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Synthesis of dimethyl carbonate by transesterification with various $MgO–CeO_2$ mixed oxide catalysts

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The transesterification of ethylene carbonate (EC) with methanol to co-generate dimethyl carbonate (DMC) and ethylene glycol over the MgO, CeO_2 and mixed oxide thereof was studied using a fixed-bed isothermal tube reactor. In all mixed oxide, the presence of cerium led to a decrease of BET surface area and pore volume as compared to pure magnesia. X-ray diffraction (XRD) revealed that no mixed phases were observed, but MgO (periclase) and CeO_2 (cerianite) phases. The catalytic activity intensely depends on the surface basicity and the base strength distribution, but not on the surface area and pore volume. It was found that a high EC conversion of 67% with DMC selectivity of 95% could be obtained by catalyst with cerium content around 25 mol%.

KEY WORDS: dimethyl carbonate; transesterification; Mg–Ce mixed oxide; surface basicity.

1. Introduction

Dimethyl carbonate (DMC) has been appealing to much interest in recent year as an environmentally benign chemical and known as a useful compound having versatile uses. In many aspects, DMC can be variously applied as a starting material for organic synthesis *via* carbonylation and methylation, substituting high-risk and toxic agents such as dimethyl sulfate, methyl halides and phosgene due to its negligible toxicity [1–3]. DMC is also a candidate for replacing methyl *tert*-butyl ether (MTBE) as an oxygen-containing additive for gasoline because it has high oxygen content, a good blending octane, low toxicity, and quick biodegradation [4, 5]. Moreover, DMC can be used in lithium batteries as an electrolyte due to its high dielectric constant [6].

Since the process methanolysis of phosgene has been losing attraction recently due to the use of virulent phosgene [6], a number of DMC synthetic methods have been suggested as an environmental benign process. DMC can be synthesized *via* the oxidative carbonylation of methanol and the carbonylation of methylnitrite processes [2]. Furthermore, DMC can be produced concurrently with ethylene glycol (EG) by the transesterification process between methanol and ethylene carbonate (EC) [7].

For transesterification of cyclic carbonate with methanol, various homogeneous and heterogeneous, acid and base catalysts have been reported as being effective. Knifton and Duranleau [8] found that bases were generally more effective than acids for this reaction. The use of inorganic base, such as alkali metal alkoxide, carbonates and hydroxide *etc*. as catalyst had been patented by Bayer and Dow companies [9, 10]. Bayer's corporation also patented the application of organic base, usually tertiary amine, as catalyst [11]. Even though the homogeneous catalysts had pretty high activity due to their homogeneous nature, there are still some drawbacks such as separation, regeneration, *etc*. Under these circumstances, it paved the way to apply solid base catalysts as alternative routes for the synthesis of DMC. There were some reports on these transesterification over solid bases. Knifton and Duranleau [8] proposed free organic phospines supported on partially cross-linked poly-styrene. Various heterogeneous catalysts such as alkali treated zeolite [12, 13], basic metal oxides [14, 15], and hydrotalcite [16] have also been applied. Nevertheless, these catalysts required a long reaction time and the activity and selectivity were not so high.

In the present study, magnesia–ceria catalysts have been prepared and characterized. The catalytic performance was investigated *via* transesterification between methanol and EC in the concurrent synthesis of DMC and EG. The mixed oxide of MgO and CeO_2 exhibited a good performance and could be a promising catalyst for DMC synthesis *via* transesterification. It is shown that the catalytic activity strongly depends on the basicity and base strength of the catalysts.

2. Experimental

Mixture of $Mg(OH)_2–Ce(OH)_4$ hydroxide gels were prepared from their salt solutions as precursors by co-precipitation method. About 1 M NaOH (>98%, Daejung, Korea) aqueous solution was slowly added to

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an aqueous solution containing $MgCl_2{\cdot}6H_2O$(>98%, Kanto, Japan) and $Ce(NO_3)_3 \cdot 6H_2O$(>98.5%, Kanto, Japan) in the desired Mg:Ce ratio at room temperature until the pH value of the mixture reached 10 with stirring. The precipitate was further aged at room temperature for 5 h in the mother liquid. After filtration and washing with distilled water, the obtained solid was dried at 110 °C for 12 h and then calcinated at 500 °C for 5 h in air.

