Structure and activity of Cu/ZnO catalysts co-modified with aluminium and gallium for methanol synthesis

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Abstract

This contribution describes the modification in the structure and activity of Cu/ZnO catalyst in the methanol synthesis reaction induced by the co-modification with a low amount of Al and Ga (Al + Ga = 3% atom). To elucidate the effect of the co-modification, the catalysts were characterized by means of variety of techniques (XRD, N₂ physisorption, FTIR, TGA, TEM, TPR and N₂O chemisorption) and tested in the methanol synthesis reaction carried out in a flow reactor at 250 °C and total pressure of 3 MPa using syngas. The combined characterization and activity tests demonstrated that the co-doping with Al and Ga affects the structure and activity of Cu/ZnO catalysts in a different manner depending on the Al/Ga ratio used. The best catalyst co-loaded with Ga and Al in equal amount shows an improvement in the activity for methanol synthesis respect to the activity obtained on catalysts individually loaded with Al and Ga. The difference in the activity of the samples co-loaded with Al and Ga normalized by N₂O chemisorption point to a different participation of the copper surfaces in combination with the defect sites of ZnO depending on the Al and Ga loading.

Keywords: Methanol, Copper, Zinc, Gallium, Syngas

1. Introduction

The production of methanol is one of the most important chemical processes because methanol is used as a chemical feedstock for production of a range of important industrial chemicals (acetic acid, formaldehyde, methyl methacrylate and MTBE) and it is also used directly as a fuel or fuel supplement. In addition to the clear industrial importance of methanol, there is also an increasing interest in the synthesis of C₁ chemicals because of their potential for the conversion of CO₂ and the storage and handling of renewable energies [1]. Most methanol is produced today from synthesis gas mixtures (H₂/CO₂/CO) at medium pressure and temperature (50–80 bar and 220–280 °C) using copper-based catalysts. Formulations based on Cu/ZnO-Al₂O₃, with molar Cu/Zn/Al ratio near 66-63/29-27/5–10 are widely employed at commercial scale as catalysts for methanol synthesis since its development by ICI [2]. In spite of the high activity and selectivity of the Cu/ZnO-Al₂O₃ catalysts sustained efforts are still made in order to improve its performance to address the emerging challenges in the methanol synthesis from renewable sources.

Active sites in the Cu/ZnO-Al₂O₃ based catalysts are related with metallic copper but there is not unanimity about its exact nature. The synergetic effect of ZnO in the activity of Cu for methanol synthesis has been widely studied in the literature and several models have proposed to elucidate its nature. These models include the lattice strain and defects in the Cu particles [3], Zn species sitting on Cu steps [4], changes in the morphology of the Cu particles [5], wetting of Zn atoms over the Cu surface by strong metal support interaction (SMSI) [6], dissolved Cu⁺ in ZnO [7]. The promotional effect of aluminium in the Cu/ZnO catalysts has been less studied than the one of ZnO and aluminium is usually considered as structural promoter enhancing the activity, stability and thermal resistance [8]. However recent findings indicate that promotion of Al in the Cu/ZnO catalysts also includes, besides the structural promotion, electronic effects related with the incorporation of Al into the ZnO lattice which influences on the formation and intrinsic activity of the copper active sites [9]. These studies demonstrated that aluminium content around 3 mol % is sufficient to promote the activity of Cu/ZnO systems. The electronic effect is derived from the incorporation of Al³⁺ into ZnO lattice which modifies its reducibility thereby affecting the extent of the dynamical SMSI effect over the copper surface increasing by this way its intrinsic activity [10]. Similarly, gallium has been also studied as promoter of Cu/ZnO catalysts because Ga³⁺ has ionic properties similar to Al³⁺ ions. However the origin of the Ga promotion has been less studied and is not yet completely understood. First works reported the stabilization of Cu/Cu⁺ species by Ga₂O₃ as the origin of the gallium promoter effect [11]. However, recent studies point to the facilitation of the reduction of ZnO by Ga insertion [10,12] as the mechanism to explain the promoter effect of Ga in Cu/ZnO catalysts. The replacement of Zn²⁺ ions with Ga³⁺ into the lattice of ZnO modifies the electronic structure and reducibility of ZnO which alters the intrinsic activity of the active Cu surface by SMSI [9] or by formation of metallic Cu-Zn interactions (Cu steps decorated with Zn atoms) [12]. As can be seen, the studies published in the literature about the promotional effect of Al and Ga on Cu/ZnO catalysts have been performed using the Al or Ga individually. Last findings point out that small amount of Al or Ga promoters produced significant changes on the structural and electronic properties of ZnO that strongly affects its defect chemistry, electronic structure and redox properties [9,10]. The modification of ZnO by n-type doping with group III elements (Al, Ga, In) has been widely studied in the literature as a way to alter its electronic properties in semiconductor and optoelectronic applications. These studies show that the different size and electronic structure of Al³⁺ and Ga³⁺ ions modify in a different way the electrical and defect properties of ZnO. The same dopant/Zn ratio leads to a very different doping efficiency when comparing Al and Ga, being the Ga cation a more effective dopant of the ZnO. The differences between Al- and Ga-doped ZnO are explained with the hypothesis that different quantities of these dopant cations are able to enter substitutionally in the ZnO matrix. Ga cations seem to behave as perfect substitutional dopants, while Al cation might occupy either substitutional or interstitial sites. Moreover, the subsequent charge balance after doping appear to be related with the formation of different intrinsic defects that depends on the dopant cation. Co-doping of ZnO with Al³⁺ and Ga³⁺ ions has

