



Influence of the synthesis method of Cu/Y zeolite catalysts for the gas phase oxidative carbonylation of methanol to dimethyl carbonate

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ABSTRACT

Dimethyl carbonate is an environmentally friendly molecule with increasing applications as reactant, solvent, and fuel additive. Oxidative carbonylation of methanol, with reactants in the gas phase and catalyzed by copper-exchanged Y zeolites, is a promising alternative route for dimethyl carbonate production. This work is focused on the improvement of the catalyst formulation and preparation methods. Catalysts were prepared using two methodologies: solid-state ion exchange and liquid-ethanol ion exchange. Five different copper salts were used as precursors and the NH_4^+ and Na^+ forms of the Y zeolite as supports. The Na^+ form of the Y zeolite removed the Brønsted acidity of the support and, therefore, the reaction rate of acid-catalyzed undesired dehydration and decomposition reactions was reduced. The use of copper chloride salts as precursors was crucial to obtain suitable catalysts for dimethyl carbonate formation. Among all the tested catalysts, those prepared using CuCl_2 precursor and the Na-Y zeolite by the liquid-ethanol ion exchange method showed the best performance (0.72 $\text{mol}_{\text{DMC}}/\text{mol}_{\text{Cu}} \text{ h}$). This catalyst exhibited the highest surface chloride content and Lewis acidity.

1. Introduction

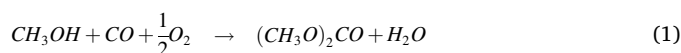
Dimethyl carbonate (DMC) is a versatile environmentally friendly molecule that can be used in carbonylation and methylation reactions, replacing other toxic compounds, such as methyl halides, phosgene, or dimethyl sulfate. The use of DMC in these reactions replaces a toxic reactant and prevents the formation of undesirable byproducts [1–3].

One of the most interesting applications of DMC can be as a fuel additive to substitute methyl tert-butyl ether (MTBE). Its non-toxicity, high octane number (116), high oxygen content, and low carbon-to-oxygen ratio make DMC a good alternative [4–6].

Phosgene methanolysis was the synthesis route of DMC until the 1980s [7,8]. Nowadays, the most important industrial processes are the Enichem process, based on the oxidative carbonylation of liquid methanol in a slurry reactor with copper (I) chloride, and the UBE process, based on the use of methyl nitrite as an intermediate [9–12]. However, these phosgene-free routes suffer from safety drawbacks, such as the use of multi-phase reactors with highly exothermic reactions, the formation of toxic intermediates, corrosive byproducts, catalyst deactivation and leaching, etc. [13–15].

There is an increasing interest in developing a methanol oxidative

carbonylation process with all the reactants in the gas phase and catalyzed by heterogeneous catalysts [16]. Such a process would solve many of the limitations of the actual liquid-phase process.



The heterogeneous catalysts proposed for this reaction consist of copper active phase and a support (active carbon, zeolites, etc.). One of the first studied catalysts was CuCl_2 supported on active carbon with optimum copper contents from 5 to 10 wt%. Also, bimetallic CuCl_2 and PdCl_2 supported on active carbon have been considered. The main drawback of these catalysts was catalyst deactivation, due to chloride losses [4].

Copper exchanged zeolites were proposed as chloride-free catalyst, creating active sites suitable for the oxidative carbonylation reaction [17] and providing higher stability than other supports, like active carbons [18,19]. Zeolite-based catalysts present high stability, low copper leaching, and little reactivity of CO to CO_2 [17]. Different types of zeolites have been considered as support: mordenite, ZSM-5, X, and Y zeolites [20–23]. The features of the active sites involved in the reaction and the reaction mechanism are still under discussion by several authors [24–26]. The most accepted active site for this reaction is Cu(I)

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exchanged on the zeolite structure, where a methoxy intermediate species can be stabilized [4,17,21]. This intermediate is generated by reaction between adsorbed methanol and oxygen. Then, carbon monoxide inserts on the methoxy species to form carbomethoxyde, which finally reacts to generate DMC [24,26].

At low temperatures, DMC is the main product of the reaction. However, dimethoxymethane (DMM), dimethyl ether (DME), and methyl formate (MF) can also be formed as byproducts, due to side methanol dehydration reactions taking place in the zeolite acid sites [27]. In previous works, it has been found that a small amount of DMC decomposes to DME and CO₂, even at 120 °C. The decomposition rate increases with temperature and, by 200 °C, all formed DMC decomposed to DME [28]. The structure and chemical properties of the zeolites have a large influence on the activity and selectivity of this reaction and the Y zeolite showed the best yield among other zeolite supports [23].

The type of catalyst preparation method and copper precursor have not been optimized for this reaction yet. The exchange of the zeolite in aqueous phase using copper (II) nitrate or acetate produces inactive catalysts for DMC synthesis. As a result, a high temperature activation step is needed to transform copper (II) into copper (I). The copper loading of the zeolite is limited in aqueous phase, due to the formation of hydrated copper species that suffer from steric limitations inside the zeolite channels [4]. Different approaches have been proposed to deal with this issue: the modification of the zeolite pore structure to facilitate the exchange [29,30], the assistance of the exchange by ultrasonication [31], the combination of different types of exchange methods [32], or the optimization of the activation conditions (limited by the thermal stability of the zeolites) [33–35].

The solid-state ion exchange method was proposed as an alternative to aqueous-phase exchange methods for salt precursors with low solubility, like copper (I) chloride. In this method, the exchange takes place at 650 °C between the zeolite and a vapor of the copper salt used as precursor [4]. Copper (I) chloride exchanged on Y zeolite was the first catalyst prepared by this method found active for DMC synthesis [17] and the most studied in the literature of the field [4,21,23,24]. This type of exchange preserves copper (I) active species from being oxidized to copper (II) [4]. Also precursors based on copper (II) have been proposed, such as, copper (II) chloride [36,37] and copper (II) acetylacetonate [38,39]. Copper in these precursors is auto-reduced to copper (I) during the high temperature exchange [36,37].

The solid-state ion exchange can produce incompletely exchanged zeolites and it is a preparation method difficult to scale-up. To overcome these issues, the present work proposes, for the first time for the DMC synthesis reaction, an alternative preparation method, based on the exchange in liquid ethanol. This method has been successfully used for the preparation of Cu-zeolite adsorbents [40]. The use of ethanol solvent eliminates the formation of hydrated copper species that make the exchange less effective. Also, other copper precursors can be used, like Cu₂O, soluble in ethanol, but insoluble in water and with high volatilization temperatures.

The scope of this work is to compare the solid-state and liquid ethanol ion exchange methods to prepare catalysts for DMC synthesis reaction. The NH₄⁺ and Na⁺ forms of the Y zeolite support and a set of copper precursors (copper (I) acetate, copper (II) nitrate, copper (I) chloride, copper (II) chloride and copper (I) oxide), have been considered to make the comparison of the preparation methods at different levels. A total of 14 catalysts were prepared and, then, characterized using textural (N₂ adsorption, SEM) and chemical techniques (ICP-MS, FTIR, XRD, XPS, SEM-EDX). The performance towards DMC synthesis reaction, measured in terms of activity and product selectivity, was studied in a fixed-bed reactor.

2. Materials and methods

2.1. Chemical reagents

The zeolite used as support for the preparation of all the catalysts was the Y zeolite in its ammoniac form with a Si/Al ratio of 12, supplied by Zeolyst International (CBV 712).

The gases used as reactants and for the analysis by gas chromatography were provided by Air Liquide: N₂ (Alphagaz 1), O₂ (Alphagaz 1), He (Alphagaz 1), air (Alphagaz 1), CO (>99 %) and dimethyl ether (>99.9 %). Other compounds used as reactants or to calibrate the analysis equipment were methanol (VWR, AnalaR NORMAPUR >99.8 %), ethanol (GPR Rectatur, VWR), methyl formate (Sigma Aldrich, reagent grade 97 %), dimethoxymethane (Sigma Aldrich, reagent plus >99 %) and dimethyl carbonate (Sigma Aldrich, anhydrous >99 %).

2.2. Catalyst preparation

The optimization of the catalyst preparation has been done by the study of three factors: the ion form of the zeolite support, the copper precursor, and the ion exchange method.

