Addition of MnO_x to the CaO/CeO₂ catalyst by simultaneous impregnation of CaO and MnO_x affects the basicity distribution by shifting the very strong to strong basic sites (923 K) regions, while the peak of 893 K shifts to 853 K, respectively. The declining basic sites distribution from very strong to strong as a result of interaction effect of CaO and MnO_x can be attributed to the synergistic effect of both metal oxides. The results in Table 1 indicate that the amounts of medium and strong basic sites are different as exhibited in the CO₂-TPD spectra (Fig. 2(b) and (c)). The binary CaO/CeO₂ catalyst gives larger number of very strong basic sites (226.6 μmol g⁻¹) compared to the ternary CaO–MnO/CeO₂ catalyst (only 106.0 μmol g⁻¹). Meanwhile pertaining to the total medium and strong basic sites, the binary CaO/CeO₂ catalyst exhibits higher number of basic sites (462.9 μmol g⁻¹) than the ternary CaO–MnO/CeO₂ catalyst (285.2 μmol g⁻¹). It is clearly revealed that the CO₂-TPD peak of medium basicity (based on the amount of medium and strong basic sites) becomes more intense for CaO/CeO₂ and CaO–MnO/CeO₂ catalysts as compared to the pure CeO₂ catalyst. As shown in Fig. 2(b) and (c), the addition of MnO to the CaO/CeO₂ catalyst shifts the CO₂ desorption peaks to lower temperature indicating that the binary catalyst has stronger CO₂ chemisorption than the ternary catalyst.

3.1.3. Reducibility of catalysts by H₂-TPR

The H₂-TPR has been extensively used to characterize the reducibility of the CeO₂-based catalysts [17,18]. Typically, the reduction profile of ceria shows two peaks as reported by Boaro et al. [19], where the first low temperature peak at about 773 K was assigned to the reduction of the most easily reducible surface-capping oxygen of ceria, while the removal of bulk oxygen of ceria was indicated by the high-temperature signal at about 1073 K. The oxygen migration in the CeO₂-based catalysts is significantly affected by the structure of ceria.

The reduction properties of the CeO₂ ternary catalyst is mainly affected by interaction of manganese oxide and calcium oxide doping. Interaction between MnO_x, CaO and CeO₂ can be revealed by the TPR study. The shifting main peak of H₂ consumption to a lower temperature as depicted in Fig. 3(a) and (c) exhibits modification of the reduction behaviour of CeO₂ due to introduction of manganese oxide [20,21]. The reducibility of bulk mixed oxide increases as the H₂-TPR peaks shift from 1043 to 1033 K for the binary CaO/CeO₂ and from 1043 to 1013 K for the ternary CaO–MnO/CeO₂ catalysts as exhibited in Fig. 3(b) and (c). The H₂-TPR peak shifts show that the reducibility of both catalysts is different. The CaO–MnO/CeO₂ catalyst exhibits the highest CeO₂ reducibility among the catalysts as indicated by the lowest temperature reduction peak (from 1043 to 1013 K). The H₂-TPR peak shifts imply that the CaO–MnO/CeO₂ catalyst is more reducible than the binary one without MnO_x. The introduction of an even relatively small amount of manganese leads to an interaction between CeO₂ support and MnO_x dopant and is believed to increase the reducibility of Ce⁴⁺. This phenomenon is in agreement with the suggestion

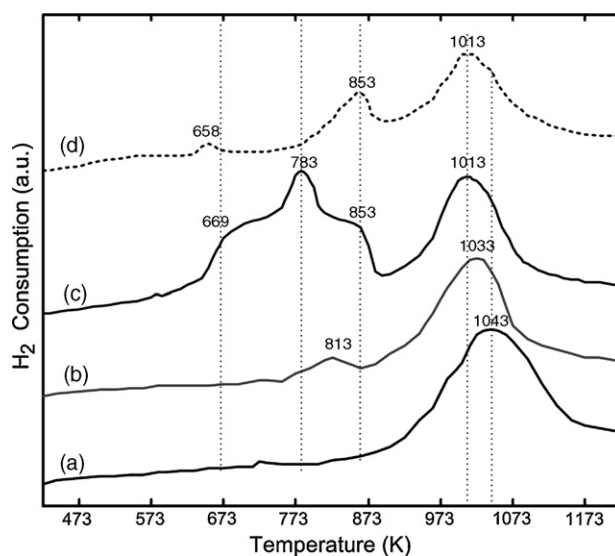


Fig. 3. H₂-TPR spectra of different catalysts. (a) CeO₂ (fresh); (b) 12.8CaO/CeO₂ (fresh); (c) 12.8CaO–6.4MnO/CeO₂ (fresh); (d) 12.8CaO–6.4MnO/CeO₂ (used).