been also studied as way for increasing the dopant solubility and increasing the carrier mobility. In this sense, enhanced electronic and defect properties of ZnO were observed by co-doping of Al and Ga respect to the values obtained with the individual doping with of Al or Ga [13,14].

Taking into account the beneficial effect of co-doping with Al^{3+} and Ga^{3+} in the electronic and defect properties of ZnO observed in the preparation of n-type ZnO systems, it should be assumed that co-modification with Al^{3+} and Ga^{3+} in the Cu/ZnO catalysts could imply some improvement respect the conventional individual promotion with Ga and Al. Therefore, bearing this assumption in mind, we present this work which was undertaken with the aim to study the changes in the structure and activity of Cu/ZnO catalysts associated with the simultaneous modification with Al^{3+} and Ga^{3+} . Changes in the properties of the co-modified Cu/ZnO catalysts were compared with those achieved with the mono-substitution with Al^{3+} and Ga^{3+} in order to analyze the possible improvement associated to a different doping efficiency over ZnO when both Al^{3+} and Ga^{3+} promoters are present in the catalyst formulation.

2. Material and methods

2.1. Catalysts preparation

Cu/ZnO catalysts modified with Al and Ga were prepared by co-precipitation of hydroxycarbonate precursors according to the benchmark methodology proposed by Schuman et al. [15] to prepare highly active Cu/ZnO based catalysts. Cu/ZnO catalysts with 70:30 Cu:Zn mol ratio (selected because this ratio maximizes the incorporation of Zn into malachite hydroxycarbonate precursor) was modified with 3 mol % of Al and/or Ga because according to the work of Behrens et al. [9] maximum promoting effect was achieved around this concentration. The Al/Ga atomic ratio in samples was varied between 1/0, 0.66/0.33, 0.50/0.50 and 0/1 (Table 1). The prepared catalysts were labelled as CZ-Al-x-Ga-y according to its Al and Ga content ($x = 1, 0.66, 0.5$ and 0 , $y = 0, 0.33, 0.5$ and 1 , Table 1). Unpromoted Cu/ZnO sample was also prepared using the same methodology as reference catalyst.

Hydroxycarbonate CZ-Al-x-Ga-y precipitates were formed from 1 M aqueous solutions of the corresponding mixture of the salts of Cu ($\text{Cu}[\text{NO}_3]_2 \cdot 2.5\text{H}_2\text{O}$, *Sigma-Aldrich* >98%), Zn ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$, *Sigma-Aldrich* >99%), Al ($\text{Al}[\text{NO}_3]_3 \cdot 9\text{H}_2\text{O}$, *Sigma-Aldrich* >99%) and/or Ga ($\text{Ga}[\text{NO}_3]_3 \cdot x\text{H}_2\text{O}$, *Alfa-Aesar* 99%) using a precipitating aqueous solution 1.6 M of Na_2CO_3 ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, *Panreac AppliChem* for analysis) added drop by drop under controlled precipitation conditions ($\text{pH} = 6.5$, $T = 65^\circ\text{C}$). Once the addition of metal nitrates and carbonate solutions were completed, the precipitate was aged in the mother liquor under continuous stirring at 65°C for 60 min after the pH drop point which indicates the beginning of the crystallization of malachite structures from the amorphous georgeite initially precipitated [16]. After aging, the precipitate was filtered and washed three times under agitation with milli-Q water to guarantee the complete removal of sodium nitrate. After

washing the precipitate was dried at 70 °C for 10 h. Dried precipitate was subjected to a thermal treatment under static air at 340 °C for 2 h (heating ramp = 2 °C/min) to form the CZ-A-x-G-y precursors in oxidized state. Finally, the CZ-A-x-G-y calcined precursors were reduced in order to obtain the catalysts in the active form under 50 mL/min of a mixture of H₂ (2.21 mol %)/Ar under the following temperature programme: room temperature (2 °C/min) → 150 °C → (1 °C/min) → 200 °C (2 h).

Table 1. Composition and labelling of the Cu/ZnO catalysts modified with Al and Ga.