2.2.1. Zeolite ion form

The zeolite was supplied in its ammoniac form. To study the influence of a support of lower acidity, the NH₄-Y zeolite was subjected to ion exchange to produce the Na-Y zeolite form. The procedure was carried out with an aqueous solution of 0.2 M of Na₂CO₃ (≥99.5 %, Sigma Aldrich) (50 mL of solution was used by every gram of zeolite), stirring at room temperature for 16 h; then, the zeolite was filtered and washed with distilled water. This procedure was repeated for three times [41].

2.2.2. Copper precursor

A total of five copper precursors were used to prepare the exchanged zeolites: copper (I) chloride (97 %, Alfa Aesar), copper (II) chloride dihydrate (ACS reagent, ≥99 %, Sigma Aldrich), copper (I) acetate (97 %, Sigma Aldrich), copper (II) nitrate trihydrate (≥99 %, Sigma Aldrich) and copper (I) oxide (≥99.99 % anhydrous, Sigma Aldrich).

2.2.3. Ion exchange methods

The *solid-state ion exchange* (SSIE) method takes place by volatilization of the copper precursor at high temperatures. The zeolite and copper precursor solids were mixed finely; the ratio was adjusted to obtain a theoretical copper loading of 16 wt%. This mixture was loaded inside a stainless steel tube, which was heated at 7 °C/min up to 650 °C for 20 h in a stream of He [17]. During this process, the copper of the precursor volatilized, and the vapor was exchanged with the zeolite. Since copper (I) oxide has an extremely high melting point (1235 °C), this precursor was not used with this preparation method. After cooling, the catalyst was recovered from the tube, pelletized, and sieved to a particle size of 0.100–0.355 mm.

The *liquid ion exchange on ethanol* (ET) solvent allows the catalyst preparation with copper precursors that are insoluble in water but with a good solubility in ethanol, like copper (I) oxide. However, copper (I) chloride cannot be used as a precursor with this method, due to its extremely low solubility, both in water and ethanol. The procedure involved the mixing of the zeolite in the copper solution of the precursor (10 mL of solution for every gram of zeolite), and stirring at 60 °C for 6 h. The concentration of the precursor in the solution was selected to obtain a theoretical copper loading of 5 wt%. Then, ethanol was removed using a rotatory evaporator and the remaining solid was dried overnight [42]. The exchange procedure was repeated twice and, finally, the catalyst was calcined at 550 °C for 4 h (temperature ramp of 1.8 °C/min).

The prepared catalysts were denoted as: precursor-zeolite form (preparation method). For instance, NitCu-Na-Y (ET) means that copper (II) nitrate was exchanged on the Na-Y zeolite by the ethanol ion

Table 1
Summary of the characterization of zeolite supports and prepared catalysts.

Catalyst	Preparation procedure ^a	Zeolite form	Copper precursor	Cu loading (wt %)	BET surface (m ² /g)	Micropore vol. (cm ³ /g)	Mesopore vol. (cm ³ /g)	Brønsted acidity (mmol/g)	Lewis acidity (mmol/g)
NH ₄ -Y	-	NH ₄ ⁺	-	-	694	0.26	0.16	0.22	0.17
Na-Y	-	Na ⁺	-	-	387	0.20	0.06	0	0.34
AcCu-Y (SSIE)	SSIE	NH ₄ ⁺	CuCOOCH ₃	15.1	492	0.19	0.13	0.03	0.22
NitCu-Y (SSIE)	SSIE	NH ₄ ⁺	Cu(NO ₃) ₂	15.8	413	0.16	0.10	0.02	0.37
CuCl-Y (SSIE)	SSIE	NH ₄ ⁺	CuCl	5.7	563	0.20	0.15	0	0.43
CuCl ₂ -Y (SSIE)	SSIE	NH ₄ ⁺	CuCl ₂	5.3	609	0.23	0.16	0	0.15
CuCl-Na-Y (SSIE)	SSIE	Na ⁺	CuCl	4.2	337	0.17	0.06	0	0.23
CuCl ₂ -Na-Y (SSIE)	SSIE	Na ⁺	CuCl ₂	4.4	317	0.17	0.06	0	0.13
AcCu-Y (ET)	ET	NH ₄ ⁺	CuCOO ₂ CH ₃	4.8	571	0.28	0.06	0.05	0.59
NitCu-Y (ET)	ET	NH ₄ ⁺	Cu(NO ₃) ₂	4.8	578	0.28	0.05	0.02	0.58
Cu ₂ O-Y (ET)	ET	NH ₄ ⁺	Cu ₂ O	4.5	586	0.28	0.05	0.09	0.35
CuCl ₂ -Y (ET)	ET	NH ₄ ⁺	CuCl ₂	4.6	568	0.29	0.03	0.08	0.22
AcCu-Na-Y (ET)	ET	Na ⁺	CuCOOCH ₃	4.0	533	0.20	0.16	0	0.05
NitCu-Na-Y (ET)	ET	Na ⁺	Cu(NO ₃) ₂	4.9	413	0.16	0.14	0	0.13
Cu ₂ O-Na-Y (ET)	ET	Na ⁺	Cu ₂ O	5.0	443	0.18	0.14	0	0.29
CuCl ₂ -Na-Y (ET)	ET	Na ⁺	CuCl ₂	5.3	404	0.13	0.20	0	0.65

^aSSIE refers to the Solid-State Ion Exchange procedure and ET to the liquid ion exchange in ethanol solvent. ^bConcentration of Brønsted acid sites per gram of catalyst at 150 °C. ^cConcentration of Lewis acid sites per gram of catalyst at 150 °C.

exchange method.

2.3. Catalyst characterization

The textural properties of the prepared catalysts were determined by nitrogen adsorption-desorption isotherms measured on a Micromeritics ASAP 2020 Plus. Physisorption data were processed using Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH) and Dubinin-Radushkevich (DR) approaches for determining surface area, total mesopores and micropores volume, respectively.

The copper content of the catalysts was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on a Thermo Scientific Neptune plus device. Prior to their analysis, the samples were digested in aqua regia and microwaved.

Pyridine adsorption on the catalysts followed by Fourier-Transform Infrared (FTIR) spectroscopy was used to quantify Brønsted (BAS) and Lewis acid sites (LAS) in a house-made system. Pyridine was introduced into the catalysts for its adsorption at 150 °C for 20 min and, then, the strength of the acid centers was determined at different temperatures by their specific FTIR bands in the 4000–400 cm⁻¹ range. The integrated molar extinction coefficients used for the concentration quantification were 1.67 cm² μmol⁻¹ for the 1545 cm⁻¹ band, characteristic of pyridine on a Brønsted acid site, and 2.22 cm² μmol⁻¹ for the 1455 cm⁻¹ band of pyridine on a Lewis acid site [43].

The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) using a SPECS system equipped with a Hemispherical Phoibos detector. A Philips FEI SX30 FEG Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-Ray (EDX) analysis was used to obtain images of the catalyst surface and analyze the surface composition.

The crystallographic structure was determined by X-ray diffraction (XRD) using a Philips PW 3040/00 X'Pert MPD/MRD diffractometer in a radiation scanning 2θ range between 5° and 90°.

2.4. Reaction tests

The catalyst activity and selectivity of the oxidative carbonylation reaction were tested in a continuous fixed-bed reactor. The stainless-steel tube, with a diameter of 6.8 mm, was loaded with 2 g of catalyst

(particle size 0.100–0.355 mm, bed length of 72 mm). The geometry of the bed and catalyst particles were selected to ensure that axial dispersion and wall channeling were negligible [44]. The reactor tube was surrounded by an electrical oven, equipped with a feedback controller, and temperature was measured inside the tube closed to the catalytic bed. The upper part of the tube was filled with 1 mm glass spheres to heat the feed upstream of the catalytic bed [28].

The reactor feed was obtained by mixing in adequate proportions the gas reactants (CO and O₂) with N₂ carrier, if necessary. The flow rate of the gas cylinders was set using mass flow controllers (BRONKHORST). The liquid reactants were introduced using a syringe pump and mixed with the gas feed. Vaporization of the liquid was ensured with the help of heating tape, maintained at 120 °C. The pressure was 1 atm for all the tests. The total flow rate was set to 155 mL/min (measured at normal conditions), which corresponds to a space velocity WHSV = 208 mol/h kg_{cat}⁻¹.

The reactor outlet was analyzed using an online gas chromatograph (AGILENT HP-6890 N), equipped with two columns: a HP Plot Q and a HP MoleSieve 5 A (to separate CO, O₂, and N₂). Two detectors were used and placed in series: a thermal conductivity detector (TCD) and a flame ionization detector (FID).