Elemental analysis of the catalysts was performed by inductively coupled plasma (ICP). The specific surface area, pore volume and pore size were measured by a Micromeritics ASAP 2020 V1.04 E instrument. X-ray powder diffraction (XRD) patterns of catalysts were recorded using X-ray diffractometer (Shimadzu XRD-6000) operated at 40 kV and 30 mA, using $CuK_\alpha(\lambda = 0.15418\ nm)$ radiation. Observation with FE-SEM (HITACHI S-4200) for the samples was carried out at an accelerating voltage of 15.0 kV. Surface composition was analyzed by EDX (Energy Dispersive X-ray).

The surface basicity and the base strength distribution were respectively analyzed by retroaldolization of diacetone alcohol (DAA) method and benzoic acid titration method using Hammett indicators according to the literature [17]. Catalytic basicity measurements by retroaldolization of DAA were carried out in a magnetically stirred liquid phase suspension of catalyst at 50 °C. DAA (99%, Fluka) was solved in 40 mL of cyclohexane resulting in a 0.05 M DAA solution. Samples of the reaction mixture were taken and analyzed by gas chromatography with a 25 m HP-FFAP Polyethylene Glycol TPA capillary column linked to a flame ionization detector at isothermally column temperature of 80 °C. The basic strength distribution of the solid bases ($H\_$) was determined from color changes of Hammett indicators (see table 1) by benzoic acid (0.02 mol/L anhydrous cyclohexane solution) titration.

The catalytic activity was measured by transesterification process of EC with methanol, which was carried out in a vertical tube reactor according to [18] with 3 g of catalyst powder, molar ratio (MeOH/EC) = 8.0 and a flow rate of 0.18 mL/min, corresponding to liquid hourly space velocity (LHSV) of 3 h^{-1}. The reaction temperature was fixed at 150 °C and the reaction pressure was maintained to be constant by BPR (Back Pressure Regulator) at 3.5 psig (0.2 MPa).

Table 1
Hammett indicators used for the benzoic acid titration

Indicator	Base strength ($H\_$)
Phenolphthaleine	8.2–9.8
Thymolphthaleine	9.3–10.5
2,4 Dinitroaniline	15.0
4-Chloro-2-nitroaniline	17.2
p-4-Nitroaniline	18.4
4-Chloroaniline	26.5

3. Results and discussion

The initial Ce content in the catalyst preparation was 0 (pure MgO), 20, 22.5, 25, 33.3, 50, and 100 (pure CeO_2) mol%. After elemental analysis using ICP, the actual Ce content was respectively 0, 19.4, 24.4, 35.4, 44.9, 55.9, and 100 mol% according to Mg/Ce mole ratio of 1/0, 5/1, 4/1, 3/1, 2/1, 1/1, and 0/1. The surface composition of the catalysts was analyzed by energy dispersive X-ray (EDX). The result has a comparable value with ICP. The values of ICP will be used for following results of analysis and discussion.

Figure 1 illustrates XRD patterns of $MgO–CeO_2$ catalysts. In the XRD profiles of the $MgO–CeO_2$ catalysts prepared by co-precipitation method ((a)–(g)), individual phases of CeO_2 and MgO were observed without producing new compounds. For the pure MgO (a), the intensive and sharp diffractions at $2\theta = 43.1°$, 62.4° and 78.7° can be primarily attributed to MgO (PDF #43-1022) to the Miller indices of (200), (220), and (222), respectively. In the XRD pattern of pure cerium oxide (g), the diffraction peaks at $2\theta = 28.8°$, 33.3°, 47.7°, and 56.6° could be assigned to CeO_2 (PDF #43-1002) corresponding to the Miller indices of (111), (200), (220), and (311), respectively. The diffraction peaks of MgO and CeO_2 both appeared for the $MgO–CeO_2$ mixed oxides ((b)–(f)). The MgO peaks in the XRD patterns faded out with increase of CeO_2 content and finally some of them disappeared at the CeO_2 content more than 45 mol%, even some peaks already disappeared at the CeO_2 content more than 20 mol%, such as peaks of (111), (311), and (222). Magnesia and ceria are known to form no solid solutions [19]. The absence of peaks MgO at higher Ce content is presumably due to suppression of crystal growth. This fact is supported by the suggestion of Saito *et al.* [20] that the MgO component is in amorphous or fine particle state due to suppression of crystal growth by CeO_2 addition.