Sample	Nomenclature	at %				wt %			
		Cu	Zn	Ga	Al	CuO	ZnO	Ga ₂ O ₃	Al ₂ O ₃
Cu/ZnO	CZ	70	30	0	0	69.5	30.5	0.0	0.0
Cu/ZnO/Al	CZ-Al-1-Ga-0	67.9	29.1	0.0	3.0	68.2	29.9	0.0	1.9
Cu/ZnO/Al-0.66-Ga-0.33	CZ-Al-0.66-Ga-0.33	67.9	29.1	1.0	2.0	67.8	29.7	1.3	1.2
Cu/ZnO/Al-0.5-Ga-0.5	CZ-Al-0.5-Ga-0.5	67.9	29.1	1.5	1.5	67.6	29.6	1.0	1.8
Cu/ZnO/Ga	CZ-Al-0-Ga-1	67.9	29.1	3.0	0.0	67.1	29.4	3.5	0.0

2.2. Physicochemical characterization

X-ray diffraction (XRD) analyses of the precipitates, calcined precursors and reduced catalysts were performed in a X'Pert Pro PANalytical polycrystalline diffractometer with a X'Celerator real time multiple strip (RTMS) detector and nickel filtered Cu K α_1 radiation (λ = 0.15406 nm, 45 kV, 40 mA). Bragg angles between 5° and 80° were scanned for each sample with a step size of 0.02° and an integration time of 50 s/step. Average crystallite sizes of zinc-malachite, CuO and Cu metallic phases were calculated from the broadening of the characteristics (020), (111) and (111) reflection peaks respectively applying the Debye-Scherrer equation. To obtain qualitative information about defects and lattice strain in the metallic Cu particles, the stacking fault was calculated from the positions of the (111) and (200) reflections of Cu-metal in the XRD profiles of reduced catalysts ($\alpha = 8.3[2/\sqrt{3} - \sin\theta(200)/\sin\theta(111)]$)

Textural properties of precipitates and calcined precursors were obtained from N₂ adsorption/desorption isotherms (-196 °C) using an ASAP 2420 Micromeritics automatic equipment. Previous to the measurement, the samples were outgassed at 120 °C for 12 h. The specific surface areas were calculated from the N₂ isotherms using the BET method within the relative $P/P_o = 0.05$ – 0.30 interval. Desorption data were used to determine the average pore size distribution of the samples according to the Barret-Joyner-Halenda (BJH) method. IR spectra of calcined precursors were recorded using a JASCO FT/IR-6300 Fourier-transform IR spectrometer equipped with attenuated total reflection accessory (ATR) and

using a MCT-M detector. Spectra were recorded in a scan range from 4000 to 400 cm^{-1} at 4 cm^{-1} resolution and 200 accumulations to have a good signal to noise ratio.

Thermal decomposition of precipitates and calcined precursors were studied by thermogravimetry using a Mettler Toledo TGA/SDTA 851e equipment. Decomposition experiments were performed under 25 mL/min of a mixture of O_2 (20 vol %)/Ar from 40 °C to 600 °C (heating ramp = 10 °C/min). To identify the nature of each mass loss, a parallel study of the thermal decomposition was performed analysing the gas produced by mass spectrometry. For these studies the samples (20 mg) were placed in a U-shaped fixed-bed reactor (4.0 mm id) and were thermally decomposed (from 40 °C to 600 °C, 10 °C/min) under 38 mL/min of a mixture of O_2 (20 vol %)/Ar. The calcination gas products were analysed with a Baltzer Prisma QMS 200 T M quadrupole mass spectrometer. The main signals (H_2O , CO, CO_2 , NO, N_2O , NO_2 and Ar) were recorded during all experiments. The results are presented as the corresponding mass spectra (m/z) normalized to Ar signal and mass of sample.

The surface morphology and chemical composition of the precipitates were studied by Scanning Electron Microscopy with energy-dispersive X-ray analyzer (SEM/EDX) using a Hitachi TM-1000 Tabletop microscope operated with an accelerating voltage of 15 kV. The nano-morphology of the primary particles in the reduced catalysts were studied by Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron microscopy (HRTEM) with a TEM/STEM JEOL 2100 F microscope operating at 200 kV of accelerating voltage with a field emission gun (FEG), obtaining a point resolution of 0.19 nm.

Temperature Programmed Reduction (TPR) experiments on calcined precursors were carried out using a semi-automatic PID Eng & Tech apparatus. The samples (20 mg) were placed into a quartz U-shaped reactor (4.0 mm id) with a coaxial thermocouple. The reduction profiles were obtained by heating the samples from 40 to 200 °C (heating rate = 2 °C/min) under 50 mL/min of H_2 (10 vol %)/Ar gas mixture. TPR tests were performed under these conditions that ensure mild reduction to control of exothermicity during reaction avoiding by this way local overheating that resulted in loss of Cu dispersion. The amount of hydrogen consumed during the temperature programmed reduction was measured with a thermal conductivity detector.

