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Study of performance of CeO₂/ZnO nanocatalysts for the oxidative coupling of methane using carbon dioxide as oxidant

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This study shows how CeO₂/ZnO nanocatalysts were prepared by combining homogeneous precipitation with micro emulsion using a conventional heating technique. The catalysts were then used in a conventional fixed bed reactor for the oxidative coupling of methane using carbon dioxide as an oxidant. Catalyst performance tests were carried out at atmospheric pressure, feed gas of 33 and 45 ml/min, and reaction temperatures was in the range of 700 to 900°C. The effect of adding promoters such as Lithium (Li), Bismuth (Bi), and Zirconium (Zr) in various loadings was studied. In this regard, it was found that proper calcination conditions can yield a nanocatalyst structure. However, the conditions for the occurrence of a nanostructure depend strongly on the type of the added promoter. The effects of the number of operating parameters were studied. Catalysts prepared with Zr were found to be more active and selective to ethylene at high calcination temperatures. Catalysts prepared with Bi, on the other hand, showed better activity at lower reaction temperatures. As with Li, the catalysts showed nearly the same activity at low calcination temperatures. As to the effect of feed ratio of methane to carbon dioxide, catalysts prepared with Li showed good activity and selectivity with the increase in the feed ratio. In opposite, catalysts prepared with Zr showed better activity and selectivity at low feed ratios. As to Bi, the increase in feed ratio has an effect on the catalyst activity but not on the selectivity. The study of the effect of different loading of Zr showed that optimal loadings have to be below 5% in weight.

Key words: Oxidative coupling of methane, carbon dioxide, CeO₂/ZnO catalyst, homogeneous precipitation, micro emulsion.

INTRODUCTION

The direct conversion of methane (CH₄) to ethane (C₂) hydrocarbons through the oxidative coupling of methane (OCM) has attracted academic and industrial interest since the eighties due to its potential to be an effective method to utilize natural gas as an industrial feed stock.

OCM is an exothermic reaction whereas some conventional non-oxidative coupling processes are strongly endothermic (causing thermodynamic limitations), are low in C₂ selectivity and may lead to coking which is strongly aggravated when using carbon dioxide (CO₂). Most of the work in the literature on the development of suitable catalysts for the OCM process makes use of oxygen (O₂). In the oxidative coupling reaction, CH₄ and O₂ react over a catalyst at elevated temperatures to form ethane (C₂H₆) as a primary product

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Table 1. Summary of performance of catalysts system for CO₂-OCM using conventional fixed bed reactor.

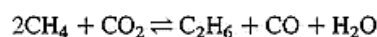
Catalysts	Temperature (K)	CH ₄ conversion (%)	CO ₂ /CH ₄ ratio	C ₂ hydrocarbons	
				Selectivity (%)	Yield (%)
La ₂ O ₃ -ZnO	1123	3.1	1.0	91	2.8
CaO-Cr ₂ O ₃	1123	6.3	2.3	63	4.0
CaO-MnO ₂	1123	3.9	2.3	68	2.7
Na ₂ WO ₄ -Mn/SiO ₂	1093	4.7	2.0	94	4.5
CaO-CeO ₂	1123	5.0	1.0	62	3.2
CaO-ZnO	1148	5.4	2.3	80	4.3
SrO-Cr ₂ O ₃	1123	2.4	2.3	37	1.3
SrO-ZnO	1123	2.8	2.3	79	2.2
SrO-CeO ₂	1123	1.5	2.3	64	1.0
SrO-MnO ₂	1123	3.9	2.3	85	3.3
BaO-ZnO	1123	0.6	2.3	74	0.4
BaO-CeO ₂	1123	0.4	2.3	55	0.2
BaO-Cr ₂ O ₃	1123	0.8	2.3	42	0.3
BaO-MnO ₂	1123	3.8	2.3	67	2.6
MnO ₂ -SrCO ₃	1148	5.7	2.3	51	4.5

and ethene (C₂H₄) as a secondary product. Unfortunately, both CH₄ and C₂H₄ may be converted to CO₂, and the single-pass combined yield of C₂ products is limited to about 25% (Lunsford, 2000). For a homogeneous catalyst, it seems that a transition metal carbene-like complex intermediate and a super acid medium are crucial for CH₄ activation (Xu and Lin, 1999). Heterogeneous catalysts were also investigated for the OCM process using O₂ (Chua et al., 2008; Fakhroueian et al., 2008; Machocki and Jezior, 2008; Takanebe and Iglesia, 2008; Gholipour et al., 2010). A C₂ selectivity of about 80% and a CH₄ conversion of 20% can be achieved using catalysts such as SrO/La₂O₃ (Mimoun et al., 1990) and Mn/Na₂WO₄/SiO₂ (Fang et al., 1992). However, because the overall reaction is exothermic, a zone within the catalyst bed may be 150 to 300°C hotter than the external temperature (Schweer et al., 1994). Heat management is therefore a serious engineering problem.