The following three types of experiments were carried out:

2.4.1. Oxidative carbonylation tests

The tests were done at 120°C with a feed concentration (in mole %) of 9 % O₂, 16 % methanol, and 75 % CO. According to previous works [28], these conditions are optimum to maximize DMC yield and reduce the side and decomposition reactions. In all the tests, methanol conversion was below 10 %, which means that the reaction rate can be easily determined using the differential fixed-bed reactor model (i.e., concentration and reaction rate is the same for all the catalyst particles):

$$r_i = \frac{dF_i}{dW} \approx \frac{F_i - F_{i0}}{W} = \text{WHSV}(y_i - y_{i0}) \quad (2)$$

In this expression, r_i is the reaction rate of compound i per weight of catalyst, F_i is the molar flow rate, y_i is the molar fraction, W is the weight of catalyst and WHSV is the space velocity. The reaction rate of the different catalysts has been normalized using the corresponding copper loadings, reaction rate per mol of Cu = r_i (63.5/% wt. Cu).

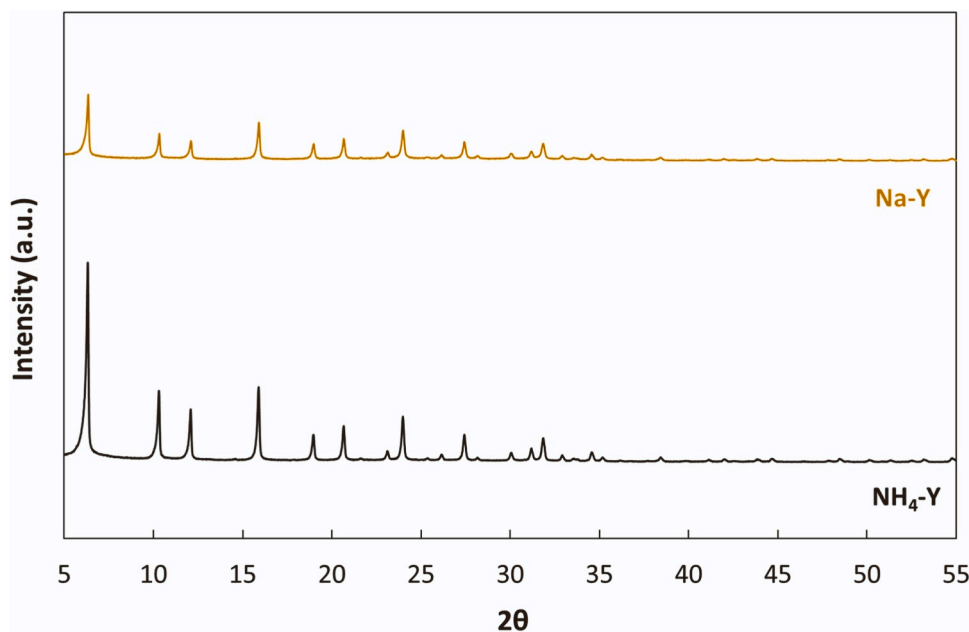


Fig. 1. XRD diffractograms for the NH_4^+ and Na^+ forms of the Y zeolite used to prepare the catalysts.

The reproducibility of the reaction tests was measured using two batches of the same catalyst prepared independently. Deviations in methanol conversion of ca. 7 % were reported for catalysts prepared by the SSIE method.

2.4.2. DMC decomposition tests

One undesired reaction is the decomposition of DMC to DME and CO_2 , which is known to occur at high temperature catalyzed by the acid sites of the zeolite. This side reaction has been studied by replacing methanol by DMC in the reactor feed (in mole %): 1.5 % DMC, 9 % O_2 , 42 % CO and 47.5 % N_2 . The reaction temperature was set at 120°C.

2.4.3. Methanol dehydration tests

It is well known that methanol dehydration to DME is catalyzed by acid catalysts, like Y zeolites [45]. To study the importance of this side reaction at the conditions of the oxidative carbonylation of methanol, tests with a reactor feed made of 16 % (mole) methanol in N_2 carrier were conducted at 120°C.

3. Results and discussion

3.1. Properties and reactivity of the Y zeolite

The Y zeolite is commercially available in the NH_4^+ form, presenting a Brønsted acidity of 0.22 mmol/g and a Lewis acidity of 0.17 mmol/g. As explained in Section 2.2.1, the Na^+ form was obtained by ion exchange with a Na_2CO_3 solution, which removed all Brønsted acidity and Lewis acidity raised to 0.34 mmol/g. The basic characterization data of these supports are summarized in Table 1. It can be observed that the Na^+ form of the zeolite presents a significantly lower BET surface area and mesoporous volume than the NH_4^+ form (44 % and 63 % lower, respectively), while the micropore volume is slightly higher. Overall, the total pore volume decreased from 0.42 cm^3/g of the NH_4^+ form to 0.35 cm^3/g of the Na^+ form. XRD patterns in Fig. 1 show that the Na-Y zeolite presents 50 % lower crystallinity than the $\text{NH}_4\text{-Y}$ zeolite.

The treatment of the Y zeolite with Na_2CO_3 to neutralize Brønsted acid sites caused a partial collapse of the cage structure of the zeolite, as evidence by the decrease in crystallinity, BET surface area and pore volume. The influence of alkali treatment on Y zeolites has been studied by Yan et al. [30]. They found that partial destruction of the zeolite

structured can favor the access of Cu during the exchange, leading to more active catalysts for DMC synthesis.

The performance at reaction conditions of the unloaded $\text{NH}_4\text{-Y}$ and Na-Y zeolites was studied with a feed mixture of CO , O_2 , and methanol, as described in Section 2.4.1. At 120°C, the $\text{NH}_4\text{-Y}$ zeolite exhibited a methanol conversion of 0.66 % with DME being the only detected reaction product, whereas the Na-Y zeolite did not catalyze any reaction. The test was repeated at 150°C, resulting in an increase of methanol conversion to 5.7 % for the $\text{NH}_4\text{-Y}$ zeolite and again not observing any reaction for the Na-Y zeolite. Methanol dehydration to DME was catalyzed by the strong Brønsted acid sites of the $\text{NH}_4\text{-Y}$ zeolite. However, in the Na-Y zeolite, all the Brønsted acid sites were removed, and the remaining weaker Lewis acid sites were not able to catalyze this reaction (at least, within the considered temperature range 120–150°C).

The activity of the unloaded zeolites towards DMC decomposition was also tested, as described in Section 2.4.2. The $\text{NH}_4\text{-Y}$ zeolite was found to be very active at 120°C, since all the fed DMC decomposed to DME and CO_2 , attributed to the presence of strong Brønsted acid sites (0.22 mmol/g) [4]. On the contrary, DMC conversion of the Na-Y zeolite was only 3.5 % at 120°C. This suggests that the weaker Lewis acid sites of the Na-Y zeolite (0.34 mmol/g) are still able to catalyze DMC decomposition to DME and CO_2 , but at lower rate than the Brønsted acid sites of the $\text{NH}_4\text{-Y}$ zeolite [41].

These preliminary tests have shown the need to eliminate Brønsted acid sites from the Y zeolites to limit the extent of undesired side reactions. This can be accomplished by a complete exchange with Cu on the $\text{NH}_4\text{-Y}$ zeolite, eliminating any residual Brønsted acidity on the prepared catalysts or, otherwise, by doing an exchange with alkali (e.g., Na or Li) before or after the exchange with copper [4,41].