The copper surface area in reduced catalysts was calculated from chemisorption of N_2O . Chemisorption on the reduced catalysts (30 mg, loaded in a U-shaped reactor) was performed passivating the sample with 7.5 mL/min of N_2O (2 vol %)/Ar flow at 25 °C for 15 min. Subsequently, the passivated catalysts were cleaned with He flow for 30 min in order to remove the excess of N_2O and reduced with H_2 /Ar flow (10 vol %, 50 mL/min) from room temperature to 280 °C (heating ramp = 10 °C/min). The H_2 consumption during the reduction of passivated samples was equivalent to the quantity of N_2O chemisorbed. The Cu^0 surface area was calculated with the premise of a molar stoichiometry of $\text{Cu(s)}/\text{N}_2\text{O} = 2$ and an average value of 1.47×10^{19} at Cu/ m^2 for the mean surface copper atom density [17].

2.3. Catalytic activity measurements

Methanol synthesis tests were performed in a continuous flow fixed-bed reactor. The catalyst bed (200 mg of calcined precursor diluted with silicon carbide (1:3 vol.)) was located in a stainless steel reactor (8.9 mm i.d.) in contact with a thermocouple to assure isothermal conditions. The calcined precursors were pelletized to obtain particles of 0.3–0.4 mm for catalytic testing. The calcined precursor was reduced under H₂/Ar flow (2.21% vol. H₂, 50 mL/min) at 200 °C for 2 h following the heating programme: 40 °C–150 °C at 2 °C/min and 150 °C–200 °C at 1 °C/min. The conditions for activation of catalysts before tests were slightly different (lower H₂ concentration) from that used in TPR because the higher mass and reactor diameter used in the catalytic tests but in both cases samples achieved nearly the same copper surface area after the reduction protocols. The methanol synthesis tests were performed at 250 °C using a syngas mixture (with a composition (vol %) of 4.5% CO₂, 22.0% CO, 58.8% H₂ and 14.7% N₂) with a flow of 75 mL/min and a total pressure of 3 MPa. The feed composition for catalysts testing was selected taking into account the ideal syngas stoichiometry for methanol synthesis ($M=2$, where M is defined as $M= (H_2-CO_2)/(CO+CO_2)$). N₂ was included as internal standard for GC quantification. Conditions for testing were selected to achieve maximum initial (CO + CO₂) conversions of 15–20% to maximize differences between samples. Preliminary tests were performed in order to assure that catalytic measurements under the selected testing conditions are obtained free of internal and external mass transfer limitations. The gas products were analysed on-line using gas chromatography (Varian 450-GC with TCD) equipped with QS-bond column (for CO₂, CH₃OH and H₂O) and molecular sieve 5A (for H₂, O₂, N₂, CO) capillary column. Activity data were presented as CH₃OH production rate normalized to the weight of calcined precursor loaded in the reactor ($\mu\text{mol CH}_3\text{OH}/\text{min g}_{\text{cat}}$).

3. Results

3.1. Characterization of precipitates

The XRD patterns of the CZ and CZ-Al-x-Ga-y precipitates are presented in Fig. 1. The unpromoted CZ precipitate shows diffraction peaks ($2\theta = 17.48^\circ, 24.04^\circ, 32.37^\circ$) related with the existence of zincian-malachite-like phase (JCPDS 041–1390 (Cu/Zn)₂ (OH)₂ CO₃) with additional weak diffraction peaks ($2\theta = 12.99^\circ, 27.85^\circ$) attributed to the small formation of aurichalcite (JCPDS 17-0743, (Cu/Zn)₅ (OH)₆ (CO₃)₂). XRD patterns of all precipitates containing Al and/or Ga (CZ-Al-x-Ga-y) only show diffraction peaks corresponding to zincian-malachite-like phase without detection of the aurichalcite phase observed in the unpromoted precipitate (CZ) or other crystalline phases containing M³⁺ ions. The inhibition of the formation of aurichalcite with the presence of Al or Ga is in good accordance with the study of Behrens et al. [9] who proposed that the relative fraction of the aurichalcite phase decreased to the benefit of the zincian-malachite when Al or Ga in concentration around 3 wt % was present in the precipitation. Apart from the differences in phase composition, the precipitates containing Al and/or Ga exhibit less defined diffraction peaks than in the

unpromoted CZ precipitate indicating less crystallinity and lower size of the zincian-malachite-like phases (Table 2). This was already observed in the literature and it was associated with a higher degree of Zn incorporation into the zincian malachite promoted by the presence of low concentration of M^{3+} ions [18]. In line with this was the slight shift in the d_{20-1} interplanar spacing of the zincian malachite phase observed in the Al- and Ga-containing precipitates (Table 2) which was associated with the incorporation of Zn^{2+} [19].

Fig. 1. XRD patterns of precipitates (after drying at 70 °C for 10 h): (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1 (o aurichalcite (JCPDS 17–743), * zincian-malachite (JCPDS 41–1390)).