In the last two decades, a number of researchers have investigated the use of CO₂ as an oxidant in the OCM process (Asami et al., 1995; Chen et al., 1996; Wang et al., 1998, 1999; Wang and Ohtsuka, 2000; Cai et al., 2003; Istadi and Amin, 2004; Wang and Zhu, 2004; Yongjun et al., 2004; Istadi and Amin, 2005; Istadi and Amin, 2006; Gao and Shi, 2010; Lee et al., 2012; Wang et al., 2012). The oxidative coupling of CH₄ with CO₂ provides a promising way of utilizing the relatively abundant natural gas resources and CO₂, the largest man-made greenhouse gas (Lunsford, 2000). The use of CO₂ presents additional advantages over O₂. Carbon monoxide (CO) is the only by-product in this case. Unlike O₂, the CO₂ does not induce gas phase radical reactions. In particular, the reactions of CH₄ and CO to produce C₂

hydrocarbons are mainly controlled by heterogeneous catalysis. It is thus expected that the development of active catalysts may achieve high selectivity to C₂ hydrocarbons. However, because of the inert nature of molecules of CH₄ and CO₂, the preparation of a catalyst with sufficiently high activity remains a big challenge to chemists all over the world. Basicity and reducibility are some of the physico-chemical criteria that are essential in designing a suitable catalyst for the CO₂ based OCM process (Wang and Ohtsuka, 2000).

The following reactions are the two main schemes for CO₂-OCM to produce C₂ hydrocarbons with CO₂ and water (H₂O) as by-products:



$$\Delta G_{1173\text{ K}}^\circ = 69.6 \text{ kJ mol}^{-1} \quad (1)$$



$$\Delta G_{1173\text{ K}}^\circ = 51.9 \text{ kJ mol}^{-1} \quad (2)$$

The equilibrium conversion of CH₄ to C₂H₆ and C₂H₄ based on thermodynamic calculations was reported by Wang et al. (1999). The conversion is enhanced when both temperature and CH₄/CO₂ ratio decreases. Lower CH₄/CO₂ ratio increases the CH₄ conversion to C₂H₆ and C₂H₄. Their yield exceeds 15 and 25%, respectively, at a temperature of 1073K and a feed ratio CH₄/CO₂ of 0.5. An efficient catalyst that is capable not only of activating both CH₄ and CO₂ but also producing C₂ hydrocarbons selectively is welcomed. Table 1 compiles the studies involving oxidative coupling of CH₄ to C₂H₆ and C₂ hydrocarbons (Wang et al., 1999; Wang and Ohtsuka,

2000; Wang and Ohtsuka, 2001; Cai et al., 2003).

Asami et al. (1995, 1997), for instance, systematically investigated the catalytic activities of more than 30 metal oxides for the conversion of CH₄ by CO₂, and found that lanthanide oxides generally showed higher activities. Among them, praseodymium oxide or terbium oxide exhibited relatively good catalytic performance with a C₂ yield of 1.5% and a selectivity of 50% at 1123K. Wang et al. (1998), on the other hand, investigated the conversion of CH₄ to C₂H₆ over praseodymium oxide and reported that the oxide could be effective at temperatures as low as 773 to 923K. In addition, binary oxides catalysts were also investigated by several research groups as shown in Table 1. However, over binary oxide catalysts, the CO₂-OCM reaction exhibits low performance at high temperature (about 1123K) with a CH₄ conversion up to 6.3%, C₂ hydrocarbons selectivity up to 91%, and C₂ hydrocarbons yield up to 4.5%.

Pertaining to ternary metal oxides system, Na₂WO₄-Mn/SiO₂ catalyst was investigated for the conversion of CH₄ and CO₂ to C₂ hydrocarbons (Liu, 1998). A CH₄ yield of about 4.5% and a C₂ hydrocarbons selectivity of 94% were obtained at 1093K. The reaction temperature was shown to favor CH₄ conversion but it did not favor the selectivity to C₂ hydrocarbons. The results of CeO₂-based catalysts screening for CO₂-OCM process over binary and ternary metal oxides revealed that the 15 wt% CaO to 5 wt% MnO/CeO₂ catalyst was the most potential (Istadi and Amin, 2004). In another investigation, single- and multi-responses optimizations of CO₂-OCM reaction over CaO-MnO/CeO₂ catalyst were developed to address the optimal process parameters and catalyst compositions (Istadi and Amin, 2005; 2006). Maximum C₂ hydrocarbons selectivity and yield of 76.6 and 3.7%, respectively, were achieved over 12.8% CaO to 6.4% MnO/CeO₂ catalyst at optimum reactor temperature of 1127K and CH₄/CO₂ feed ratio of 0.5.