3.2. Solid state ion exchange method (SSIE)

The solid-state ion exchange (SSIE) method was used to prepare the catalysts with the copper precursors and zeolite forms indicated in Table 1. Though the theoretical copper loading was set to 16 wt% for all the precursors, the final copper loading (measured by ICP-MS) was quite different for the catalysts prepared by the SSIE method (Table 1). The catalysts prepared with acetate and nitrate salt precursors had a copper loading of 15.1 and 15.8 wt%, respectively, very close to the theoretical loading. On the contrary, for chloride salt precursors, the final copper

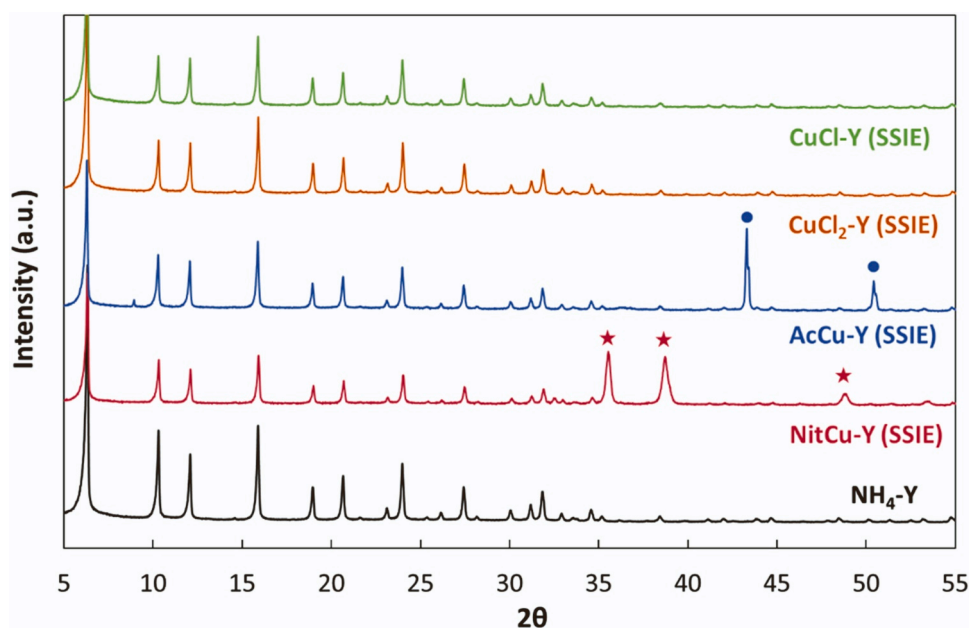


Fig. 2. XRD diffractograms for the catalysts prepared by the solid state ion exchange method. Identified peaks related to CuO (★) and Cu⁰ (●).

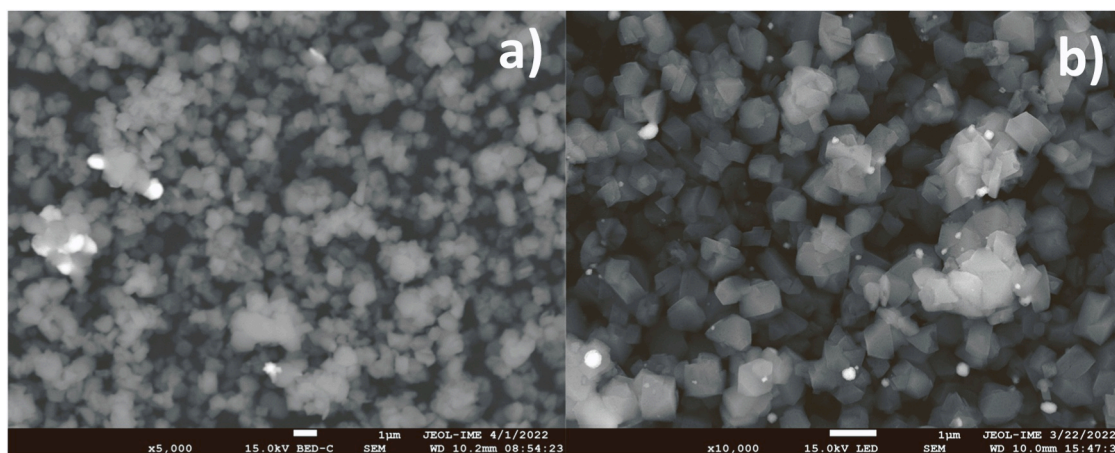


Fig. 3. SEM images of NitCu-Y zeolite (a) and AcCu-Y zeolite (b) catalysts prepared by the solid-state ion exchange method.

loading was in the range 4–6 wt%, which means that most volatilized copper was vented with the He sweep gas during the preparation method. These loadings are similar or slightly lower than those reported in the literature [17].

The XRD diffractograms of Fig. 2 show that the crystallinity of the catalysts prepared using nitrate and acetate salt precursors is much lower and several additional peaks appeared. According to the bibliography, the peaks observed at 35, 39 and 49° on NitCu-Y (SSIE) are related to CuO [46] and peaks at 43 and 51° on AcCu-Y (SSIE) to elemental copper [47]. The formation of elemental copper and copper oxide on the external surface of the zeolite also explains the observed decrease in micropore and mesopore volumes for these catalysts (Table 1). The micrographs obtained by SEM (Fig. 3) for NitCu-Y (SSIE) and AcCu-Y (SSIE) show the presence of large particles of high density distributed all over their surface. EDX analysis identified copper on these particles.

The activity towards the oxidative carbonylation of methanol of the prepared catalysts was also measured. For the of NitCu-Y (SSIE) and AcCu-Y (SSIE) catalysts, no DMC was produced and only small amounts of DME and DMM were detected. Methanol conversion was 0.51 % (39 % DME selectivity) and 0.65 % (18 % DME selectivity), respectively, for

NitCu-Y (SSIE) and AcCu-Y (SSIE) catalysts (Fig. 4a). According to these findings, it can be concluded that nitrate and acetate precursors are not adequate for the preparation of the catalyst using the SSIE method.

Copper chloride salt precursors (CuCl and CuCl₂) were used in the preparation of the catalysts using NH₄ and Na-Y zeolite supports. As shown in Table 1, the final copper loading of these catalysts was in the range 4–6 wt%. The XRD diffractograms of Fig. 2 do not show the appearance of the phases and Brønsted acidity of the catalysts prepared with the NH₄-Y zeolite dropped to zero, which suggests a complete exchange of the zeolite. The use of Na-Y zeolites resulted in a lower copper loading. This can be attributed to the lower surface area and pore volume of this support and the larger size of Na (ionic radius of 0.180 nm for Na, 0.143 nm for NH₄⁺, and 0.145 nm for Cu), which makes the exchange more difficult. The SSIE preparation method had little impact on the textural properties of the catalyst with respect to the corresponding bare support, surface area, micropore, and mesopore volumes being only slightly lower [48].

Reaction experiments for this set of catalysts are summarized in Fig. 4. The oxidative carbonylation tests showed a similar yield to DMC for both chloride salt precursors (CuCl and CuCl₂), when prepared using the same zeolite form. Thus, when CuCl₂ is used as precursor in the SSIE

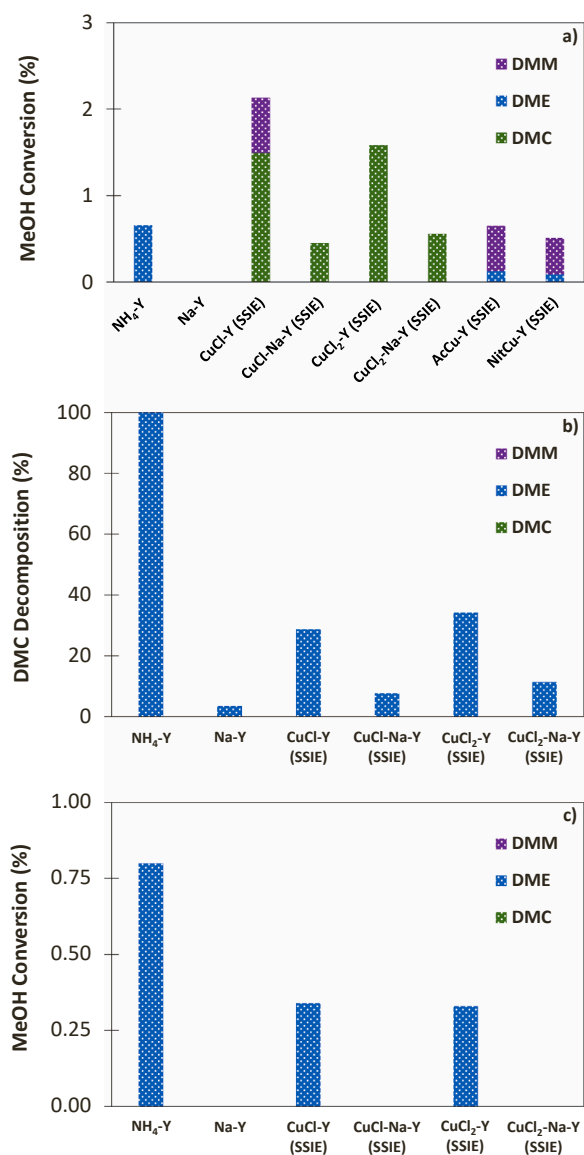


Fig. 4. Reaction results for the unsupported zeolites and the catalysts prepared via solid-state ion exchange (SSIE). WHSV = 208 mol/h kg_{cat}. a). Oxidative carbonylation tests (16 % methanol, 9 % O₂, 75 % CO) at 120°C. b). DMC decomposition tests (1.5 % DMC, 9 % O₂, 42 % CO, 47.5 % N₂) at 120°C. c). Methanol dehydration tests (16 % methanol, 84 % N₂) at 150°C.

preparation method, the salt decomposes into CuCl + Cl₂ at 350–500°C and, then, volatilized CuCl is exchanged with the zeolite. A temperature of 650°C is needed to maximize the exchange of copper and the sublimation of CuCl [36]. The textural properties of the catalysts prepared with both copper precursors are similar. However, Lewis acidity of the catalyst prepared with CuCl₂ was considerably lower (0.15 and 0.43 mmol/g, respectively, for CuCl₂-Y and CuCl-Y).

