

Preparation and characterization of Mg-modified zirconias as catalysts for the direct synthesis of dimethyl carbonate (DMC)

Preparación y caracterización de circonias modificadas con Mg como catalizadores para la síntesis directa de carbonato de dimetilo (DMC)

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Abstract

In this work sol-gel zirconia was prepared using H_2SO_4 , HNO_3 or HCl as hydrolysis catalysts. Basic and acid sites of synthesized zirconia materials were characterized by XRD, BET, FTIR, CO_2 -TPD and NH_3 -TPD. FTIR spectra and TGA confirmed the presence of sulfate in the structure of samples prepared with H_2SO_4 as hydrolysis catalyst. Different molar ratios of Mg were incorporated by co-gellation on selected zirconia materials in order to improve their basic properties. Mg loading was determined by elemental analysis. The resulting materials were tested for the direct synthesis of dimethyl carbonate (DMC) from methanol and CO_2 . The addition of Mg to zirconia samples prepared with HCl as hydrolysis catalyst increased their CO_2 adsorption capacity between 100 and 200°C. However, methanol conversions on these samples were lower than over unmodified zirconia samples.

----- *Keywords:* Sol-gel process, zirconia, basic sites, dimethyl carbonate, CO_2 -TPD

Resumen

Se preparó circonia por el método sol-gel usando H_2SO_4 , HNO_3 o HCl como catalizadores de hidrólisis. Los materiales resultantes se caracterizaron por DRX, BET, FTIR, desorción de CO_2 con temperatura programada (TPD- CO_2) y desorción de amoníaco con temperatura programada (TPD- NH_3). Los espectros FTIR de las muestras preparadas con H_2SO_4 muestran bandas típicas de sulfatos, lo cual se confirmó mediante TGA. Adicionalmente, en algunos materiales seleccionados se incorporaron diferentes proporciones

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de Mg mediante co-gelación. La carga de magnesio de los materiales modificados se determinó por análisis elemental. Los materiales se ensayaron como catalizadores en la síntesis directa de carbonato de dimetilo (DMC) a partir de metanol y CO₂. La incorporación de Mg incrementó la capacidad de adsorción de CO₂ entre 100 y 200 °C. No obstante, las conversiones de metanol obtenidas con estas muestras fueron menores a las de las muestras de circonia sin modificar.

----- *Palabras clave:* Método sol-gel, circonia, sitios básicos, carbonato de dimetilo, TPD-CO₂, TPD-NH₃

Introduction

The interest in the production of dimethyl carbonate (DMC), a compound catalogued as a “green chemical”, has been growing over the last decade. DMC is an environmentally friendly raw material of wide versatility and a possible substitute of highly corrosive or toxic reagents in organic synthesis such as: dimethyl sulfate, chloromethane and phosgene. Moreover, DMC can act as methylating and carbonylating agent or as an intermediate in the production of higher carbonates, polyurethanes, isocyanates, polycarbonates and other fine chemicals [1]. Due to its high oxygen content and reduced environmental impact, DMC has also emerged as a potential substitute for methyl tertiary butyl ether (MTBE), used as an oxygenated fuel additive (i.e., octane enhancer) [2]. The direct synthesis of DMC from methanol and CO₂ (reaction 1), which would replace the traditional synthesis via the phosgenation of methanol, is an attractive route for its production [3].



Several catalysts have been reported for the one-step synthesis of DMC (reaction 1) [4]: organometallic compounds, Ni and Ti tetraalkoxides, K₂CO₃, ZrO₂, H₃PW₁₂O₄-ZrO₂, H₃PO₄-V₂O₅, Cu-Ni/VSO, Cu-Ni/CA [5], Rh/ZSM-5 [6]. However, DMC yields are still very low, even in the presence of dehydrating agents (to shift the reaction towards products) and additives. Furthermore, almost all catalytic experiments

have been carried out in the liquid phase under high pressure conditions (supercritical conditions) showing disadvantages versus gas-phase processes in terms of controlling the process variables, catalyst recovery and associated costs.