The oxidative coupling of CH₄ to C₂H₆ and ethylene requires a high reaction temperature due to the high activation dissociation energy of most C-H bonds (Yao et al., 2000). Due to the difficulty in obtaining high yield in CO₂-OCM process, further improvements are required including the exploitation of some non-conventional technologies such as the application of plasma reactor technologies or the exploitation of some non-conventional technologies for catalyst preparation (Istadi and Amin, 2006). Recently, nanocatalysts had attracted much attention (He et al., 2003a, b). The higher activity and better selectivity of nanocatalysts over traditional catalysts are attributed to their large specific surface area, high percentage of surface atoms and special crystal structures. The preparation method such as homogeneous precipitation, micro-emulsion, gas evaporation and laser vaporization has a significant influence on the structure, size distribution, and the morphology of the nanocatalysts, which in turn greatly affects the properties of the catalysts. He et al. (2003c),

for instance, synthesized La₂O₃/BaCO₃ nanocatalysts from the coupling route of homogeneous precipitation with micro emulsion under pulsed microwave heating. They compared the performance of La₂O₃/BaCO₃ nanocatalysts with that of La₂O₃/BaCO₃ catalysts prepared by conventional homogeneous precipitation. The authors found that using La₂O₃/BaCO₃ nanocatalysts, the reaction could take place at lower temperature, the conversion of CH₄ was higher, but the carbon (C) deposition on the catalysts was more serious, and the improvement of the selectivity of C₂ was not distinct.

He et al. (2003b), on the other hand, prepared nano-CeO₂/ZnO catalysts using a novel combination of homogeneous precipitation with micro emulsion for oxidative coupling of CH₄ with CO₂ as an oxidant. The prepared catalysts were compared with those prepared using the conventional impregnation. The effects of reaction temperature, amount of ZnO doped in the catalysts, and the average size were investigated. Their experimental investigation demonstrated that CH₄ conversion over the nano-CeO₂/ZnO catalysts prepared by the combined technique was higher than that obtained over catalysts prepared by the conventional impregnation. The authors also found that CH₄ conversion increased with increasing fractal dimension of the nanocatalysts.

In this study, we extend the work of He et al. (2003a) by examining the effect of a number of promoters. The following chemicals were tested as promoters:

- i) Lithium nitrate (LiNO₃),
- ii) Zirconium nitrate (Zr(NO₃)₄),
- iii) Bismuth nitrate (Bi(NO₃)₃),
- iv) Barium nitrate (Ba(NO₃)₂)
- v) Lanthanum nitrate (La(NO₃)₃),
- vi) Cobalt nitrate (Co(NO₃)₂),
- vii) Thallium nitrate (TlNO₃) and
- viii) Potassium nitrate (KNO₃).

More than 160 catalyst samples were prepared and tested. In this work, we show the results of the most promising promoters, namely Lithium (Li), Bismuth (Bi) and Zirconium (Zr). We also investigate the effect of a number of operating parameters such as the calcination temperature, calcinations time, feed ratio of CH₄/CO₂, and the different loading percentages of selected promoters.

EXPERIMENTAL

Catalyst preparation

The catalyst samples were prepared using a combination of homogeneous precipitation and micro emulsion. Hexane was used as a solvent, cetyl tri-methylamine bromide (CTAB) as a surfactant and 1-hexanol as a co-surfactant. The nitrates were dissolved in water (solution A), the dimethyl oxalate (DMOX) was dissolved separately in water (Solution B) while CTAB was dissolved in

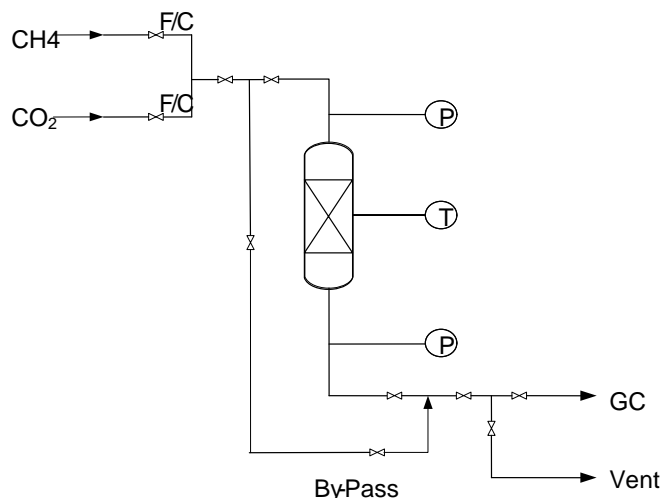


Figure 1. Schematic diagram of experimental set-up.

hexanol and then added to hexane (solution C).

Solution B was added to solution C under vigorous stirring. Afterwards, solution A was added very slowly to the combined solution of B and C at room temperature. The resulting solution was then heated at 45°C for about 2 h. The solvent was evaporated using a vacuum oven. The solid product was then washed by water and then by ethanol 3 times. The resulting solid was dried under vacuum at 50°C. The precursor, Cerium (Ce) and Zinc (Zn) oxalates were calcined at 500 to 900°C in a muffle furnace for different periods of time.