The only reaction product was DMC, except for the CuCl-Y (SSIE) catalyst that also generated dimethoxy methane (DMM) with a selectivity of 30 % (Fig. 4a). According to the literature [28,49], DMM by-product is formed in the presence of extra-framework CuO_x when adsorbed methoxide is oxidized to formaldehyde; then, formaldehyde and methanol react on the acid sites of the zeolite to generate DMM. Hence, an important selectivity towards DMM is indicative of presence of CuO_x species on the CuCl-Y (SSIE) catalyst [49]. Conversely, the CuCl₂-Y (SSIE) catalyst did not catalyze the formation of any by-products and DMC yield was actually higher than that of CuCl-Y (SSIE) catalyst.

The rate of reaction of the catalysts prepared using the Na-Y zeolite was lower than those prepared using the NH₄-Y zeolite, though selectivity to DMC was 100 %. This agrees with the lower copper loading of these catalysts and, also the lower surface area and pore volume caused by the previous exchange with Na.

According to the literature, the copper species most active in DMC synthesis reaction is copper (I) exchanged in the zeolite framework [4, 17]. The use of copper acetate and nitrate as precursors in the SSIE preparation method resulted in CuO_x extra-framework copper species, as evidenced in the XRD diffractograms and SEM images. These species were not active towards DMC, but they catalyzed the oxidation of the methoxy intermediates to formaldehyde, which further reacts to DMM [26,49]. Conversely, the use of copper chloride precursors led to the formation of copper (I) species on the structure of the zeolite able to generate the methoxide intermediate when methanol adsorbs [21,24]. Either copper (I) or copper (II) chloride precursors produced active catalysts, given that copper (II) chloride is decomposed into copper (I) chloride during the exchange at high temperature [36,37].

The catalysts were also tested for DMC decomposition to DME and CO₂. As discussed in Section 3.1, DMC decomposition can be catalyzed by the acid sites of the bare zeolite [41]. After the exchange of Cu on the NH₄-Y zeolite, Brønsted acid sites were removed and the activity dropped considerably, as observed in Fig. 4b. The activity of the catalysts prepared with Na-Y zeolites increased a bit with respect to the bare support. This can be due to the adsorption of DMC on Cu, making DMC more reactive in adjacent acid sites. The catalysts prepared using the Na-Y zeolite exhibited considerably lower decomposition rate. Thus, for the same copper precursor, the use of Na-Y zeolite for the preparation of the catalysts resulted in lower Lewis acidity, which explains the lower observed reaction rate towards DMC decomposition.

The presence of parallel reactions responsible for methanol consumption by dehydration to DME was also evaluated. The tests at 120°C do not yield any reaction product, suggesting that DME generation in the oxidative carbonylation tests is caused by DMC decomposition. A further increase in temperature to 150°C resulted in DME formation as the only product, with methanol conversions of 0.34 % and 0.32 %, respectively, for CuCl-Y (SSIE) and CuCl₂-Y (SSIE) catalysts. The conversion was lower than that of unsupported NH₄-Y zeolite, which may be explained by the elimination of Brønsted acidity after the exchange with copper. The catalysts prepared using the Na-Y zeolite did not produce any DME at any of the tested temperatures.

The use of Na-Y zeolites as support resulted in lower activity towards DMC, but undesired reactions were eliminated or considerably reduced.

3.3. Liquid ethanol ion exchange method (ET)

The liquid ion exchange in ethanol solvent was proposed to overcome the limitations caused by hydrated copper species formed in water solution. The catalysts were prepared by this method using all the copper precursors as for the SSIE method previously tested, except the insoluble CuCl that was replaced by Cu₂O. Both the NH₄ and Na-Y zeolite forms were used as supports. Eight catalysts were prepared following this procedure.

This preparation method resulted in very similar copper loadings for all the catalysts, close to 5 wt% (Table 1). Regarding the textural properties, the catalysts based on the NH₄-Y zeolite suffered a decrease in the BET surface area and micropore volume, but this decrease was particularly important for the mesopore volume, with reductions of up to 80 %. On the other hand, the catalysts based on Na-Y zeolites showed an increase in BET surface area and mesopore volume with respect to the bare support, while the micropore volume suffered a small reduction. The decrease in the micropore volume may indicate a deterioration of the zeolite framework caused by the introduction of copper, which was confirmed by the XRD diffractograms of Fig. 5b. NiCu-Na-Y (ET) and CuCl₂-Na-Y (ET) are the catalysts with the lower micropore volume and the ones showing a stronger crystallinity reduction in their XRD

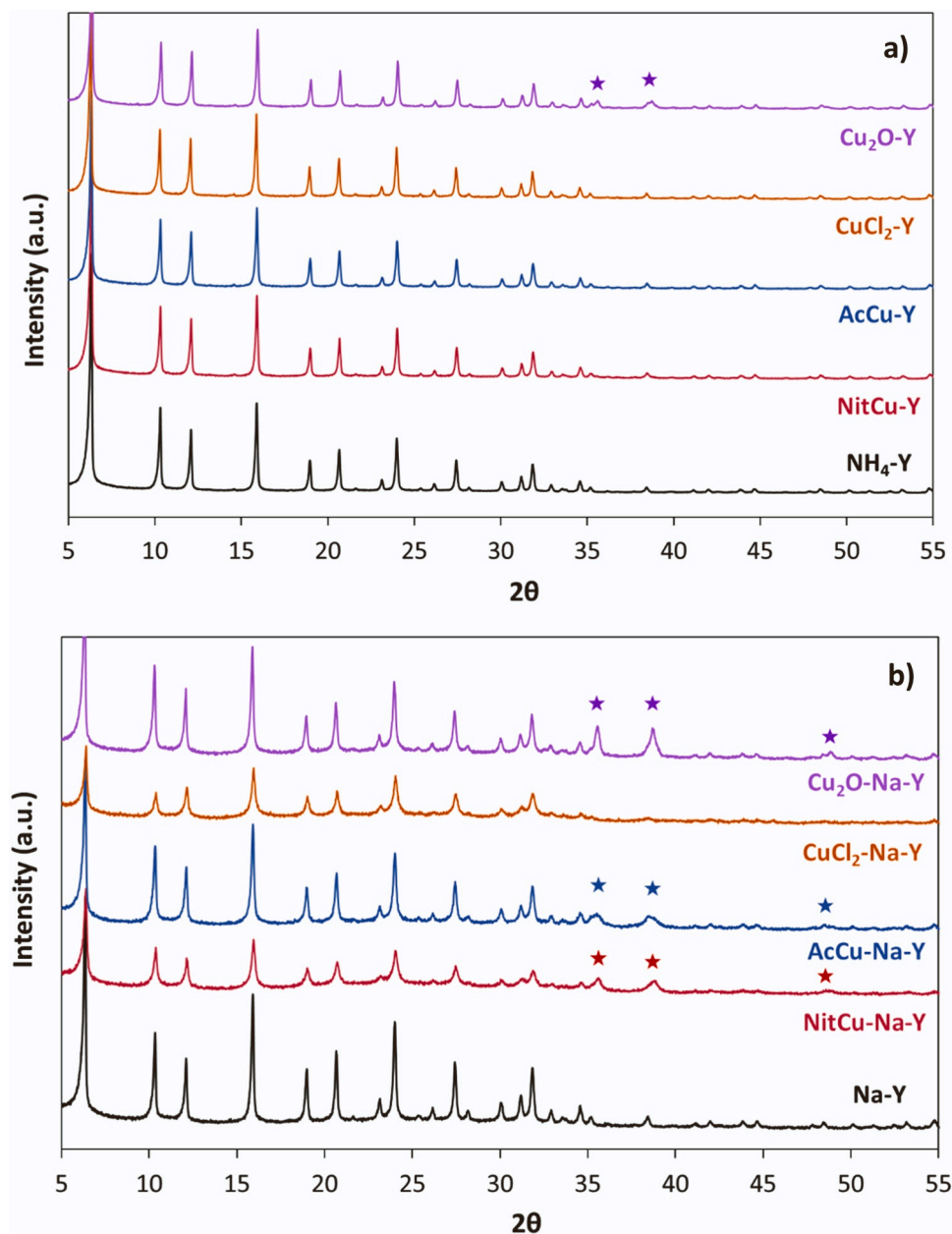


Fig. 5. XRD diffractograms for the catalysts prepared by the liquid ion exchange in ethanol using the $\text{NH}_4\text{-Y}$ zeolite (a) and Na-Y zeolite (b). Identified peaks related to CuO (★).

diffractograms.