The width of peaks of $MgO–CeO_2$ in the X-ray diffraction curve reflects the average grain size and it can be calculated using Scherrer's formula. The average crystallite sizes of the catalysts were calculated and illustrated in figure 2. With increase of cerium content, the crystallite sizes of mixed oxides were radically increased. As expected, XRD (Fig. 1) and SEM (figure 3) analysis show that crystallite size is increased with increase in the Ce content. The average pore diameters of these catalysts were also increased monotonically with the Ce content. First, pore diameter increased from 11.08 to 14.81 nm of pure MgO and mixed oxide with Ce content of 19.9 mol%, respectively. Then, pore size was slightly increased from 14.81 to 17.61 nm with an

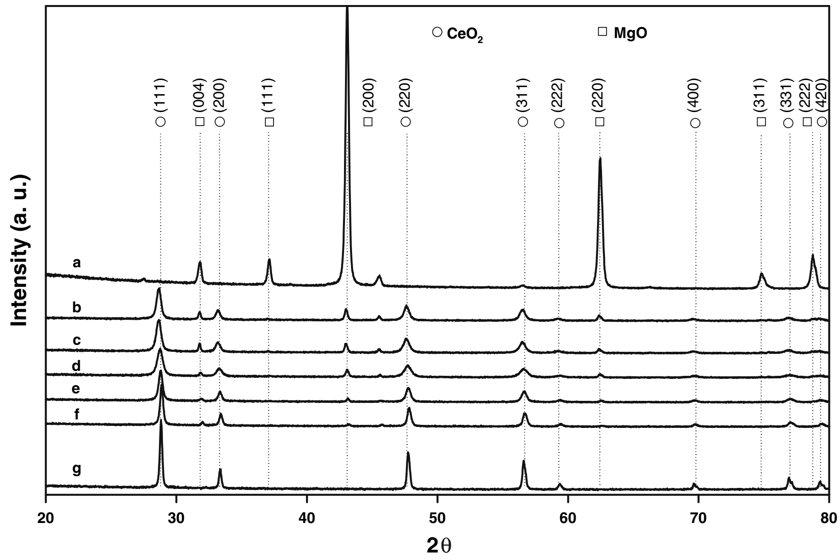


Figure 1. XRD profiles of MgO–CeO$_2$ mixed oxide catalysts with various cerium contents (mol%): (a) 0.0 (MgO), (b) 19.4, (c) 24.4, (d) 35.5, (e) 44.9, (f) 55.9, and (g) 100.0 (CeO$_2$).

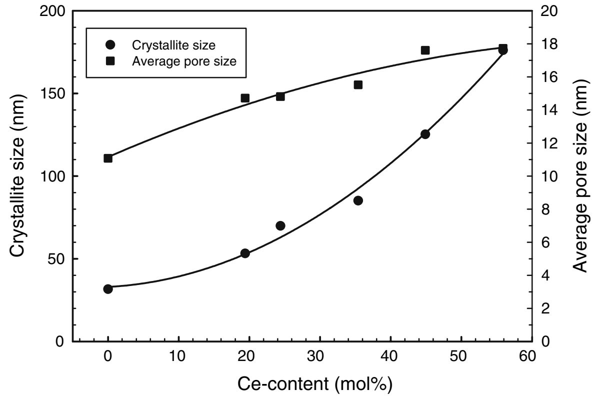


Figure 2. The effect of Ce content on the crystallite size and average pore size of the mixed oxides.

increase of Ce in the mixed oxide from 14.9 to 55.9 mol%, respectively. Figure 3(a)–(c) are the SEM images of MgO and MgO–CeO$_2$ with Ce content of 19.4 and 24.4%. We observed an increase in the MgO–CeO$_2$ phase with an increase in the Ce content. In particular, figure 3(a) shows the agglomerate of MgO.

The structural properties of the magnesium–cerium mixed oxides together with the pure MgO and CeO$_2$ are shown in figure 4. It can be seen that the surface area and pore volume of mixed oxides are smaller than those of the pure MgO. It is worthy noting that the addition of cerium to MgO decreased the surface area dramatically, from 26.3 to 11.6 m^2/g respectively for MgO and cerium content of 19.4 mol%, while the pore volume decreased from 0.073 to 0.051 cm^3/g. An increase of cerium content in the mixed oxide from 19.4 to 55.9 mol% decreased the surface area and pore volume gradually from 11.6 to 7.3 m^2/g and from 0.051 to 0.032 cm^3/g, respectively. This indicates that the particles of mixed oxides are greater than MgO particles.