Insertion of Al^{3+} or Ga^{3+} into zincian malachite is also possible for contents below 3 wt % and therefore part of the contraction observed in the d_{20-1} spacing could be associated to this fact. Co-incorporation of Zn^{2+} and Al^{3+} ions into the zincian-malachite precursors was reported [19] in which AlO_6 units contribute to the dilution of Cu^{2+} in the malachite matrix leading to an additional decrease in the interplanar spacing due to the smaller ionic radius of Al^{3+} . Co-incorporation of Ga^{3+} with Zn^{2+} ions into the zincian-malachite structure is also described but in this case the larger ionic radius of Ga^{3+} ($IR = 0.47 \text{ \AA}$) respect the Al^{3+} ions ($IR = 0.39 \text{ \AA}$) [20] produces less contraction in the malachite. In our case the precipitates only promoted with Al and Ga shows similar shift in the (20-1) diffraction peak (Table 2) which notes similar co-incorporation of Zn and Al^{3+} or Ga^{3+} into the malachite. The precipitates co-modified with Al and Ga show a slight increase in the contraction of the d_{20-1} spacing respect to the samples only promoted with Al or Ga (Table 2) which denotes a small increase in the incorporation of Zn^{2+} and Al^{3+}/Ga^{3+} into the malachite structure. The reason for the slight

increase in the incorporation of Zn^{2+} and Al^{3+}/Ga^{3+} in the co-modified samples is not easy to understand. An explanation might be related with the different sites occupied by Al and Ga in the malachite structure derived from the different radii of these ions [21] which are optimally occupied when both ions are at the same time during the precipitation and growth of the zinc-malachite structures. In line with this, the energy-dispersive X-ray spectroscopy on CZ-Al-x-Ga-y precipitates revealed the homogeneous distribution of Al and Ga on the precipitates.

Table 2. Domain size (from (002) diffraction peak) and shift in the (20-1) diffraction peak of zincian malachite structures calculated from the XRD patterns of precipitates (after drying at 70 °C for 10 h).

	(002) peak Domain size (nm)	(20-1) peak 2θ (°)	D (20-1)(Å)
CZ	9.4	32.38	2.762
CZ-Al-1-Ga-0	8.9	32.44	2.756
CZ-Al-0.66-Ga-0.33	8.8	32.51	2.749
CZ-Al-0.5-Ga-0.5	8.9	32.52	2.748
CZ-Al-0-Ga-1	8.9	32.47	2.753

Table 3. Textural properties from N_2 isotherms and quantification of mass loss and HT- CO_3 species from thermogravimetric decomposition of precipitates (after drying at 70 °C for 10 h).

	S_{BET} ($m^2 \cdot g^{-1}$)	V_{pore} ($cm^3 \cdot g^{-1}$)	Average pore diameter (nm)	Total mass loss (%)	HT- CO_3 (*)	
					T_{max} (°C)	(%)
CZ	57	0.405	26	28.7	–	–
CZ-Al-1-Ga-0	111	0.471	17	29.0	529	47.2
CZ-Al-0.66-Ga-0.33	126	0.571	16	29.1	536	45.0
CZ-Al-0.5-Ga-0.5	121	0.578	16	28.6	535	45.1
CZ-Al-0-Ga-1	118	0.530	19	28.2	527	46.6

(*) percentage of CO_2 (to the total CO_2) produced at $T > 400$ °C measured by EGA.

Textural properties of the precipitates (Table 3) were calculated from the adsorption/desorption isotherms of N_2 (Fig. 2). All precipitates show isotherms characteristics of mesoporous materials (type IV) with hysteresis loops type H2 characteristic of disordered porous materials. The CZ-Al-x-Ga-y precipitates show differences in the shape and size of their hysteresis cycles respect to that observed in the CZ

reference which could be derived from the differences in the domain size and structure of the solid particles present in the precipitates. The BET surface area of the CZ-Al-x-Ga-y precipitates was in all cases much higher than that developed by the CZ reference (Table 2). This result is well in line with the results reported [16] on the beneficial effect of Al on the development of meso-structure and porosity in the precipitates respect to the binary CZ counterparts as results of the formation of a higher fraction of zincian malachite with meso-structure. All the CZ-Al-x-Ga-y precipitates show high values of BET surface area, in the range of 110-120 m²/g, with higher surface development in the co-doped samples attributed to a decrease in the average pore size (BJH, Table 3) since the domain size of the zincian malachite structures was similar in all precipitates (Table 2).

Fig. 2. N₂ isotherms of precipitates (after drying at 70 °C for 10 h): (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1.

Thermal decomposition of precipitates was followed by thermogravimetry in order to study the decomposition of anions of the precipitates to form nano-sized CuO and ZnO which act as precursors of the catalysts. The decomposition profile of the CZ precipitate presents a main decomposition peak composed of three components at 336, 364 and 421 °C (Fig. 3a-b). Conversely, the thermogravimetric curves of CZ-Al-x-Ga-y precipitates (Fig. 3) show a decomposition through two steps with maximum peaks around 250–300 °C and 530 °C. The separation in two main steps with the addition of Al to CZ precipitate was already described in the literature [15] which indicates the shifting in the decomposition of the zinc malachite phases to lower temperature and the stabilization of the second decomposition step to higher temperature in ternary CZ-Al respect to binary CZ precipitate.