The catalysts prepared using Cu_2O precursor showed new peaks in their XRD diffractograms. In Fig. 5a, a small broadening and disturbance of the peaks around Bragg's angles of 35° and 39° , related to the presence of CuO , can be observed for $\text{Cu}_2\text{O-Y}$ (ET). These peaks are more clearly observed in $\text{Cu}_2\text{O-Na-Y}$ (ET) catalyst in Fig. 5b. The presence of Na^+ on the zeolite framework probably makes the ion exchange more difficult and promote the formation of copper oxide particles on the surface. The presence of this kind of particles is confirmed by the micrographs obtained with SEM, as Fig. 6d shows the presence of local large aggregates of high copper content on the $\text{Cu}_2\text{O-Na-Y}$ (ET) catalyst.

On the other hand, AcCu-Na-Y (ET) micrographs (Fig. 6b) show the presence of more dispersed smaller particles all over the surface of the zeolite. NitCu-Na-Y (ET) images (Fig. 6a) show that copper dispersion is lower, with larger copper aggregates than AcCu-Na-Y (ET), but with different texture and lower density than $\text{Cu}_2\text{O-Na-Y}$ (ET). Only the catalysts prepared using the CuCl_2 precursor (Fig. 6c) does not present any

kind of copper aggregates on its surface (at least, within the resolution of the SEM images). The XRD diffractograms of these catalysts do not show the appearance of new peaks, though crystallinity is reduced with respect to the bare zeolite.

Residual Brønsted acidity of the catalysts prepared by the ET method using the $\text{NH}_4\text{-Y}$ zeolite is considerably higher than that of the SSIE preparation method (Table 1). This may be attributed to a poor copper exchange in the liquid phase, leaving more residual acid Brønsted sites available. When the Na-Y zeolite (with no Brønsted acidity) is used as support, the residual Brønsted acidity is negligible for all the prepared catalysts.

The activity towards the oxidative carbonylation reaction of the catalysts prepared by the liquid ethanol ion exchange method is summarized in Fig. 7a. Only the catalysts prepared using the CuCl_2 precursor formed DMC product. This might suggest that, in the rest of the catalysts, the exchange of copper to form the active phase required for the reaction was not successful. This is supported by the presence of copper

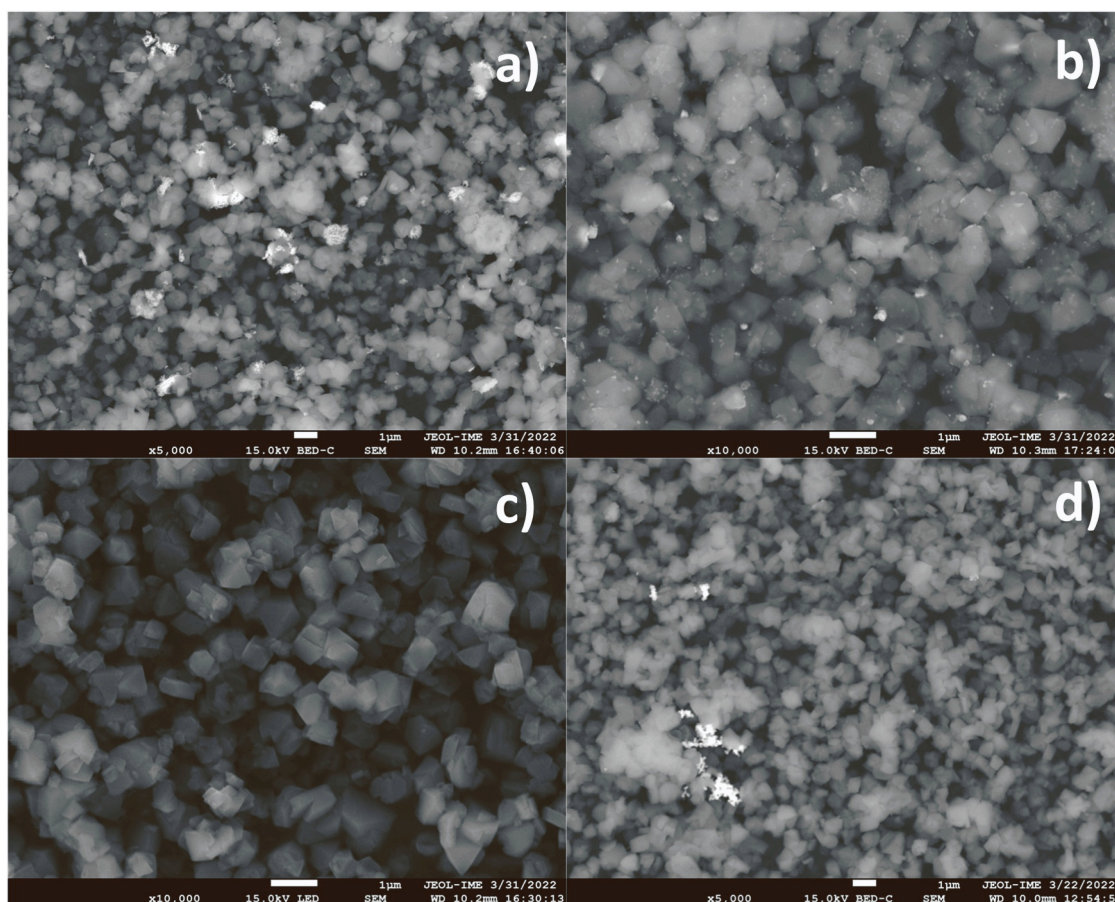


Fig. 6. SEM images of NitCu-Na-Y zeolite (a), AcCu-Na-Y zeolite (b), CuCl₂-Na-Y zeolite (c), and Cu₂O-Na-Y zeolite (d) catalysts prepared by the liquid ethanol ion exchange method.

aggregated in these catalysts, as evidenced by the characterization tests (XRD diffractograms and SEM images) discussed previously.

The CuCl₂-Y (ET) catalyst only yielded DMC as reaction product. Conversely, the CuCl₂-Na-Y (ET) catalyst formed DMC and also small amounts of DME and DMM with selectivity of 2 % and 8 %, respectively. Despite the presence of these by-products, the CuCl₂-Na-Y (ET) catalyst showed considerably higher activity to DMC: methanol conversion of 4.3 % and DMC yield of 3.8 % (ca. 5 times higher than for the CuCl₂-Y (ET) catalyst). Traces of CO₂ were also detected, indicating possible DMC decomposition to DME and CO₂.

The activity of the catalysts towards DMC decomposition was confirmed with additional tests in which DMC was fed as reactant (Fig. 7b). At 120°C, DMC conversion was 40 % for the CuCl₂-Y zeolite (ET) catalyst and 26 % for the CuCl₂-Na-Y zeolite (ET) catalyst. In these tests, the decomposition products were DME and CO₂, and no methanol was detected. This behavior is correlated with the residual Brønsted acidity of the prepared catalysts, higher acidity leading to a higher DMC decomposition rate, as evidenced by the reaction tests done with the unsupported zeolites and previous works [41].

One important side reaction of this type of catalyst is methanol dehydration. Specific reaction tests were performed on the catalysts prepared with CuCl₂ precursor. At 120°C, no reaction was observed with any of the catalysts. However, by increasing the temperature to 150°C, the conversion of methanol to DME raised to 0.63 % for the CuCl₂-Y zeolite (ET) catalyst. The CuCl₂-Na-Y zeolite (ET) catalyst did not show any reaction with methanol, which means that the DME detected during the oxidative carbonylation reaction test was generated by DMC decomposition.