Previous studies [7, 8] have shown the simultaneous presence of acid and basic sites on zirconia, which are believed to be the active sites for the direct synthesis of DMC. However, low methanol conversions have been obtained (less than 1%) due to the difficulty of CO₂ activation. Those reports also emphasized that the strength of the basic sites would favor CO₂ activation in that reaction [9]. The use of metal oxides as dopants is proposed not only to improve the chemical stability but also, to increase the oxygen anion concentration and basicity of zirconia [10].

The synthesis of sol-gel zirconia materials has been previously reported. Montes et al. [11] reported a 100% tetragonal phase using H₂SO₄ while about 63.6% tetragonal phase was obtained using HNO₃. At a calcination temperature of 600 °C crystalline materials with defined properties and surface areas up to 67 m²/g were obtained. On the other hand, Bokhimi et al. [12] mostly obtained the monoclinic phase (97%) when HCl was used as hydrolysis catalyst and the material was calcined at 800 °C.

In this paper magnesium oxide –which displays CO₂ adsorption capacity [13]– was added by cogellation to several sol-gel zirconia materials. It was found that Mg increases the CO₂ adsorption capacity of zirconia in the temperature range

(100 - 200°C) where the formation of DMC occurs. However, methanol conversions to DMC over Mg modified zirconia are lower than on unmodified zirconia materials.

Experimental

Catalyst preparation

Zirconia was prepared by modifications of previously reported methods [11, 12]. Solution A, containing 10 mL of zirconium (IV) butoxide (Aldrich) $Zr(OC_4H_9)_4$ in 85 mL of isopropanol (J.T. Baker), was stirred at room temperature. Then HCl (37%, Merck), HNO_3 (65%, Merck) or H_2SO_4 (95-98%, Merck) was added to solution A in order to favor alkoxide hydrolysis. After aging the gel for 24 h at room temperature without stirring, solution B, containing 5 mL of H_2O and 42 mL of isopropanol, was added drop-wise to solution A under vigorous stirring until gellation. Finally, the gel was dried at 100 °C during 60 h. The samples prepared using H_2SO_4 , HNO_3 and

HCl were coded as ZrO_2 -S, ZrO_2 -N and ZrO_2 -C, respectively.

Magnesium-modified zirconia was prepared as follows: about 5.5 g of $Mg(NO_3)_2 \cdot 6H_2O$ (Merck) were dissolved in solution B, prior to mixing with solution A. The Mg/Zr molar ratio was 1. The resulting magnesium-loaded materials were coded: Mg/ZrO_2 -N (prepared with HNO_3) and Mg/ZrO_2 -S (prepared with H_2SO_4). Both materials were calcined in a static air furnace at 600 °C (873 K) and 800 °C (1073 K) for two hours at a heating rate of 1 °C/min. The highest calcination temperature was used only for comparison purposes. Other materials were prepared by varying Mg loading following a similar procedure, but using HCl as initiator of the alkoxide acid hydrolysis. These samples were calcined at 800 °C in order to obtain a stabilized monoclinic phase as reported by Bokhimi [12]: The Mg/Zr molar ratios were 0, 0.1, 0.5 and 1. The codes of the samples are summarized in table 1.

Table 1 Zirconia materials prepared via sol-gel

<i>Material</i>	<i>Hydrolysis Catalyst</i>	<i>Mg/Zr Molar Ratio</i>	<i>Calcination Temperature (°C)</i>
ZrO₂-S	H ₂ SO ₄	-	600
ZrO₂-S	H ₂ SO ₄	-	800
ZrO₂-N	HNO ₃	-	600
ZrO₂-N	HNO ₃	-	800
ZrO₂-C	HCl	-	800
Mg/ZrO₂-S	H ₂ SO ₄	1	600
Mg/ZrO₂-N	HNO ₃	1	600
0.1 Mg/ZrO₂-C	HCl	0.1	800
0.5 Mg/ZrO₂-C	HCl	0.5	800
1 Mg/ZrO₂-C	HCl	1	800