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Catalyst characterization

A scanning electron microscopy [(SEM) Cambridge S360], was used to study the morphology of the catalyst. The images were recorded in secondary electron imaging mode (SE) at different magnifications. An energy dispersive X-ray spectroscopy (Oxford ISIS300, Instrument ID: EDX-1) was used for the analysis of the catalyst. The composition of metals was estimated by EDX system software and pure metal standard spectra.

Catalyst testing

The prepared catalysts were tested for their performances using a conventional reactor shown in Figure 1. The feed section contains two gas cylinders for C_2H_6 and CO_2 . Gases coming from regulators pass through the in-line filters (molecular sieves, 5A) and are introduced into mass flow controllers (Bronkhorst, Netherland). The gases were mixed and passed to the reaction section. Online samples (reactor by-pass) from the feed gas mixture are directed to gas chromatograph for analysis. The micro reactor overall length is 300 mm with an inside diameter of 8 mm. Surrounding temperature

can be controlled with the controller built in the heater. The temperature in the reactor is measured by a thermocouple located in the catalyst bed. The outlet from the reactor (bottom end) is passed through a back pressure regulator (BPR) to control the pressure in the reactor, and the product gases from the BPR are sent to the analysis section. Reaction products were analyzed online using Varian system model CP-3800 RGA gas chromatograph. Thermal conductivity detector (TCD) and flame ionization detector (FID) were used for analysis using Haysepe A columns.

RESULTS AND DISCUSSION

The first part of this section examines the catalyst performance while in a later section we investigate the effect of some parameters on the catalyst size and morphology.

Effect of promoter type and calcinations temperature

This work has investigated the use of three types of promoters: Li, Bi, and Zr. During all the investigation, the following concentrations were maintained: CTAB = 0.0006 g/ml hexane and hexane/hexanol = 5 while thratio of cerium nitrate and zinc nitrate to the dimethyl oxalate ($Ce(NO_3)_3/DMO$) was maintained at 0.24.

Table 2 summarizes the effect of calcination temperature on the performance of the catalyst with the selected promoters. For Li used as promoter, Table 2 shows nearly the same activity (conversion) at the calcination temperatures of 500 and 600°C. At reaction temperature of 800°C, the conversion is 0.373 for a calcination temperature of 500°C compared to 0.45 for a calcination temperature of 600°C. The activity, on the other hand, decreases to almost zero at higher calcination temperature of 700°C. As to the selectivity, it is clear that the catalyst selectivity to produce ethylene increases with increasing reaction temperature. For example, for calcination temperature of 600°C, a 72.8% selectivity can be reached at reaction temperature of 900°C compared to 39.13% at reaction temperature of 800°C. The high calcination temperature of 700°C is detrimental to both the conversion and selectivity.

When Bi is selected as a promoter, the catalyst behaves in a different way. Table 2 shows that the catalyst calcined at 500°C is active only at the high reaction temperature of 900°C. When, on the other hand, the catalyst is calcined at 700°C, there is activity at both reaction temperatures of 800 and 900°C. The table also shows that the selectivity at reaction temperatures of 700 and 800°C is the same for all calcination temperatures that is, they are 100% selective to C_2H_6 , but the selectivity goes towards ethylene at the higher reaction temperature of 900°C. For example, at the reaction temperature of 900°C, 64.21% selectivity can be reached for calcination temperature of 700°C compared

Table 2. Effect of calcination temperature on the catalyst performance for different promoters (feed rate 33 ml/min, CH₄/CO₂ = 1, calcinations time = 1 h).

Promoter	Reaction temperature (°C)	Calcination temperature 500°C		Calcination temperature 600°C		Calcination temperature 700°C	
		Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)
Li	700	0.0	0.0	0.0	0.0	0.0	0.0
	800	0.373	0.0	0.45	39.13	0.0	0.0
	900	1.0	100.0	1.1	100.0	0.0	0.0
Bi	700	0.0	0.0	-	-	0.0	0.0
	800	0.0	0.0	-	-	0.35	0.0
	900	1.4	62.65	-	-	0.50	64.21
Zr	700	0.0	0.0	0.0	0.0	0.0	0.0
	800	0.0	0.0	0.0	0.0	0.489	39.80
	900	0.541	54.0	0.62	62.1	0.53	48.30

Table 3. Effect of feed ratio on the catalyst performance for different promoters (Calcination temperature = 700 °C, calcination time = 1).

Promoter	Reaction temperature (°C)	(CH ₄ /CO ₂) = 1:1; Feed rate = 33 ml/min		(CH ₄ /CO ₂) = 2:1; Feed rate = 45 ml/min	
		Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)
None	700	0.0	0.0	0.0	0.0
	800	0.0	0.0	0.0	0.0
	900	0.525	62.16	0.70	100.
Li	700	0.0	0.0	0.0	0.0
	800	0.0	0.0	0.978	36.76
	900	0.0	0.0	1.562	62.34
Bi	700	0.0	0.0	0.164	0.0
	800	0.0	0.0	0.369	0.0
	900	0.35	0.0	0.755	76.0
Zr	700	0.503	64.2	0.0	0.0
	800	0.49	34.0	0.0	0.0
	900	0.53	48.3	0.15	100.0

to 62.65% when the catalyst is calcined at 500°C.