The catalytic performance of the catalysts was examined by transesterification between EC and methanol in a vertical tube reactor. The DMC yields formed and the conversions of reacted EC are plotted with the surface basicity (rate constant of DAA) against the Ce-content in figure 5. The catalytic activity for the formation of acetone from DAA can be used as a direct measure of basicity [17]. The catalyst activity could be characterized by the first-order rate constant (k_{DAA}) per unit surface area. The reaction rate was obtained by following the consumption of DAA with time. Obviously, the EC conversion increased slowly with the cerium content in the catalysts below 20%. An increase of cerium content the activity enhanced dramatically and reached the maximum point with EC conversion of 67% and DMC selectivity of 95% at cerium content about 25%. Beyond this value, an increase of cerium content leads to a decrease of catalytic activity. This trend happened also to DMC yield. First, DMC yield increased with the cerium content and then decreased remarkably at cerium content beyond 25 mol%. It has been seen that there is obviously relationship between the surface basicity and catalytic activity. The addition of cerium to the mixed oxides definitely leads to an increase of the surface basicity of the catalyst. With further increase of cerium, basicity is enhanced up to a maximum value of $13.1 \times 10^{-3} \mathrm{m}^{-2} \mathrm{s}^{-1}$ at 24.4 mol%. The basicity drops down at higher cerium content and its value is less than the value of MgO at cerium content more than 50 mol%.

The activity and selectivity of mixed oxide with Ce content of 25 mol% with 67% EC conversion and 95% DMC selectivity are high as compare with earlier reports

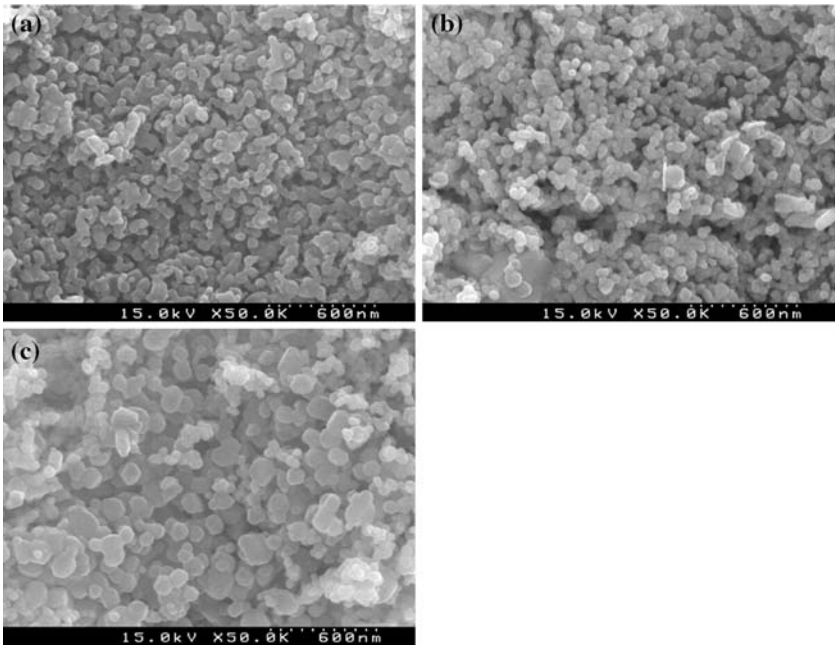


Figure 3. SEM images of MgO–CeO$_2$ catalysts with cerium content (mol%): (a) 0 (MgO), (b) 19.4, and (c) 24.4.

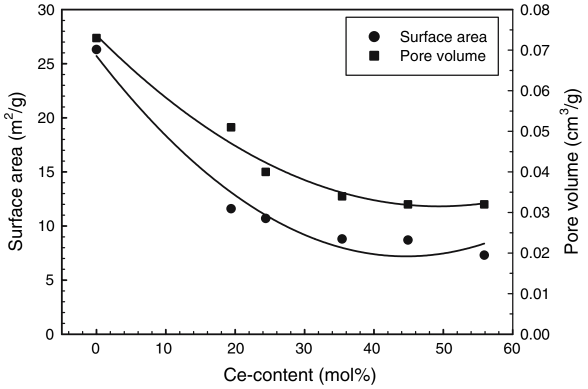


Figure 4. The effect of Ce content on the surface area and pore volume of the mixed oxides.