Characterization

The crystallinity of synthesized materials was determined by X-ray diffraction (XRD) on a Phillips PW 1710 diffractometer using $Cu K\alpha$ radiation and Ni filter operated at 30 kV and 20 mA

at room temperature. The scanning range was $2\theta=20-60^\circ$, step of 0.014° . Magnesium loading was determined by atomic absorption spectroscopy (AAS) on a Philips PU9200. Specific surface areas were determined by N_2 adsorption at 77 K in an AutoChem II 2920 (Micromeritics).

The basic and acid sites of the samples were characterized by temperature programmed desorption using 99.9% CO₂/He and 0.3% NH₃/He, respectively. TPDs were performed in a Micromeritics AutoChem II 2920 apparatus coupled to a mass spectrometer (Thermostar-QMS 200, Pfeiffer Vacuum), where the mass signals m/e⁻ 44 (basic sites) and m/e⁻ 17 (acid sites) were monitored. In addition, signals m/e⁻ 30 for the decomposition of anions NO₃⁻ and m/e⁻ 64 for the decomposition of sulphate anions SO₄⁻² were monitored. Samples (0.1 g) were pretreated in 25 mL/min flowing He (99.99%) up to 500 °C for 1 hour at 10 °C/min. Samples were then cooled to 50 °C and saturated with 50 mL/min CO₂ (basic sites) or NH₃ (acid sites) for 1 hour. CO₂ or NH₃ loosely bound to the surface were removed by flowing 50 mL/min of He for 1 hour at 10°C/min up to 900 °C. FTIR spectra of selected samples pressed in KBr pellets were collected with a Nicolet Avatar 330 spectrometer. The sulfur content of samples prepared with H₂SO₄ was determined by TGA using a 2950 TGA/HRV6 instrument where the sample was heated up to 950 °C at 10 °C/min in flowing nitrogen (100 mL/min).

Catalytic tests

Catalytic tests were performed in a tubular quartz reactor (ID 10 mm) packed with 0.5 g of catalyst sample. The products were analyzed using a mass spectrometer QMS Thermostar 200 (Pfeiffer) with a resolution of 0.01 ppm. The reaction mixture consisted of a 2:1 molar ratio of CO₂ (99.9%) and methanol-saturated helium (grade UAP). The reactions were carried out at 80, 120, 160, and 200 °C for 60 min. The reactor pressure was 720 mmHg, and the total flow was maintained about 20 mL/min.

Results and discussion

Catalyst characterization

XRD patterns of figure 1 indicate that ZrO₂-N and ZrO₂-S are crystalline. Sulfated zirconia, ZrO₂-S exhibits a tetragonal phase (diffraction peaks at 2θ = 30.5, 35.5, 50°), whereas two phases,

monoclinic (diffraction peaks 2θ = 28.5 and 31.5°) and tetragonal were identified in ZrO₂-N [14]. Magnesium-modified zirconia materials, Mg/ZrO₂-S and Mg/ZrO₂-N, were amorphous and no diffraction peaks were observed in the 2θ interval examined. This change of crystallinity has been reported by Liu et. al. [15], where MgO was incorporated on sol-gel zirconia samples. For different MgO loadings only appreciable diffraction peaks were observed at 2θ = 1°. Those materials, which are described as mesoporous, were strongly influenced by MgO incorporation. Their observations were explained in terms of the solubility of the magnesium precursor salt during the sol-gel process, specifically on hydrolysis/condensation of zirconium alkoxide and the self-assembly of the gel. Thus, excessive magnesium salt added to the system could influence or even damage the formation of the mesoporous framework. As can be observed in Figure 1, Mg/ZrO₂-S and Mg/ZrO₂-N show no XRD peaks indicating that the tetragonal structure disappeared.

