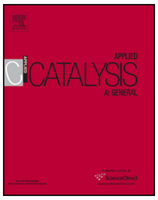
Applied Catalysis A: General xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Metal-impregnated zeolite Y as efficient catalyst for the direct carbonation of glycerol with CO_2

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ARTICLE INFO

Article history:
Received 16 September 2014
Received in revised form
25 November 2014
Accepted 3 December 2014
Available online xxx

Keywords:
Glycerol
CO_2
Glycerol carbonate
Zeolite
Metal oxide

ABSTRACT

Metal-impregnated zeolite Y catalysts were prepared by treatment of a NaY zeolite with an aqueous solution of $AgNO_3$, $Zn(NO_3)_2$ and $SnCl_2$, followed by water evaporation. The materials were then calcined in air at 450 °C and evaluated in the reaction of CO_2 with glycerol at 180 °C for 3 h at 100 Bar. The parent NaY zeolite was inactive under these conditions, but the metal-impregnated zeolites, as well as the calcined salt precursors, showed yields of glycerol carbonate up to 5.8%. The TON of the zeolite catalysts were significantly higher than that of the calcined salts, suggesting the formation of a highly active metal oxide phase at the external surface of the zeolite.

1. Introduction

The burning of fossil fuels liberates huge amounts of CO_2 in the atmosphere every day. Since the beginning of the industrial revolution, the concentration of carbon dioxide in the atmosphere has increased by about 40%, imposing the discussion of global warming and the establishment of goals for the reduction of CO_2 emissions to the society and the governments. As a consequence, CO_2 capture and storage has gained importance in the past years [1–4], with many technologies being commercially implemented. Nevertheless, the economical utilization of the captured CO_2 is still poorly exploited. Indeed, carbon dioxide can be used as feedstock for the chemical industry [5,6]. Several approaches, such as electrochemical [7–9], photochemical [10–12] and thermocatalytic [13–16] methods can be used for the production of different substances from CO_2. Organic carbonates appear as one of the main products that can be obtained from CO_2. Cyclic organic carbonates, such as ethylene and propylene carbonates can be prepared by means of the reaction of carbon dioxide with oxiranes like ethylene and propylene oxides, respectively, in the presence of different type of catalysts [17]. The use of polyfluoroalkylphosphonium iodides as catalyst presents high conversion and selectivity for propylene carbonate in the reaction of supercritical CO_2 with propylene oxide [18]. Today, the Japanese company Asahi Kazei Chemicals produces polycarbonates through this route, avoiding the emission of 1750 ton of CO_2 per 10,000 ton of polycarbonate produced [19]. Dimethyl carbonate (DMC) may also be produced by the direct carbonation of methanol with the use of metal-complex catalysts [20]. DMC has been used to produce polycarbonates and is an efficient octane booster additive [21].

Glycerol carbonate (GC) is another important product in this category. It is gaining increased applications every year. Today, it is mostly used as solvent, emulsifier and chemical intermediate. Glycerol is a by-product of biodiesel production through trans-esterification of triglycerides, with an increasing surplus in the world [22]. Therefore, there are many studies concerning the use of glycerol as a renewable feedstock for the production of different chemicals [23–25]. The preparation of GC is usually carried

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http://dx.doi.org/10.1016/j.apcata.2014.12.010
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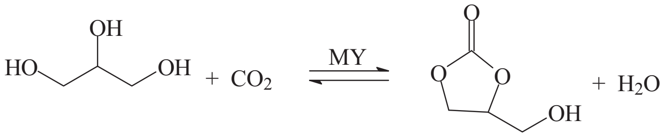

Scheme 1. Production of glycerol carbonate by reacting glycerol and CO_2 in the presence of metal-impregnated zeolite Y (MY).

out via the reaction of urea with glycerol in the presence of zinc salts [26]. The reaction can also be catalyzed by lanthanum oxide [27] or metal-impregnated zeolites as catalysts [28]. Since urea can be obtained from CO_2, this is an indirect route to obtain GC from this greenhouse gas. On the other hand, the direct carbonation of glycerol is still poorly studied. Aresta and collaborators have used [29,30] tin complexes as homogenous catalysts in the reaction of glycerol with CO_2. The yield of GC was around 5.5% at 180 °C, 50 Bar and 15 h of reaction time. Glycerol carbonate have also been prepared by the reaction of glycerol with ethylene carbonate in supercritical CO_2 and presence of 13X zeolite [31]. However, the direct reaction between CO_2 and glycerol was not observed under these conditions.

We wish to report the use of metal-impregnated zeolite Y as heterogeneous catalysts for the reaction of glycerol with CO_2 to produce glycerol carbonate (Scheme 1). There are few studies on the use of heterogeneous catalysts in this reaction, which can be easily separated from the medium and eventually reused.