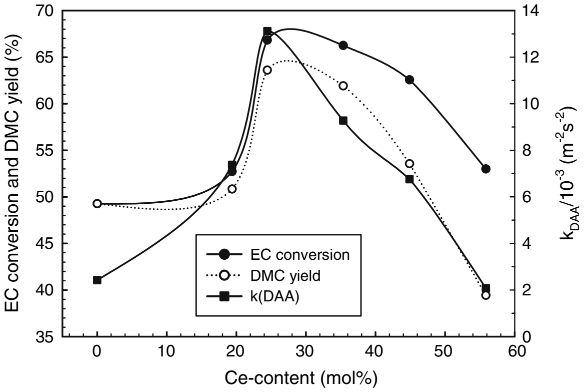


Figure 5. Correlation of EC conversions and DMC yields with the first order constant by retroaldolization of diacetone alcohol represents surface basicity of catalysts.

on the title reaction using the similar tube reactor for measuring the catalytic performance. For instance, Feng *et al.* report 41.7% EC conversion for MCM-41 [12]. Urano *et al.* [14] report 59% EC conversion with 32% DMC yield, using rare earth oxides. Table 2 illustrates the activity of MgO–CeO$_2$ and other heterogeneous catalysts of previous authors. It is obviously that MgO–CeO$_2$ catalyst yielded DMC higher with good selectivity compare to other catalysts. TOF value of this mixed oxide is 0.19 s^{-1} as high as that of hydrotalcite from ref. [16]. Although EC conversion of hydrotalcite was little bit higher (70%) than MgO–CeO$_2$, but it produced lower DMC selectivity (83%). It is worthy to note that MgO–CeO$_2$ produced DMC more pure than the other catalysts.

Over the cerium content around 45%, the EC conversion was high but DMC yield was almost the same with the cerium content of 20%. This indicates that some of reacted EC converted to by-products. The viable by-products, which have been formed in this transesterification over the MgO–CeO$_2$ mixed oxide catalysts, are described in table 3. It has been found that the increase of cerium content in the mixed oxide increase by-products concentration in the reaction. The phenomenon could occur due to the high value of strong basic site, which are seized by catalysts with higher cerium content. The formation of byproducts in this reaction might be occurred by some factors such as decomposition of EC, decomposition of EG, reaction between EC and EG, *etc*. Ethylene carbonate reacts with methanol form 2-hydroxyethylmethyl carbonate as intermediate of DMC (Scheme 1). EC could be

Table 2
Activity of $MgO–CeO_2$ and other heterogeneous catalysts of previous authors

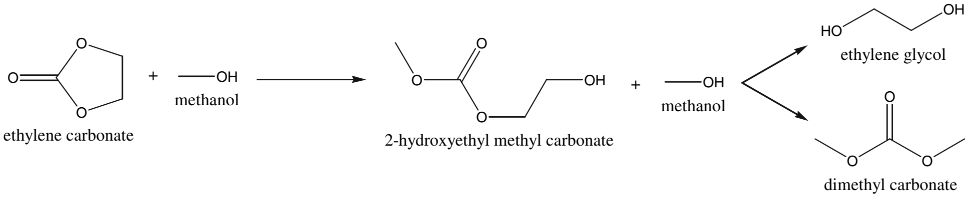
Catalyst	DMC		TOF[a]	Reactor	Reference
	Yield (%)	Selectivity (%)	(1/s)		
$MgO–CeO_2$ (Ce = 24.4 mol%)	64	95	0.19	SS-tube reactor	This work
MCM-41	42	N/A	–	SS-tube reactor	[12]
K-TS-1 (Si/Ti = 92)	57	84	–	Autoclave	[13]
Rare earth oxide	32	54	–	SS-tube reactor	[14]
Metal oxide	60	73	–	Autoclave	[15]
Hydrotalcite (Mg/Al = 2.5)	58	83	0.19	Autoclave	[16]

[a] Based on DMC yield.

Table 3
By-products and their concentrations[a]

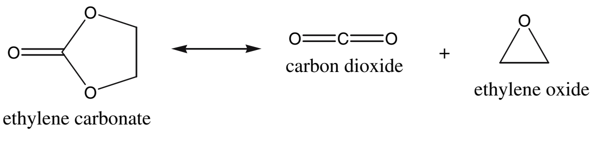
Ce-content (mol%)	19.4	24.4	35.4	44.9	55.9
CO_2	0.79	0.88	1.16	1.06	0.65
Ethylene oxide	0.20	1.20	0.69	0.22	0.86
2-methoxy-ethanol	2.04	3.75	6.51	2.58	4.73
2-hydroxyethylmethyl-carbonate	0.00	0.30	0.45	8.61	0.25
2-(2-methoxyethoxy) ethanol	5.91	2.78	3.61	4.05	3.65
2-ethoxy-ethanol	2.66	2.22	1.21	0.00	1.36
Diethylene glycol	0.00	6.69	7.32	8.35	15.28
Diethylene glycol dimethyl ether	0.63	0.77	0.66	1.15	1.08
Total concentration (%)	12.23	18.50	21.61	26.02	27.86

[a] Analyzed using GC-MS HP 6890 with 25 m capillary column HP-FFAP.