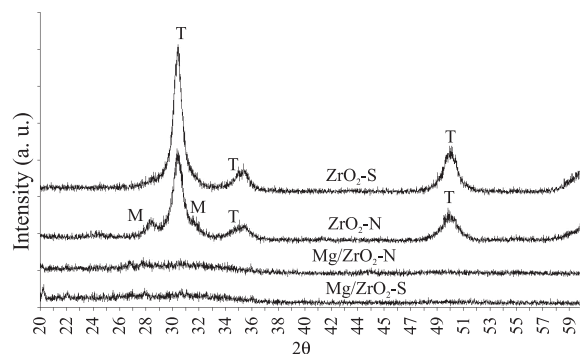


Figure 1 XRD patterns of zirconia and Mg-modified zirconia prepared by the sol-gel method. (M) monoclinic; (T) tetragonal

As shown in figure 2, ZrO₂-C synthesized using HCl as hydrolysis catalyst and calcined at 800 °C showed diffraction peaks at 2θ = 28.5 and 31.5° associated with the monoclinic phase. However, incorporation of Mg to zirconia samples prepared with HCl as hydrolysis catalyst resulted in crystalline materials with predominantly tetragonal phase. It can be noticed in figure 2

that increasing calcination temperature to 800 °C and using HCl as hydrolysis catalyst for the sol-gel synthesis of zirconia improves crystallinity of the Mg-containing materials. Jung and Bell [8] reported that either monoclinic or tetragonal zirconia, or a mixture of both, can catalyze the reaction of methanol and CO₂ to DMC. In this sense, the purpose of this study was to determine whether Mg incorporation on zirconia would improve conversion of methanol to dimethyl carbonate (DMC). ZrO₂-N samples were calcined at 800 °C to compare their crystallinity with ZrO₂-C samples (also calcined at 800 °C). XRD pattern for ZrO₂-N (calcined at 600 °C) shows the presence of both crystalline phases, monoclinic and tetragonal. The increase in the calcination temperature from 600 to 800 °C did not significantly modify the crystalline phase of ZrO₂-N samples but, the surface area decreased (see table 2).

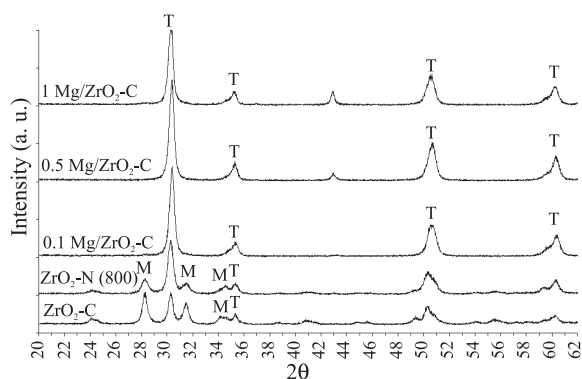


Figure 2 XRD patterns of zirconia and Mg-modified zirconia. (M) monoclinic; (T) tetragonal

Surface area and Mg content

Table 2 lists the surface area of Mg-modified zirconia materials. ZrO₂-N and ZrO₂-S have higher surface areas than their Mg-modified counterparts. The surface areas of ZrO₂-N and ZrO₂-S samples decreased when calcination temperature increased to 800 °C. In general, materials prepared with different Mg loadings showed lower surface areas than zirconia samples synthesized with nitric or sulfuric acid.