As for Zr, Table 2 shows that, at calcination temperatures of 500 and 600°C, the catalyst is active only at the high temperature of 900°C. At calcination temperature of 700°C, the catalyst shows activity at reaction temperatures as low as 800°C. For example, at calcinations temperature of 700°C and reaction temperature of 900°C, the catalyst selectivity to ethylene reaches 48.3%.

Effect of feed ratio

The effect of feed ratio of CH₄ to CO₂ was studied by

testing the activity and selectivity of catalysts prepared without and with different promoters (Li, Zr, and Bi). Table 3 shows the results at calcination temperature of 700°C for feed ratios of 1 and 2, respectively. The table shows that when the catalyst is prepared without promoter, the feed ratio is not a very sensitive parameter, given that the catalyst is active in both cases only at the high temperature of 900°C. Catalysts prepared with Li showed on the other hand, good activity and selectivity with the increase in the feed ratio. For the feed ratio of 1, both conversion and selectivity were at lowest values for all reaction temperatures. Increasing the feed ratio shows increasing activity and selectivity at both reaction

Table 4. Effect of Zr loadings on the catalyst performance at different reaction temperatures (Calcination temperature = 700°C; calcination time = 1 h; CH₄/CO₂ = 1; feed rate = 33 ml/min).

Loading (%)	700°C		800°C		900°C	
	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)
0	0.157	0.0	0.0	0.0	0.0	0.0
5	1.234	53.5	0.143	57.6	0.222	0.0
20	1.360	81.4	1.426	80.7	0.827	61.7

Table 5. Effect of calcination time on the catalyst performance with 0.1% Zr loading (Calcination temperature = 600°C; CH₄/CO₂ = 1; feed rate = 33 ml/min).

Reaction temperature (°C)	30 min		60 min	
	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)
700	0.0	0.0	0.0	0.0
800	0.55	53.5	0.65	28.6
900	1.31	41.3	1.35	70.7

Table 6. Effect of calcination time on the catalyst performance with 0.1% Zr loading (Calcination temperature = 800°C; CH₄/CO₂ = 1; feed rate = 33 ml/min).

Reaction temperature (°C)	30 min		60 min		90 min	
	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)	Conversion of CH ₄ (%)	Selectivity of C ₂ H ₄ (%)
700	0.0	0.0	0.0	0.0	0.0	0.0
800	0.0	0.0	0.0	57.6	0.0	0.0
900	0.21	100.0	0.43	51.4	0.85	71.7

temperatures of 800 and 900°C.

In opposite to Li, catalysts that prepared with Zr showed better activity and selectivity at the lower feed ratio of 1. The increase in feed ratio reduces substantially the activity of the catalyst at the temperatures of 700, 800 and 900°C.

As to Bi, Table 3 shows that the increase in feed ratio has an effect on the catalyst activity but not on the selectivity. Larger value of the feed ratio increases the activity of the catalyst for all reaction temperatures, but this increase is not reflected in the sensitivity to ethylene.

Effect of promoter loading

In this section, the effect of different loadings of Zr is investigated. Zr was selected as promoter since the results of the earlier section yielded promising behavior. The catalysts were prepared using a calcination temperature of 700°C and weight percent of 0, 5, and 20%, respectively. All samples were tested with a feed ratio of 1 and reaction temperatures of 700, 800, and 900°C.

Table 4 shows that the choice of loading of 5 and 20 wt% are detrimental to the performance, since catalysts prepared without promoter showed better performance than those with loadings of 5 or 20%. Moreover, the activity and selectivity of the catalysts prepared with 5% were comparable with the basic catalyst only at high reaction temperature of 900°C. We can conclude therefore that, optimum loadings of Zr have to be between the range of 0 and 5 wt%.

Effect of calcinations time

In this section, a sample of 0.1% Zr was tested for different calcinations times of 30, 60, and 90 min using calcination temperatures of 600 and 800°C, respectively. The results are shown in Tables 5 and 6. Table 5 shows that at the moderate calcination temperature of 600°C, the activity is unaffected by the increase in calcination time. The selectivity, on the other hand, increases with calcinations time, especially at high reaction temperatures. For the higher calcination temperature of 800°C, Table 6 shows that both the catalyst activity and