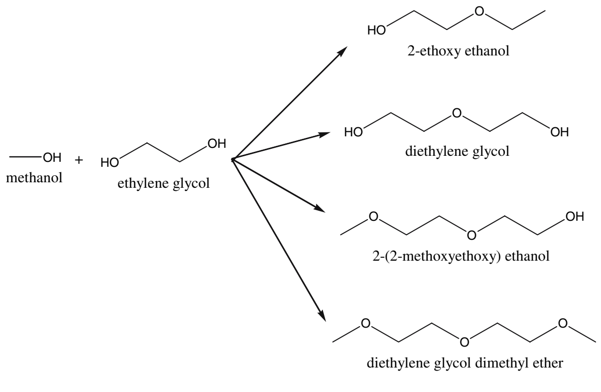
Scheme 1.

decomposed due to high temperature to ethylene oxide and carbon dioxide (Scheme 2). Reaction between ethylene oxide and methanol produced 2-methoxy ethanol (Scheme 3). Methanol and EG produces alkyl glycol ether and dimer, trimer or oligomer of EG (Scheme 4).



Scheme 2.

Scheme 3.



Scheme 4.

Table 4
Base strength distribution (H_) of MgO–CeO_2 mixed oxide catalysts

Cerium content (mol%)	Base strength distribution (H_) (%)[a]				
	8.2–10.5	10.5–15.0	15.0–17.2	17.2–18.4	18.4+
0.0	34.8	24.2	20.6	6.4	3.9
19.4	24.9	24.3	24.9	7.8	4.8
24.4	26.4	27.0	29.3	11.4	5.9
35.4	18.9	22.8	31.2	18.0	9.1
44.9	14.0	17.2	31.1	27.9	9.8
55.9	12.1	13.2	26.8	35.6	12.2
100.0	3.5	5.8	30.8	43.5	16.4

[a] Measured from the color changes of Hammett indicators by benzoic acid titration.

The base strength distribution of the MgO–CeO_2 mixed oxides catalysts are recapitulated in table 4. The number of basic sites per unit surface area was determined for certain ranges of base strength (H_). The base strength distribution was obtained from the color changes of Hammett indicators. The amount of strong basic sites in the range 17.2 ≤ H_ ≤ 26.5 increases with the cerium content, whereas the medium basic sites show the tendency like the surface basicity (rate constant of DAA). It was suggested that moderately basic sites are active for the reaction [15, 16]. It can be seen between cerium content 19.4% and 44.9%, and between pure MgO and cerium content 55.9%. Although the basicities are almost the same, but the value of strong basic site (17.2 ≤ H_ ≤ 26.5) of catalyst with cerium content 44.9% is three times more than that of the catalyst with 19.4% cerium content. The similar case happened also with the catalyst with cerium content 55.9%, which has the value of strong basic site (17.2 ≤ H_ ≤ 26.5) more than four times than that of MgO. The results indicate the high concentration of strong basic site can give negative effect on the DMC yield by producing by-products (see table 4).

4. Conclusion

Magnesia–ceria solids catalysts with different cerium content were synthesized by the co-precipitation method. A comparative study of surface properties (BET) showed the tendency of reduction of surface area and pore volume by cerium addition. Surface areas and pore volumes of mixed oxides are lower than those of pure magnesia, suggesting the possibility of a suppression of crystal growth by cerium addition. XRD analysis revealed that no mixed phases are present, but MgO (periclase) and CeO_2 (cerianite) phases. The crystallite size increased significantly with the cerium content in the mixed oxides. The highest catalytic activity of the mixed oxide catalyst with EC conversion of 67% and DMC selectivity of 95% could be obtained by Ce-content around 25%. However, an increase of cerium content in mixed oxides beyond 25% increased the EC conversion but not the DMC yield. The strong basic site enhanced the EC conversion to by-products. It has been found, that the catalytic activity depends on the surface basicity and the base strength distribution rather than the surface area of the catalysts.

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