Table 2 BET surface area of synthesized materials

Sample (Calcination Temperature)	BET Surface Area ^a , (m ² /g)	Mg %
MgO	7	-
ZrO ₂ -S (600)	91	-
ZrO ₂ -S (800)	40	-
ZrO ₂ -N (600)	97	-
ZrO ₂ -N (800)	41	-
Mg/ZrO ₂ -S	17	11.7
Mg/ZrO ₂ -N	2	9.7
ZrO ₂ -C	10	-
0.1 Mg/ZrO ₂ -C	1	3.1
0.5 Mg/ZrO ₂ -C	2	8.3
1 Mg/ZrO ₂ -C	1	14.8

^a Single-point measurements of N₂ adsorption-desorption at 77 K

CO₂-TPD

The intensity and the relative strength of basic sites were examined by CO₂-TPD (figures 3 and 4). The CO₂ desorption profiles of Mg-containing materials synthesized with HNO₃ and H₂SO₄, respectively, are shown in figure 3. Peaks at 640 and 700 °C suggest the presence of strong basic sites. Furthermore, a significant enhancement of CO₂ adsorption capacity is obtained on Mg-modified zirconia. ZrO₂-N profile also revealed strong basic sites at 600 and 680 °C but CO₂ adsorption capacity was lower; ZrO₂-N shows a faint line of CO₂ desorption between 100-400 °C, a somewhat similar behavior to Mg/ZrO₂-N.

Mg/ZrO₂-N shows a signal at 580 °C for m/e⁻ 30 assigned to the decomposition of NO₃⁻ either from the Mg precursor or nitric acid. Mg/ZrO₂-S showed weak basic sites around 100 °C with very low adsorption capacity in addition to decomposition of nitrate and sulfate anions related to signals m/e⁻ 30 and m/e⁻ 64, respectively, around 580 °C. From figures 3 and 4 it can be noticed that the use of HCl during the sol-gel synthesis of zirconia

(ZrO₂-C and Mg/ZrO₂-C) affects the strength of the basic sites of the resulting material, since desorption peaks shift to lower temperatures. Moreover, CO₂ adsorption in the region between 100 °C and 200 °C increases with Mg content.

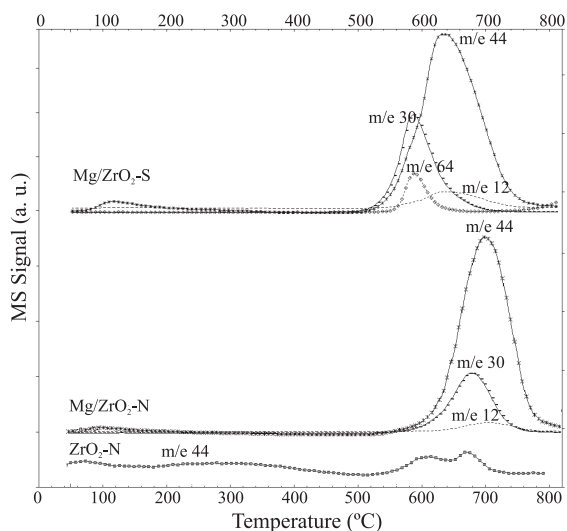


Figure 3 TPD-CO₂ profiles of materials prepared by the sol-gel method

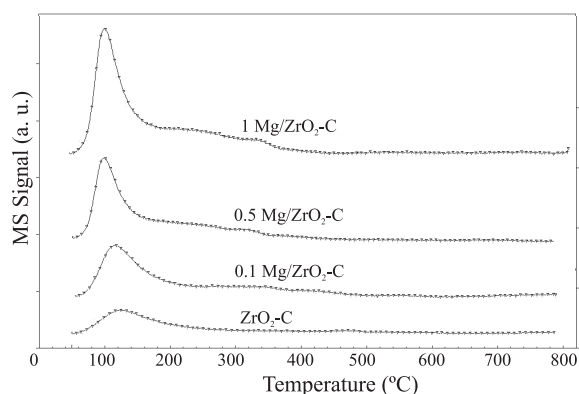


Figure 4 TPD-CO₂ profiles (m/z 44) of materials prepared by the sol-gel method using HCl as hydrolysis catalyst

NH₃-TPD

Figure 5 shows the NH₃-TPD profiles of magnesium-modified zirconia samples using HCl as hydrolysis catalyst. The NH₃-TPD profiles indicate that the acid sites of zirconia are affected

by Mg incorporation. A broad region of NH₃ desorption between 50 and 600 °C is evidenced in the trace corresponding to unmodified zirconia –indicating the presence of acid sites– whereas none of the Mg-modified materials (different Mg loadings) show NH₃ desorption signals in the temperature range examined. Since the surface area of ZrO₂-C decreased by the addition of Mg (see table 2), it may be possible that surface Mg could block NH₃ access to zirconia acid sites.