2. Experimental method

A parent zeolite NaY was purchased from Zeolyst Company (CBV 100). About 10 g of the zeolite was put in contact with 200 mL of a 0.02 mol L^{-1} solution of the metal salt ($AgNO_3$ or $SnCl_2 \cdot 2H_2O$) or 200 mL of a 0.04 mol L^{-1} solution of $Zn(NO_3)_2 \cdot 6H_2O$ in deionized water. The water was then carefully evaporated in a rotary evaporator leaving a humid solid, which was dried overnight at 120 °C and further calcined in an oven at 450 °C for 3 h to obtain the metal-impregnated catalysts, which were designated AgY, ZnY and SnY, respectively. The prepared catalysts were characterized by chemical analysis, using X-ray fluorescence (XRF), and BET surface area, using nitrogen adsorption isotherm. X-ray diffraction (XRD) analyses were also carried out. X-ray photoelectron spectroscopy (XPS) was performed at Soft X-ray Spectroscopy (SXS) beamline of the Brazilian Synchrotron Laboratory. XPS spectra were recorded using monochromatized synchrotron radiation at 1840 eV and a Phoibos HSA350 analyzer with 40 eV pass energy for survey spectra and 30 eV pass energy for high resolution spectra. The binding energy (BE) was corrected considering the charge shift observed for the C 1s photopeak that was adjusted at 285 eV.

The catalysts were catalytically evaluated in a 100 mL Parr autoclave, loaded with 25.2 g of glycerol (analytical grade) and about 0.5 g of the catalysts, which were dried at 300 °C for 1 h just prior to use. The system was heated to 180 °C and pressurized with 100 Bar of CO_2, reacting at these conditions under stirring for 3 h. At the end, the pressure was relieved and about 30 mL of ethanol were introduced in the reactor to facilitate the filtration of the catalyst. The liquid phase was then concentrated in a rotary evaporator and subjected to analysis by gas chromatography coupled with a mass spectrometer.

The yield of glycerol carbonate (GC) was obtained from the analysis of the liquid phase obtained after the reaction. At the end of the reaction, about 30 mL of ethanol was added to the reaction mixture to help the separation of the catalyst by filtration. The liquid phase was then carefully concentrated by evaporating the ethanol and 0.5 g of the remaining liquid phase was diluted with ethanol in a 5.0 mL volumetric flask. Samples of this diluted solution were then injected in a GC/MS equipment (Agilent 5975) and the amount of GC was obtained using a calibration curve constructed with a standard sample of glycerol carbonate prepared according to literature procedure [26]. A mixture of glycerol and urea in the presence of $ZnSO_4$ as catalyst was heated to 150 °C for 3 h under reduced pressure. The GC was extracted from the reaction medium with dichloromethane and obtained pure by GC/MS analysis after carefully solvent evaporation.

Table 1
Chemical and textural characterization of the catalysts.

Catalyst	Si/Al ratio	Metal content (wt%)	Surface area (m^2/g)	Pore volume (mL/g)
NaY	2.4	–	760	0.320
AgY	2.4	5.9	289	0.123
ZnY	2.5	6.0	407	0.176
SnY	2.4	10.3	442	0.175

Table 2
Yield of glycerol carbonate (GC) obtained from GC/MS analysis.

Catalyst[a]	Yield of GC (%)
NaY	0.0
AgY	5.6
ZnY	5.8
SnY	5.1
$AgNO_3$	3.5
$Zn(NO_3)_2$	2.7
$SnCl_2$	2.6

[a] Calcined at 450 °C for 3 h.

3. Results and discussion

Table 1 shows the chemical and textural analysis of the catalysts. One can see that the impregnation did not affect the Si to Al ratio of the catalyst, but significantly reduced the surface area. This is consistent with deposition of metal oxide after the calcination, which may be located on the external surface of the zeolite, thereby causing partial pore blockage. The higher amount of Sn may be attributed to partial hydrolysis of the parent $SnCl_2$ salt, which was not purified before the impregnation procedure.

Table 2 depicts the yields of glycerol carbonate for all the catalysts, as well as for the precursor salts calcined at the same conditions (450 °C for 3 h). With the exception of the parent NaY, all the metal-impregnated zeolites and calcined metal salts were active in the reaction of glycerol with CO_2 to produce glycerol carbonate. The inactivity of the NaY zeolite is in agreement with literature data [31], which reported that zeolite 13X was not able to catalyze the direct carbonation of glycerol. Since the 13X zeolite is structurally similar to the NaY zeolite, differing basically on the Si/Al ratio, it would be expected that both zeolites will have the same catalytic behavior for the carbonation of glycerol. The GC yields for the zeolite catalysts were in the range of 5.5%, whereas the calcined metal salts showed yields in the range of 3.0%. A similar yield of GC was reported [29,30] with the use of tin complexes as homogeneous catalysts, but at significantly longer reaction time. The yields of GC are within the thermodynamic limit for this reaction at similar conditions [32].

Since the amount of metal in each catalyst varied, the turnover number (TON) was calculated and expressed as the amount (%) of GC formed per atom of the metal in the reaction medium. The results are presented in Fig. 1. One can see that metal-impregnated zeolites showed a significantly higher TON than the calcined metal salts, indicative of higher catalytic activity. Aiming at understanding the reason for the higher catalytic activity of the metal-exchanged zeolites XRD analysis of the catalysts, as well as of the calcined salts, were carried out. Figs. 2–4 show the XRD results

Please cite this article in press as: L.P. Ozorio, et al., Appl. Catal. A: Gen. (2014), http://dx.doi.org/10.1016/j.apcata.2014.12.010