of Kaspar et al. [20] and Terribile et al. [21] that the introduction of relatively small amount of smaller Zr⁴⁺ or Mn^{3+/4+} into CeO₂ generates defects throughout the matter and brings about an increase of oxygen mobility and pronounces the increasing reducibility of CeO₂. Besides, manganese has several oxidation states as active redox behaviour. In this work, the reduction of CeO₂-based catalysts starts at about 573 K and two broad peaks are observed at about 813 K (weaker intensity) and 1043 K. The TPR peak at 813 K is assigned to the reduction of surface-capping oxygen of ceria [17–19], while the peak at about 1043 K can be ascribed to the reduction of bulk oxygen of CeO₂. The reduction of surface capping oxygen over CaO–MnO/CeO₂ catalyst shifts to higher temperature (from 813 to 853 K) due to the strong interaction effect of MnO_x and CeO₂ support. The interaction also generates a new strong H₂-TPR peak at about 783 K which is attributed to the reduction of Mn₂O₃ or MnO₂ to Mn₃O₄. Meanwhile a small new peak also appears at about 669 K due to the interaction effect. As reveal by the CO₂-TPD results, the ternary CaO–MnO/CeO₂ catalyst has less amount of medium and strong basic sites (284.2 μmol/g) than the binary CaO/CeO₂ catalyst (462.9 μmol/g). The total amount of very strong basic sites for the ternary catalyst is lower than the binary one. MnO_x doping significantly reduces the catalyst basicity as the distribution of weak basic site increases slightly. Both the H₂-TPR and CO₂-TPD spectra suggest that the ternary CaO–MnO/CeO₂ catalyst is more reducible and less basic by having considerable amount of medium and strong basic sites than the binary CaO/CeO₂ catalyst.

In relation to the possible oxidation states of manganese species, the reduction of manganese oxide might occur in three probable stages: MnO₂–Mn₂O₃–Mn₃O₄–MnO. From Fig. 3(c) the TPR peak at 669 K is attributed to the reduction of MnO₂ to Mn₂O₃. The very small peak within the temperature range of 653–673 K indicates that the catalyst synthesis method brings about a small proportion of MnO₂ form to the surface of the

Table 2
Catalysts activity results of CeO₂-based catalysts toward CO₂ OCM

Catalysts	CH ₄ conversion (%)	C ₂ ^a selectivity (%)	C ₂ ^a yield (%)
CeO ₂	13.2	9.1	1.2
12.8% CaO/CeO ₂	2.7	75.0	2.0
6.4% MnO/CeO ₂	8.8	3.1	0.3
12.8% CaO–6.4% MnO/CeO ₂	5.1	75.6	3.9

$T = 1127$ K, $\text{CO}_2/\text{CH}_4 = 2$, weight of catalyst loaded = 1 g, total feed flow rate = $50 \text{ cm}^3 \text{ min}^{-1}$.

^a C₂ hydrocarbons = 44% C₂H₄ and 56% C₂H₆.