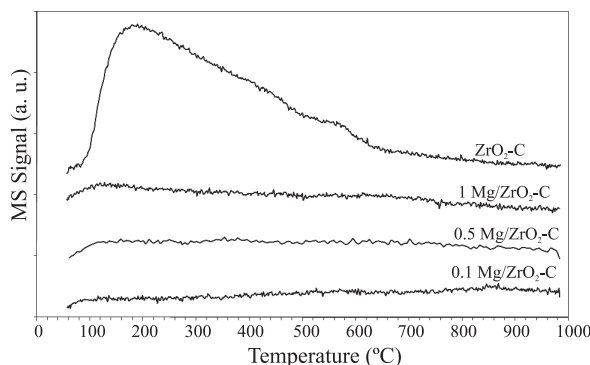


Figure 5 TPD-NH₃ profiles (m/z 17) of materials prepared by sol-gel method using HCl as hydrolysis catalyst

Thermal analysis

Figure 6 shows the TGA profile of a ZrO₂-S sample. Two major weight loss regions are identified. The first weight loss of 6.5% observed up to about 400 °C is associated with the release of physisorbed water with a minor contribution from oxidation of organic species. The second weight loss of about 5.6% is observed above 500 °C and is attributed to decomposition of surface sulfate [17].

FTIR

Figure 7 shows the FTIR spectra of samples calcined at 600 °C. ZrO₂-S and Mg/ZrO₂-S samples have a common broad band located at 1120 cm⁻¹ assigned to the presence of surface sulfate complex in a bidentate configuration [17]. Furthermore, the spectrum of ZrO₂-S shows a broad peak at 1223 cm⁻¹ typical of a bidentate

sulfate ion coordinated to a metal cation [16, 18]. ZrO_2 -N and ZrO_2 -C samples show no bands in the region from 800 cm^{-1} to 1300 cm^{-1} . Spectra for sample ZrO_2 -C showed a very intense and sharp band at 2340 cm^{-1} . This band has been assigned to CO_2 trapped inside the bulk structure of the oxide [19]. Bands between 1550 - 1556 cm^{-1} have been assigned to the stretching vibrations of Zr-O and between 1637 - 1642 cm^{-1} (observed in all samples from Fig. 7) are attributed to stretching and flexion vibration of hydroxyl from water. [16].

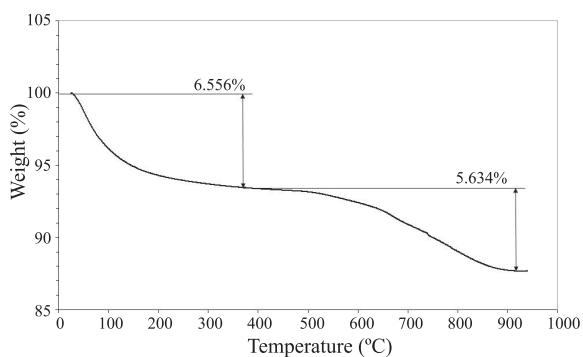


Figure 6 TGA of sample ZrO_2 -S, prepared by sol-gel method using H_2SO_4 as hydrolysis catalyst