3.4. Comparison of the preparation methods

An important conclusion of this study is that only the catalysts prepared using copper chloride precursors were found active for the production of DMC. Both preparation methods, the solid-state ion exchange and the liquid ion exchange in ethanol, have been found suitable. Fig. 8 compares the activity of the prepared catalysts in terms normalized by Cu content, which is the DMC formation rate, calculated using Eq. (2), normalized for the different catalysts using the corresponding copper loadings (see Table 1). The copper loading of this set of catalysts is very similar (in the range of 4.2–5.7 wt%), despite the different zeolite supports and preparation methods.

As observed in Fig. 8, the catalyst prepared using the CuCl₂ precursor and the Na-Y zeolite by the liquid ion exchange method points out in terms of activity. For this catalyst, the DMC formation rate was 0.72 h⁻¹, which is ca. 3 times the reaction rate of the following most active catalyst. The selectivity to DMC of this catalyst was also high, at 88 %. To explain the outstanding behavior of the CuCl₂-Na-Y zeolite (ET) catalyst, the Lewis activity has also been included in Fig. 8. As shown, it is suggested a correlation between the Lewis acidity and DMC formation rate, with the CuCl₂-Na-Y zeolite (ET) catalyst having the highest Lewis acidity (0.65 mmol/g). Oxidative carbonylation is a reaction that needs the oxidation function of copper to activate methanol as a methoxy species, but also the acid function of the support to form the DMC product. Note that the acid function also catalyzes side reactions, responsible for the formation of DME and DMM by-products [28]. In this context, the Y zeolite offers a balance between these two functions aimed at maximizing the formation of DMC.

In the preparation of the CuCl₂-Na-Y zeolite (ET) catalyst, first, the

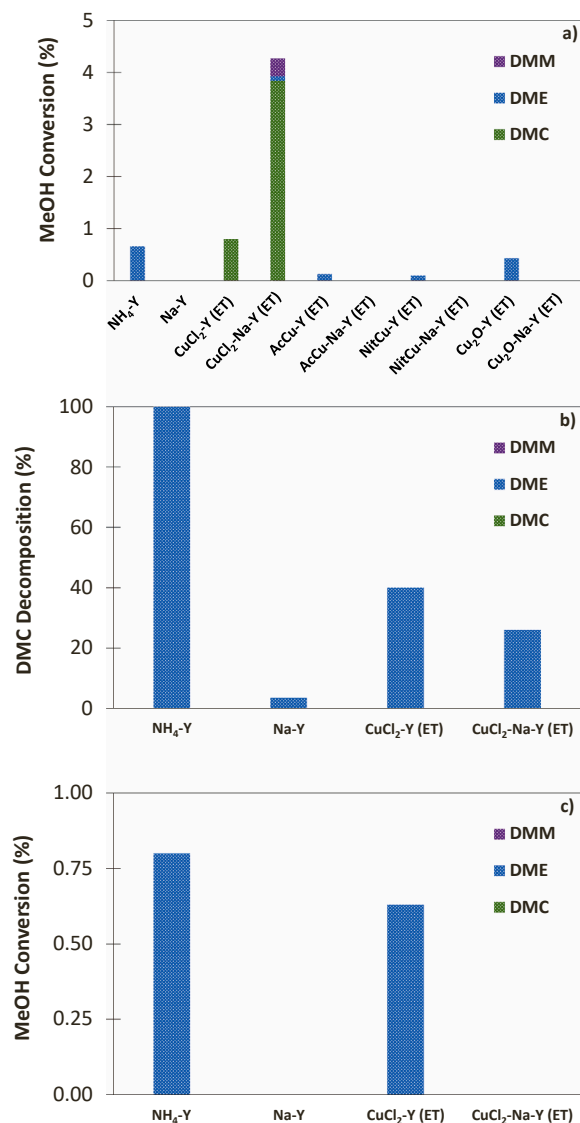


Fig. 7. Reaction results for the unsupported zeolites and the catalysts prepared via liquid ion exchange in ethanol (ET). WHSV = 208 mol/h kg_{cat}. a). Oxidative carbonylation tests (16 % methanol, 9 % O₂, 75 % CO) at 120°C. b). DMC decomposition tests (1.5 % DMC, 9 % O₂, 42 % CO, 47.5 % N₂) at 120°C. c). Methanol dehydration tests (16 % methanol, 84 % N₂) at 150°C.

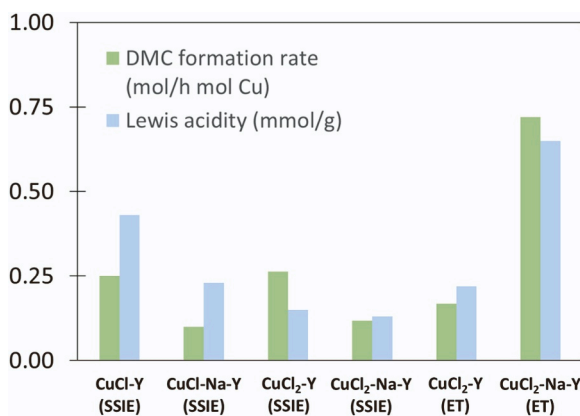


Fig. 8. Comparison of DMC formation rates and Lewis acidity for the catalysts prepared with copper chloride precursors. WHSV = 208 mol/h kg_{cat}, 120°C and mole fractions: 16 % methanol, 9 % O₂, 75 % CO.

NH₄⁺ of the commercial Y zeolite was exchanged by Na⁺, which removed Brønsted acidity and Lewis acidity increased from 0.17 to 0.34 mmol/g. Then, copper was exchanged using the CuCl₂ precursor dissolved in ethanol, resulting in a further increase in Lewis acidity to 0.65 mmol/g. None of the other precursors was so successful in increasing Lewis acidity during the copper exchange.

The EDX microanalysis performed on the SEM images has revealed the presence of copper and chloride on the surface of the catalysts prepared by the liquid ethanol methanol (Fig. 9). For the CuCl₂-Y (ET) catalyst, the exchange takes place between NH₄⁺ from the Y zeolite and Cu²⁺ from the promoter with precipitation of NH₄Cl after the evaporation of the solvent. This salt has a boiling point of 520°C, so it is removed during the activation step (4 h at 550°C). Consequently, the presence of chloride must be due to occlusions on the zeolite channels of CuCl₂ promoter, transformed into CuCl at 350–500°C during the activation step. Also, part of CuCl is sublimated above 500°C [36]. Conversely, for the CuCl₂-Na-Y (ET) catalyst, the exchange occurs between Na⁺ and Cu²⁺ with formation of NaCl deposits after the evaporation of the solvent. Given that NaCl is not volatile, the chloride of the promoter is not removed during the activation step. For this reason, high concentration of surface chloride was identified on this catalyst by EDX microanalysis. The XRD diffractograms and the SEM images did not reveal the present of other phases on these catalyst (Figs. 5 and 6).

The presence of copper-chloride species on the zeolite channels when these salts are used as precursors has been identified by different authors [50,51]. The commercial DMC synthesis process occurs in the liquid phase catalyzed by dissolved CuCl, which forms the intermediate cupric methoxy chloride. The high surface chloride content of the CuCl₂-Na-Y (ET) zeolite might imply higher density of copper chloride occlusions that can be responsible of the increase in the activity of this catalyst. As explained before, this can be related to the higher Lewis acidity of this catalyst, which is a consequence of the preparation methodology, based on the use of the Na-exchanged Y zeolite and the CuCl₂ precursor.

The catalyst surface was also characterized by XPS. Fig. 10 shows the Cu 2p XPS spectra of the most active catalysts. The existence of Cu(0) species has been discarded, due to the absence of the characteristic peak from binding energies (BE) from 916 to 920 eV [52]. The Cu 2p spectra exhibited two large peaks: in the range 931–934 eV and 951–953 eV of BE, respectively attributed to the Cu 2p_{3/2} and Cu 2p_{1/2} levels of Cu⁺/Cu²⁺ species. The spectra also present the satellite peak corresponding to the Cu²⁺ 2p_{3/2} level for BE 943–945 eV, which confirms the existence of Cu²⁺ specie [38,53]. However, the size of this satellite peak is very small compared to the Cu 2p_{3/2} peak, suggesting that Cu²⁺ is not the most abundant specie. Thus, during the preparation of the catalyst at high temperature, there is a shift on the surface equilibrium between Cu²⁺ and Cu⁺ species with preferential stabilization of Cu⁺ [54]. By means of curve fitting, the positions and surface concentrations of the two Cu species can be obtained (Fig. 10, right graphs).