CaO–MnO/CeO₂ catalyst which may be due to formation of solid solution of Ca_xMn_{1-x}O as corroborated by the small MnO₂ peak in the XRD diffractogram (Fig. 1). The strong H₂-TPR peak at about 783 K is assigned to the reduction of Mn₂O₃ or MnO₂ to Mn₃O₄, while the peak at about 853 K is assigned to the final reduction from Mn₃O₄ to MnO. The final reduction of the fresh catalyst from Mn₃O₄ to MnO is confirmed by the TPR peak of the used catalyst (CaO–MnO/CeO₂) as exhibited in Fig. 3(d). From Fig. 3(d), it is suggested that final oxidation state of the used catalyst is mainly Mn^{2.7+} (Mn₃O₄), while the MnO₂ peak is only apparent weakly. The presence of weak MnO₂ peak in the used catalyst reveals that simultaneous oxidation and reduction process occurred during the catalytic reaction. Both Fig. 3(c) and (d) reveal that the reducibility of the fresh and used catalyst was sustained during the reaction. In addition, the phases of the manganese oxide can also be identified physically by the catalyst color, i.e. MnO₂ (black), Mn₂O₃ (black), Mn₃O₄ (brown) and MnO (gray) as reported by Cadus and Ferreti [22], but it is not scientifically precise. In this research, the change in the catalyst colour from black (fresh catalyst) to brown and/or grey (used catalyst) suggested that the oxidation state of manganese oxide changed during the reaction from mixed MnO₂ and Mn₂O₃ to Mn₃O₄ and/or MnO. It is interesting to note that the colour change and therefore the oxidation states of the catalyst during the reaction are consistent with the H₂ TPR peaks.

3.2. Catalyst activity testing for CO₂ OCM reaction

The present study indicates that there exists a correlation between basic sites distribution and reducibility of the catalyst and catalytic activity toward methane and carbon dioxide reactions. The catalytic activity of CeO₂-based catalysts towards CO₂ OCM reaction is presented in Table 2 with respect to CH₄ conversion, C₂ selectivity and C₂ yield. The C₂ hydrocarbons resulted from this process consist of 44% ethylene (C₂H₄) and 56% ethane (C₂H₆), while acetylene (C₂H₂) is not detected in this process.

Proper amount of medium and strong basic sites and lower amount of very strong basic sites as well as high reducibility of the catalyst are important in CO₂ OCM process and hence these sites are responsible for the OCM activity. Although considerable amount of medium and strong basic sites are evident in the binary CaO/CeO₂ catalyst, the large amount of very strong basic sites is detrimental to the CO₂ OCM activity possibly due to CO₂ being strongly adsorbed on the very high basic sites and

may block the catalyst surface. The results in Table 2 reveal that CH₄ conversion and C₂ yield over the CaO–MnO/CeO₂ catalyst (5.1% and 3.9%, respectively) are somewhat higher than that of CaO/CeO₂ catalyst (2.7% and 2.0%, respectively), but the C₂ selectivity is constant. Meanwhile, the role of catalyst basicity (due to CaO function) on the significant improvement of C₂ selectivity is shown in Table 2 on the comparison between MnO/CeO₂ catalyst with CaO/CeO₂ and CaO–MnO/CeO₂ catalysts. Earlier studies on the OCM by O₂ over rare earth oxides [23] indicated that both catalyst basicity and acidity play important roles in OCM as the strong and medium acid sites are required for obtaining high catalytic activity and selectivity in OCM. In CO₂ OCM, it is suggested that CO₂ chemisorption plays important roles leading to high C₂ hydrocarbons selectivity [2–4], while the high reducibility favour CH₄ conversion. The chemisorption of CO₂, as an acid component, can be enhanced by increasing the catalyst basicity, particularly medium and strong basic sites. Meanwhile, the carbon dioxide activation on the catalyst surface is favoured by catalyst reducibility [3].

In Table 2, the ternary metal oxide (12.8CaO–6.4MnO/CeO₂) is compared to the binary metal oxide (12.8CaO/CeO₂) and pure metal oxides (CeO₂). The 12.8CaO–6.4MnO/CeO₂ catalyst shows better activity which demonstrates higher methane conversion and higher C₂ yield than that of binary catalysts. From the CO₂-TPD characterization as revealed in Table 1, the ternary catalyst shows large number of medium and strong basic sites with low number of very strong basic sites. There exists a relation between the distribution of basic sites, reducibility and the catalyst activity towards CO₂ OCM. With the addition of MnO_x to the 12.8CaO/CeO₂ catalyst, the catalyst reducibility increases, hence the methane conversion improves due to enhanced CO₂ activation on the catalyst surface to produce more oxygen active species. It is suggested that the synergistic effect between the catalyst basicity and reducibility enhances the catalytic activity towards CO₂ OCM as confirmed by the CO₂-TPD and the H₂-TPR characterizations.