EGA analyses of gases during the thermal decomposition of precipitates (Fig. 3 c–d) show a simultaneous decarbonation and dehydroxylation during the first decomposition step of both the CZ and CZ-Al-x-Ga-y precipitates while only decarbonation takes place in the second decomposition step. Therefore the decomposition profile indicates that there are two carbonate species only in the CZ-Al-x-Ga-y precipitates, with the carbonates decomposed at higher temperature ($T > 400\text{ }^{\circ}\text{C}$) assigned as HT-CO₃, which agree fairly well with that reported in the literature for zincian malachite [22]. However other studies reported decomposition of zincian malachite in just a single mass loss [23]. The factors that influence the decomposition of zincian malachite in one or two steps were not fully understood [24,25] but the stability and quantity of these carbonate species are associated with the development of small crystalline domains of CuO in contact with ZnO which are precursors of catalysts with high activity and stability under methanol synthesis conditions [26]. Residual carbonates after calcination affect the microstructure and defectivity of the Cu particles during the reduction [22]. In this sense, the presence of low amount of carbonates in the calcined precursors (3%) seems to result in improved activity and stability of Cu/ZnO catalysts derived from zincian malachite precipitates [22]. The total mass losses of all precipitates (Table 3) correlates well with the theoretical mass loss calculated for aurichalcite (27.2 wt %) and zincian malachite (27.7 wt %) what corroborates the existence of these structures with minimum contribution of other by-phases in both the CZ and CZ-Al-x-Ga-y precipitates. The abundance of HT-CO₃ in the CZ-Al-x-Ga-y precipitates was also determined from TGA-EGA analysis (Table 3) because as indicated previously these species remain after calcination and they play a key role in the activity of the derived catalysts [14,27]. The abundance of HT-CO₃ was relatively constant in all CZ-Al-x-Ga-y precipitates but the temperature at which decompose slightly shifts to higher temperature in the case of the co-promoted samples (CZ-Al-0.66-Ga-0.33 and CZ-Al-0.5-Ga-0.5). The nature of this HT-CO₃ is still debated in the literature [27] but previous results by Schumann et al [15] indicated the stabilising effect in the HT-CO₃ with addition of Al to the binary CZ precipitates which denotes a relationship between the stronger stability of HT-CO₃ with higher Zn (Al) incorporation into zincian malachite. Similar effect was described for Ga which also outlines the stabilising effect in the HT-CO₃ with the higher incorporation of Zn (Ga) into the malachite precursors [14]. In line with this argumentation appears the slightly higher stability of HT-CO₃ observed in the co-promoted samples that could be derived for the small increase in the incorporation of Zn²⁺ and Al³⁺/Ga³⁺ into the malachite structure as the previous XRD of the precipitates indicated.

Fig. 3. TGA (a), DTA (b) and EGA ($m/z = 18$ (c); $m/z = 44$ (d)) corresponding to the thermal decomposition of precipitates: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1.

3.2. Characterization of the calcined precursors and reduced catalysts

The structure of the copper and zinc oxides after calcination of the CZ and CZ-Al-x-Ga-y calcined precursors was analysed by XRD (Fig. 4). The crystallinity of all calcined precursors was low with broad diffraction peaks ($2\theta = 35.56^\circ$, 38.66°) corresponding to CuO

with tenorite structure (JCPDS: 41-0254) and small contributions ($2\theta = 31.88^\circ, 34.56^\circ$) of hexagonal ZnO (JCPDS: 89-0510). This characteristics means no strong segregation of CuO after calcination as expected from precipitates which contain aurichalcite (in the case of CZ reference) and Zn malachite structures with high degree of insertion of Zn [22,28]. Other crystalline phases corresponding to Al/Ga spinels, Ga oxides, hydroxides or residual hydroxycarbonate phases were not detected.

Fig. 4. XRD patterns of calcined precursors: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1 (■ ZnO, ○ CuO).

Crystalline domains size of CuO were measured from the diffraction peaks corresponding to (1 1 1) planes in the calcined precursors (Table 4). Crystalline size of CuO in CZ calcined precursor was slightly higher than that observed in the calcined CZ-Al-x-Ga-y precursors. Little changes in the crystalline size, intensity or positions of the CuO reflections were observed among the calcined CZ-Al-x-Ga-y precursors. It is known that segregation and contact of CuO with ZnO after calcination depends on both the structure of precipitates (aurichalcite or malachite) and the degree of insertion of Zn in the aurichalcite or malachite structures present in the precipitates what defines the intergrowth of the copper and zinc oxides. Considering this fact, the nano-structuration of CuO and ZnO observed for all the calcined CZ-Al-x-Ga-y precursors is in agreement with their previous XRD profiles which showed the presence of malachite structures with similar Zn insertion in all CZ-Al-x-Ga-y precipitates (Fig. 1). The increase in the crystalline domains of CuO observed in the CZ calcined precursor is in line with the above argument taking into account the lower insertion

of Zn in the malachite structures together with the small presence of aurichalcite phase observed in the CZ precipitate (Fig. 1).