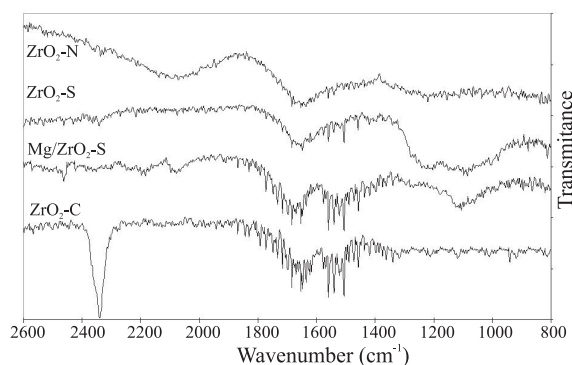


Figure 7 FTIR of samples ZrO_2 -N, ZrO_2 -S, Mg/ ZrO_2 -S and ZrO_2 -C

Catalytic experiments

Only crystalline synthesized materials which exhibited basic sites in the range of 100 - 200°C (temperature region where high DMC yields have been obtained over zirconia) were tested

as catalysts for the reaction between methanol and CO_2 . Thence, only ZrO_2 -C and Mg/ ZrO_2 -C catalysts series were used. Zirconia samples synthesized with HNO_3 or H_2SO_4 and modified with Mg were not tested because they showed no defined morphology, and high strength basic sites (CO_2 desorbed above 600°C).

Table 3 shows the concentration of DMC and the conversion of methanol (MeOH) on zirconia materials synthesized with HCl and modified with Mg. As can be observed in table 3, higher conversions are obtained over ZrO_2 -C than those obtained over Mg-modified samples. In addition, the concentration of DMC remains relatively constant in the temperature range examined. Methanol conversions, although very low ($<0.5\%$), are comparable to those reported by Tomishige et al. [17], where conversions around 0.36% were reached over commercial zirconia in a batch reaction system at considerably higher pressure (5 MPa).

The incorporation of Mg affected methanol conversion. The conversions achieved over Mg-modified materials are 50% lower than those obtained over the unmodified samples (ZrO_2 -C). In the temperature range evaluated, no methanol conversion was observed over materials containing higher magnesium loadings (0.5% Mg/ ZrO_2 -C and 1% Mg/ ZrO_2 -C). Therefore, although the addition of Mg stabilizes the tetragonal phase of zirconia and increases its CO_2 adsorption capacity in the temperature region 100 to 200°C , methanol conversion to DMC at moderate pressures is not improved.

Conclusions

The type of hydrolysis catalyst and the incorporation of Mg influence the surface area, crystallinity, basic strength, and CO_2 adsorption capacity of zirconia materials. Mg-modified zirconia exhibited higher CO_2 adsorption capacity than unmodified zirconia, regardless of the type of hydrolysis catalyst used; however, the strength of basic sites depends on the acid used for hydrolysis, i.e. the tetragonal phase of zirconia and adsorption capacity in the

range 100 to 200 °C is obtained when HCl is used. On the other hand, amorphous materials and stronger basic sites with increased CO₂ adsorption capacity at temperatures between 600 and 800 °C are obtained for those materials prepared with HNO₃ and H₂SO₄. Mg-modified zirconia exhibited

more basic sites in the temperature range where zirconia has been reported to be active for the direct synthesis of dimethyl carbonate (DMC). Nevertheless, it appears that not only basic sites but also, acid sites are required to obtain DMC from methanol and CO₂.

Table 3 Concentration of DMC and MeOH conversion over Mg modified zirconia catalysts ^a

Sample	Reaction Temperature (°C)	DMC Concentration (ppm)	MeOH Conversion (%)
ZrO ₂ -C	80	134.5	0.471
	120	118.3	0.410
	160	130.2	0.448
	200	127.9	0.441
0.1 Mg/ZrO ₂ -C	80	84.4	0.260
	120	53.6	0.196
0.5 Mg/ZrO ₂ -C	160 - 200	n.d	0
	80 - 200	n.d	0
1 Mg/ZrO ₂ -C	80 - 200	n.d	0

^a Reaction conditions: catalyst weight 0.5 g, CH₃OH/CO₂ = 2, pressure = 745 mmHg, reaction time: 60 min/at either temperature, total flow = 20 mL / min. n.d: not detected

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