The distribution of basic sites, particularly proper amount of medium and strong basic sites and low number of very strong basic sites [11] are important factors that govern the catalytic activity towards CO₂ OCM. Large number of very strong basic sites, however, does not improve the performance since the CO₂ gas may be adsorbed strongly on the very strong basic sites, thus blocking the active sites. It is suggested that the reducibility of Ce⁴⁺/Ce³⁺ is enhanced by the introduction of MnO_x which accounts for the activation of CO₂ and CH₄. However, Wang and Ohtsuka [24] suggested that proper amount of catalyst basicity, particularly medium and strong basic sites, greatly enhances the selectivity to C₂ hydrocarbons. Enhancing CO₂ chemisorption by the proper amount of medium and strong basic sites leads to CH₄ abstraction using oxygen from CO₂ and prevents the role of lattice oxygen which is only converted to synthesis gas and is not selective to C₂ hydrocarbons [2,3,24]. From the catalyst testing, the ternary CaO–MnO/CeO₂ may be regarded as the effective catalyst for the CO₂ OCM process.

The following are the proposed reaction mechanism based on the characterization results. The most distinct feature of the composite catalyst consisting of CaO, MnO_x, and CeO₂ is the

crucial roles of CO₂ being adsorbed on the surface in the formation of C₂ hydrocarbons. In the presence of chemisorbed CO₂, the proper amount of CO₂ pool on the CaO–MnO/CeO₂ catalyst may inhibit the reaction via redox mechanism involving the lattice oxygen and promote the defect sites or oxygen vacancy on the Mn^{2.7+} (due to mainly Mn₃O₄) and/or Ce³⁺ which may be responsible for CO₂ activation. Active ternary catalysts (Ca, Mn, and Ce) are present in the form of solid solution (Fig. 1), and some impregnated metal oxides, as well as rich in Ca species at the outermost layer which also includes Ce³⁺ and Mn^{2.7+} sites during reaction. Thus, CO₂ first adsorbs on the catalyst surface due to interaction with basic Ca²⁺ sites, and then the Ce³⁺ and Mn^{2.7+} sites activate CO₂ to form CO and active oxygen species, possibly O⁻, which converts CH₄ to CH₃^{*} radical. The possible formation of solid solution or the presence of neighbouring Ca²⁺, Mn^{2.7+} and Ce³⁺ sites, is efficient for CO₂ adsorption and its subsequent activation. Furthermore, the incorporation of Ca²⁺ and Mn^{2.7+} cations into CeO₂ lattice generates defect sites which promote redox reaction of Ce⁴⁺/Ce³⁺, and even Mn^{2.7+}/Mn²⁺. The interaction effect of possible solid solutions of CaO and MnO_x (Fig. 1), CaO and CeO₂, and/or MnO_x and CeO₂ increases the CH₄ conversion which may be attributed to enhanced reducibility and proper basicity of the catalyst.

4. Conclusions

The present investigation on the surface properties and activity of CaO–MnO/CeO₂ catalyst suggests the vital role of synergistic effect of catalyst basicity and reducibility in enhancing the CO₂ OCM process. Methane conversion and C₂ yield correlate to the distribution of basic sites and reducibility of the catalyst. The activity is enhanced by the proper amount of medium and strong basic sites and high catalyst reducibility. The weak and very strong basic sites are inappropriate for the CO₂ OCM. Introduction of MnO_x on the CeO₂-based catalyst modifies the reduction behaviour of CeO₂ and leads to enhancement of methane conversion and C₂ yield. The 12.8CaO–6.4MnO/CeO₂ catalyst with proper number of medium and strong basic sites, less number of very strong basic sites and high reducibility seems suitable for the CO₂ OCM reaction.

Acknowledgments

The authors would like to express their sincere gratitude to the Ministry of Science, Technology and Innovation (MOSTI) Malaysia for the financial support received under IRPA Project No. 02-02-06-0016 EA099. The authors would also like to thank Miss Shamsina Sabdin of Petronas Research and Scientific Services (PRSS), Kajang, Malaysia for her assistance in the CO₂-TPD and H₂-TPR characterizations.

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