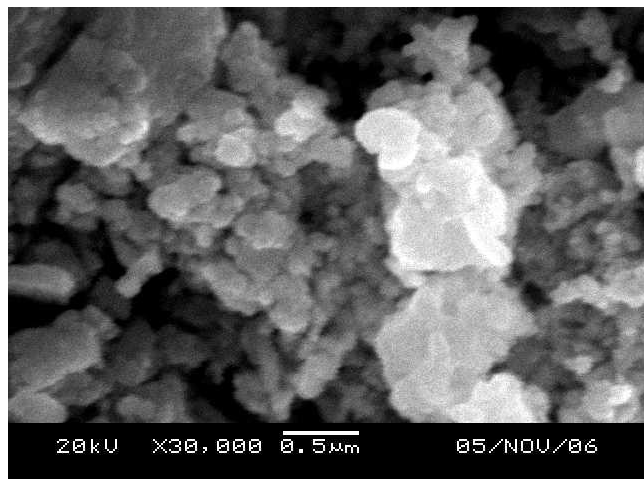


Figure 2. SEM image for $\text{Ce}_2\text{O}_3/\text{ZnO}$ parent catalyst, $T_c = 600^\circ\text{C}$, $t = 1$ h.

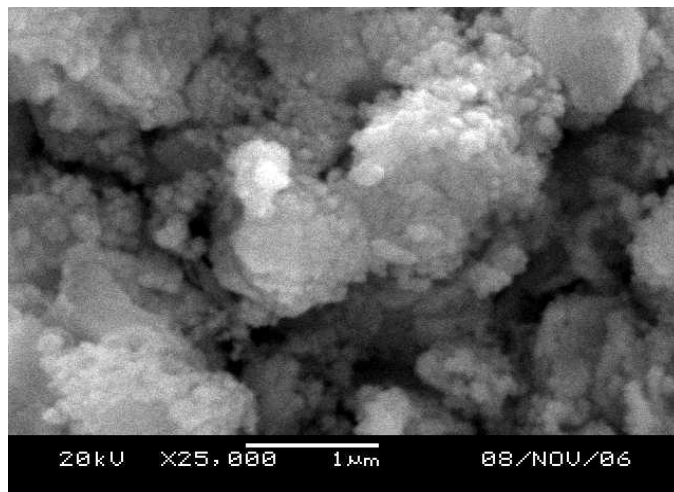


Figure 4. Effect of calcinations time. SEM image for $\text{Ce}_2\text{O}_3/\text{ZnO}$ parent catalyst, $T_c = 700^\circ\text{C}$, $t = 1.5$ h.

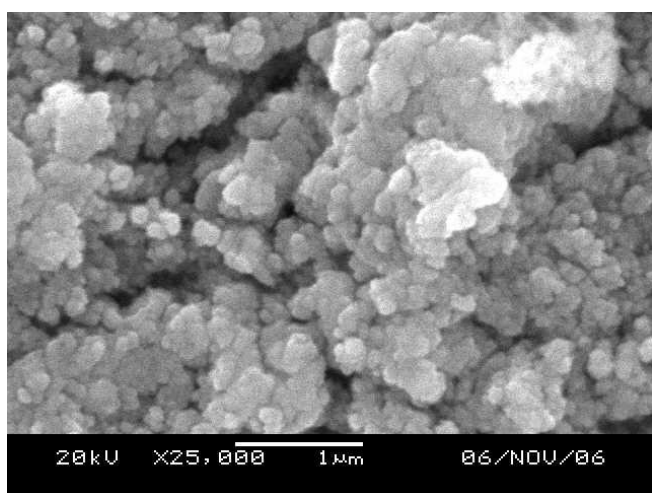


Figure 3. Effect of calcinations temperature SEM image for $\text{Ce}_2\text{O}_3/\text{ZnO}$ parent catalyst, $T_c = 700^\circ\text{C}$, $t = 1$ h.

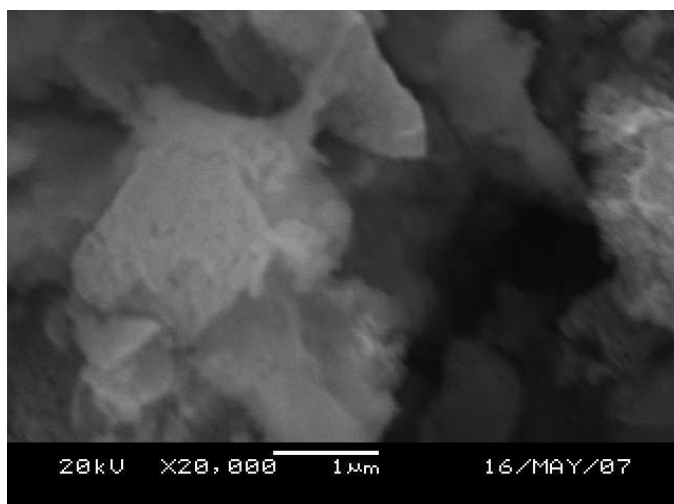


Figure 5. SEM image for $\text{Ce}_2\text{O}_3/\text{ZnO}$ with Zr as promoter, $T_c = 600^\circ\text{C}$, $t = 1$ h.

selectivity clearly deteriorate with the increase in calcination time.

A scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) results

In this section we investigate the effect of some parameters on the morphology of the catalyst. Figure 2 shows the microstructure of the parent catalyst calcined at 600°C for 1 h. Due to agglomeration, it is difficult to determine the exact particle size but it is evident that the crystallite size of the catalyst falls in the nanometer scale range. With increasing calcination temperature, Figure 3 shows that the crystals begin to grow and become more

prominent and more ordered at 700°C as compared to 600°C .

Figures 4 shows on the other hand, the effect of calcination time. It is clear from the SEM micrographs that increasing calcination time has a drastic effect on crystallite size. The crystallites began to grow in a more rapid way as compared to previous results (Figure 3), and are fully agglomerated.

Figures 5, 6, and 7 show the effect of the different studied promoters on the nanostructure of the catalysts. The figures correspond to the same calcinations conditions (calcination temperature of 600°C and calcinations time of 1 h). The agglomeration seen in the three figures makes it difficult to determine the exact

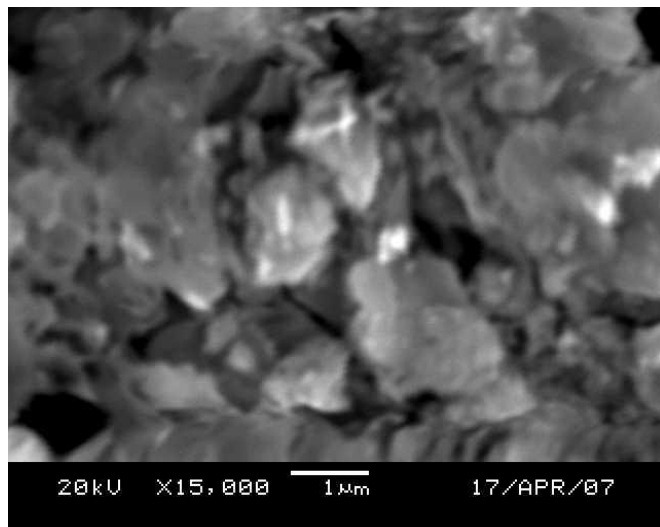


Figure 6. SEM image for $\text{Ce}_2\text{O}_3/\text{ZnO}$ with Bi as promoter, $T_c = 600^\circ\text{C}$, $t = 1$ h.

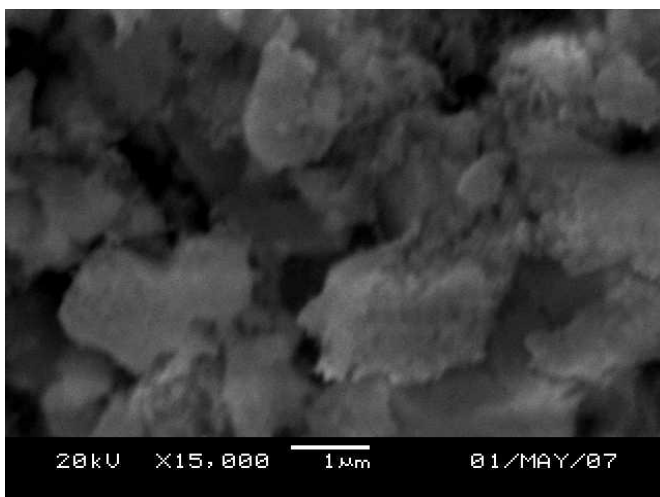


Figure 7. SEM image for $\text{Ce}_2\text{O}_3/\text{ZnO}$ with Li as promoter, $T_c = 600^\circ\text{C}$, $t = 1$ h.

particle size but it is clear that the crystallite sizes of the different catalyst are in the nanometer scale range. Moreover, it can be seen that catalysts with Bi promoter show more ordered structure than those prepared with Li or Zr. However, no further conclusions can be made at this point as we found no clear correlation between the conversion of CH_4 and the average size of the nanoparticles. This is also the conclusion reached by He et al. (2003b). The composition of the catalyst was analyzed using EDS which confirmed the presence of Zn, Ce, and O in the parent catalyst. An example of this analysis was shown in Figure 8.

Conclusions

CeO_2/ZnO nanocatalysts were prepared by combining homogeneous precipitation with micro emulsion. The performance of these nanocatalysts on the oxidative coupling of CH_4 with CO_2 was investigated for a number of promoters and under various operating conditions. The SEM images confirmed the nanostructure of the parent catalyst. With increasing calcination temperature, crystals begin to grow and become more prominent and more ordered. Increasing calcinations time, on the other hand, makes the crystallites to grow in a more rapid way and become fully agglomerated. The nanostructure depends strongly on the added promoters. At the same calcinations temperature of 600°C and time of 1 h, the crystallites with Li as promoter are more ordered than those associated with Zr and Bi.