The curve fitting of the Cu 2p_{3/2} peak was very similar for the CuCl₂-Na-Y zeolite (ET) (a) and the CuCl₂-Y zeolite (SSIE) (b) catalysts (Fig. 10); the peak was split into a large peak (85 % of the peak area) attributed to Cu⁺ specie, respectively, at BE 931.5 and 931.8 eV, and a small peak (15 % of the peak area) attributed to Cu²⁺ specie, respectively, at BE 934.1 and 934.3 eV [38,52,54]. Surface chloride was also detected for both catalysts on the Cl 2p XPS spectra at BE of 198 eV; the surface concentration of Cl on the CuCl₂-Na-Y (ET) catalyst was found to be 3.4 times higher. This finding agrees with the results of the SEM EDX characterization discussed previously (Fig. 9).

The curve fitting of the Cu 2p_{3/2} peak for the CuCl₂-Y zeolite (ET) catalyst (c) suggests that there is only one copper specie (with at least more than 95 % of the peak area) with a BE of 933.1 eV (Fig. 9). This peak is attributed to Cu⁺ specie, since the satellite Cu²⁺ peak is almost negligible for this catalyst. In this catalyst (c), the BE of the Cu⁺ peak is shifted +1.3 eV with respect to the equivalent peak of the CuCl₂-Y zeolite (SSIE) (b). This can be explained by a difference in acidity, since the CuCl₂-Y zeolite (ET) preserves 0.08 mmol/g of Brønsted acidity after

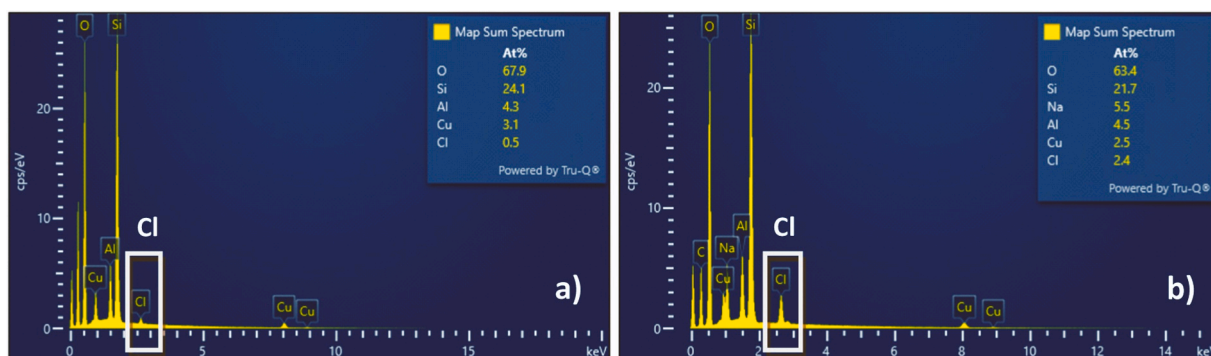


Fig. 9. EDX microanalysis of a) CuCl₂-Y (ET) and b) CuCl₂-Na-Y (ET).

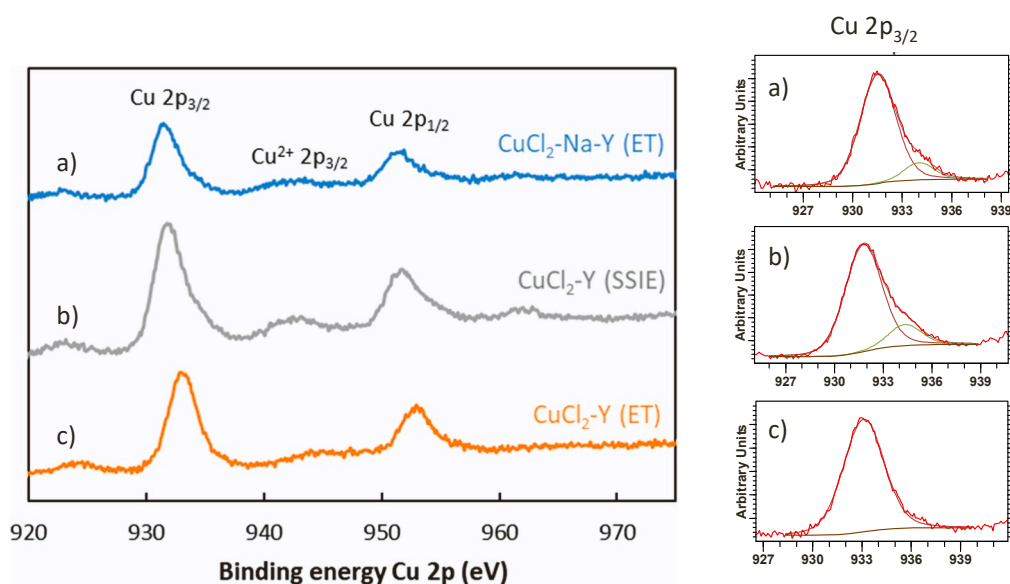


Fig. 10. Cu 2p XPS spectra (left) and gaussian deconvolution for Cu 2p_{3/2}: a) CuCl₂-Na-Y (ET), b) CuCl₂-Y (SSIE) and c) CuCl₂-Y (ET).

the Cu exchange (Table 1). Conversely, the other two zeolites present no Brønsted acidity, due to the pre-treatment with Na₂CO₃ (CuCl₂-Na-Y (ET)) or the complete exchange of Cu with NH₄⁺ (CuCl₂-Y (SSIE)). Thus, it is well known that as zeolite acidity decreases, the peaks of the O 1s XPS spectra shift towards lower binding energies [55]. By comparing the O 1s peaks of CuCl₂-Y (ET) and CuCl₂-Y (SSIE) zeolites, the BE are 532.2 eV and 531.2 eV, respectively. This shift of +1 eV of the first zeolite is attributed to a higher acidity of the zeolite framework. We suggest that the Cu 2p_{3/2} peaks are shifted in a similar way, according of the acidity of the zeolite environment. This is in agreement with the XPS results obtained with other Cu-Y zeolites from the literature. For catalysts prepared using the Na form of the Y zeolite or in alkali metal hydroxide media that guarantee the removal of Brønsted acidity, the Cu 2p_{3/2} peak appeared in the range 930–931 eV [38,54]; otherwise, in catalysts with residual Brønsted acidity, the peak shifted to 933–934 eV [52,54].

4. Conclusions

The purpose of the work has been the optimization of the preparation of copper supported on Y zeolite catalysts for the oxidative carbonylation of gas-phase methanol. The type of copper precursor, the form of Y zeolite support, and the preparation methodology were studied.

Regarding the copper precursor, it was found that only the use of copper chloride salts, CuCl and CuCl₂, produced catalysts with activity towards the formation of dimethyl carbonate (DMC) considering all the

Y zeolite forms and preparation methods.

The exchange with Na⁺ of the commercial NH₄⁺ form of the Y zeolite caused a removal of Brønsted acidity and an increase on Lewis acidity. It also had a significant effect on the crystallinity of the material. The catalysts prepared with the Na-Y zeolite support presented some advantages in terms of DMC yield, such as, the reduction of DMC decomposition to DME and methanol dehydration to DME.

The two catalyst preparation methods followed in this work were suitable to obtain active catalysts for DMC synthesis when copper chloride salts were used as precursors. It was found that, differently from the solid-state ion exchange method, the liquid ion exchange in ethanol was a method capable of increasing the Lewis acidity with respect to the unloaded Y zeolites. This, together with the use of the Na-Y zeolite form, was determinant to obtain the CuCl₂-Na-Y (ET) catalyst with the highest DMC formation rate (0.72 mol_{DMC}/mol_{Cu} h with 88 % DMC selectivity at 120°C and WHSV = 208 mol/h kg_{cat}).

CRediT authorship contribution statement

Mauro Álvarez: Investigation, Data curation, Writing- Original draft preparation. **Jennifer Cueto:** Conceptualization, Methodology, Writing- Reviewing and Editing. **David P. Serrano:** Supervision, Writing- Reviewing and Editing. **Pablo Marín:** Conceptualization, Supervision, Writing- Reviewing and Editing. **Salvador Ordóñez:** Funding acquisition, Writing- Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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