Table 4. Textural properties, domain size of CuO and HT–CO₃ retention on calcined precursors.

	S_{BET} (m ² ·g ⁻¹)	V_{pore} (cm ³ ·g ⁻¹)	Average pore diameter (nm)	Domain size CuO (nm)	% of HT-CO ₃ retained %	T max (°C)
CZ	67	0.519	28	5.1	0.96	427
CZ-Al-1-Ga-0	83	0.569	22	4.2	1.40	428
CZ-Al-0.66-Ga-0.33	87	0.656	24	4.5	1.54	422-517
CZ-Al-0.5-Ga-0.5	83	0.647	25	4.6	1.52	427-530
CZ-Al-0-Ga-1	81	0.600	26	4.6	1.50	426-543

The carbonate retention on CZ-Al-x-Ga-y precursors after calcination of precipitates were analysed by TGA (Fig S2) and FTIR (Fig. 5). The IR spectra of calcined CZ and CZ-Al-x-Ga-y precursors present bands at 1483 and 1402 cm⁻¹ what are characteristics of the asymmetric C–O stretching ν_3 mode bands of carbonates. Quantification of carbonate retention on calcined precursors was done from TG experiments (Fig S2) and the results were presented in Table 4. As it was observed by FTIR, the carbonate concentration after calcination was similar on all CZ-Al-x-Ga-y precursors and higher than in the calcined CZ precursor in agreement with the lower thermal stability of carbonates in the CZ precipitate. The carbonate concentration on calcined precursors was relatively low, around 1.5 wt %, in comparison with the amount of HT–CO₃ determined in the precipitates (Table 2). The low retention of carbonates on calcined samples may mean that the kinetics of decomposition during the calcination (2 °C/min and 340 °C) has been relatively high. In spite of this, the amount of carbonates remaining on calcined CZ-Al-x-Ga-y precursors is sufficient to avoid a strong segregation of CuO. The carbonates on the calcined CZ-Al-x-Ga-y precursors exhibited small differences in their stability (Fig S2). In this sense the calcined precursors with Ga samples show higher relative concentration of carbonates which decompose at temperatures higher than 500 °C (Table 3). Since the presence of these carbonates appears only in the samples with Ga it appears that remaining carbonates on calcined precursors were more strongly bonded when Ga cations are present than in the case of Al.

Fig. 5. FTIR spectra (carbonate region) of calcined precursors: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1.

The isotherms of the calcined CZ and CZ-Al-x-Ga-y precursors are shown in Fig. 6. All calcined precursors show similar isotherms with characteristics typical of mesoporous materials (type IV) with hysteresis loops type H2. The calcined CZ precursor develops lower BET surface area than in the case of the calcined CZ-Al-x-Ga-y precursors (Table 4) as consequence of the lower meso-porosity of the precipitate from which it is derived. The calcined CZ-Al-x-Ga-y precursors exhibited similar values, around 85 m²/g, below the surface area developed by their precipitates (around 110-120 m²/g). This means that the nano-structuration of CuO and ZnO occurring during the calcination does not maintain the initial meso-structuration of the precipitates which they derive. The model of subsequent meso- and nano-structuring of Cu/ZnO catalysts [16] states that the precipitates initially pre-determine the porosity of the final catalysts because they form a loose network of zincian malachite nanostructures. The zincian malachite nanostructures need to be carefully decomposed into nanoparticles of CuO and ZnO during calcination (nano-structuration) without destroying the meso-structure and the porosity of the initial precipitates. In spite of the no strong segregation of the CuO observed after calcination of our samples, they still suffer some segregation during calcination which diminishes the initial porosity (meso-structuration) of the nanostructures of the precipitates. This could be related with the protocol used for the calcination of the precipitates what, as commented above, did not guarantee the

total retention of the HT-CO₃ responsible for the preservation of the mesostructuration developed in the initial precipitates. Although the calcination temperature used was not optimal to preserve the meso-structuring level achieved in the precipitates, the surface area developed by all CZ-Al-x-Ga-y precursors was high enough to guarantee high catalytic activity in the resulting catalysts.

Fig. 6. N₂ isotherms of the calcined precursors: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1.