The effect of some operating parameters on the performance of the catalysts was also studied. Generally, it can be said that the activity was almost the same for catalysts calcined at 500 and 600°C except for Bi for which the catalysts calcined at 700°C showed better activity at the lower reaction temperature of 800°C . Catalysts prepared with Zr, on the other hand, preferred higher calcination temperature for both activity and selectivity.

The study of the effect of feed ratio showed that catalysts prepared without promoter were not sensitive to changes in the feed ratio. Catalysts prepared with Li showed, on the other hand, good activity and selectivity with the increase in the feed ratio. In opposite, catalysts prepared with Zr showed better activity and selectivity at the lower feed ratio. As to Bi, the increase in feed ratio has an effect on the catalyst activity but not on the selectivity.

The study of the effect of calcination temperatures on the catalyst prepared with 0.1% Zr showed that at moderate calcination temperatures, the activity was unaffected by the increase in calcination time. The selectivity, on the other hand, increased with calcinations time. For higher calcination temperatures, both the catalyst activity and selectivity clearly deteriorated with the increase in calcinations time.

A final note should be made about future research directions. There are a number of other parameters that may also affect the size of the precursor and hence the size of the catalyst. These may include the concentration of CTAB in hexanol, the ratio of hexanol to hexane, and the ratio of nitrates to oxalates. These parameters are worth being investigated in future work.

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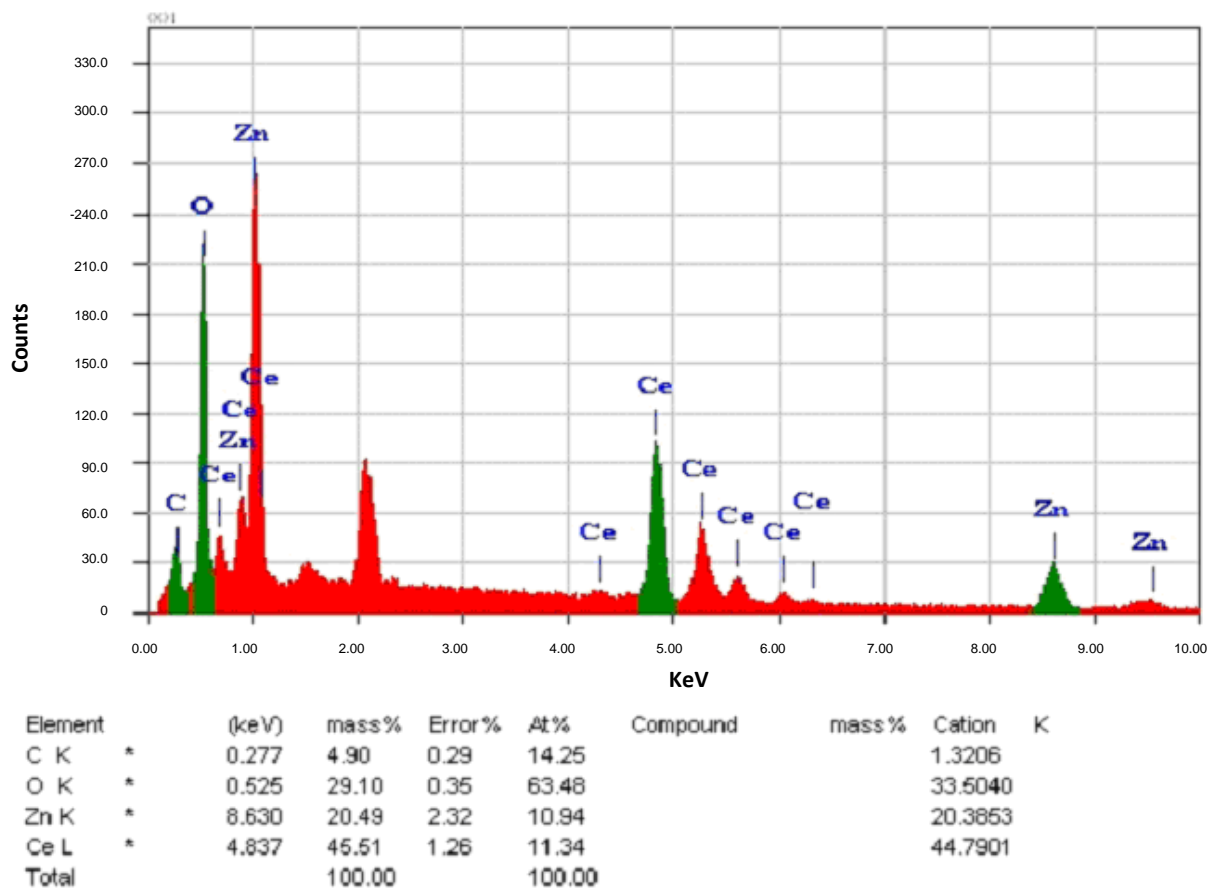


Figure 8. Chemical composition of $\text{Ce}_2\text{O}_3/\text{ZnO}$ parent catalyst, $T_c = 700^\circ\text{C}$, $t = 1.5$ h.

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