The reducibility of calcined CZ and CZ-Al-x-Ga-y precursors was investigated by temperature-programmed reduction (Fig. 7). Most of the studies about reduction of CuO [29,30] indicated that reduction proceeds through two consecutive steps with amorphous Cu₂O as intermediate product. The reduction of CuO proceeds according to an autocatalytic mechanism in which the copper formed facilitates the dissociative adsorption of H₂. The TPR profile of the calcined CZ precursor exhibits a first small broad peak around 135 °C followed by a main stronger reduction peak around 150 °C with a shoulder at 163 °C. The small broad reduction peak at low temperature could be ascribed to highly dispersed CuO [30] or to the reduction of the undecomposed carbonate species present in the precursors [31]. The subsequent contributions above 150 °C were attributed to the reduction of more crystalline CuO species in contact with ZnO. For these species the stronger embedment of CuO in the ZnO matrix hinders the reduction process shifting the reduction to higher temperature [29]. However, it cannot be ruled out the contribution to this reduction peak of the partial reduction of ZnO to ZnO_{1-x} because the hydrogen consumption is higher than that would be expected if only CuO reduces. For CuO in contact with ZnO the strong metal-support interaction (SMSI) effect has been reported in the literature [33] Fig. 7 shows that the calcined CZ precursor reduces at lower temperature than the calcined CZ-Al-x-Ga-y precursors. In the case of the calcined CZ-Al-x-Ga-y precursors, the formation of CO₂, detected by mass spectrometry, points to the participation of undecomposed carbonates species in the first reduction step [15]. Taking into account that reduction of CuO includes two linked steps, the reduction at

higher temperature observed in the calcined CZ-Al-x-Ga-y precursors respect to the binary CZ precursor may be caused by the participation of the undecomposed carbonate species in the first reduction step which retard the onset of the reduction process [32]. Following the same reasoning, the precursors containing Ga show a little more intense first reduction shoulder at lower temperature than in the case of the precursors containing only Al in agreement with the slightly higher concentration of undecomposed carbonates observed in the Ga containing precursors after calcination (Table 3). However the shift in the reduction of the CZ-Al-x-Ga-y precursors respect to unpromoted CZ precursor might be also related with the formation of a more extended embedment of CuO in the ZnO matrix which might slow the hydrogen consumption as observed by Schumann et al [10]. The second reduction peak, which is observed in the temperature range of 168–176 °C, also shows clear differences in the calcined CZ-Al-x-Ga-y precursors. Taking into account that this reduction peak is related with the reduction of CuO nanoparticles interacting with ZnO [29], the observed differences might suggest some modification in these interactions. The TPR peak of the precursor containing only Al shows a main reduction peak at 176 °C which indicates homogeneous reduction of CuO nanoparticles in contact with ZnO species. The homogeneity of the reduction of the CuO species in the Ga- precursors also changes with the Ga loading presenting the sample with equal concentration of Al and Ga (CZ-Al-0.5-Ga-0.5) two overlapped reduction peaks suggesting heterogeneous reducibility of CuO and their contacts with ZnO.

Fig. 7. Temperature-programmed reduction profiles of calcined precursors: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1.

In general the precursors containing Ga show the main reduction peak a lower temperature than in the case of the precursor containing only Al. This might be derived from the shift in the beginning of the reduction of these precursors, previously commented, which could facilitate the reduction of copper taking into account that reduction proceeds according to an autocatalytic mechanism. Considering the relative hydrogen consumption for the reduction of CZ-Al-x-Ga-y precursors (Table 5), only the sample with lower Ga content (CZ-Al-0.66-Ga-0.33) shows higher hydrogen consumption than the sample only substituted with Al. Taking into account that in the reduction of the CuO species in contact with ZnO, the partial reduction of ZnO to ZnO_{1-x} in the vicinity of Cu is also produced, the less hydrogen consumption may be related to changes in the reducibility of ZnO. It is known that the reducibility of ZnO changes when it contacts with Cu and when small amounts of Al³⁺ or Ga³⁺ are incorporated in its lattice and this effect on the oxygen vacancy formation in ZnO depends on the Al³⁺/Ga³⁺ incorporation [10,5]. Therefore, the changes in the reducibility of ZnO with the variation in the Ga concentration observed in the calcined precursors may be related with variations in the contacts CuO-ZnO and/or changes in the partial substitution of Al and Ga in the ZnO lattice derived from the varying proportion of Al and Ga incorporated. Studies in literature report the relative better promoter effect of Al³⁺ than Ga³⁺ in redox properties of ZnO which is in line with the lower reducibility of ZnO with the increase in the Ga observed in this study with the exception of the sample with lower Ga substitution (CZ-Al-0.66-Ga-0.33) that shows higher hydrogen consumption probably related with improvements in the contacts CuO-ZnO developed for this specific Al/Ga ratio.

Table 5. Quantitative data from temperature-programmed reduction of calcined precursors.

	Peak I^a T (°C)	Peak II^a T (°C)	H₂ consumption mmol H₂/g_{cat}
CZ	135 (1.5)	150 (60) 163 (38.5)	8.85
CZ-Al-1-Ga-0	156 (2.2)	176 (97.8)	8.68
CZ-Al-0.66-Ga-0.33	151 (3.4)	170 (96.6)	9.06
CZ-Al-0.5-Ga-0.5	150 (4.0)	170 (67.2) 177 (28.8)	7.91
CZ-Al-0-Ga-1	149 (4.2)	169 (57.5) 173 (38.3)	8.11

^a Peaks obtained from the mathematical deconvolution used for the quantification of H₂ consumption. The percentage of each peak to the total H₂ consumption is given in parenthesis.

Nanostructured changes in reduced CZ and CZ-Al-x-Ga-y catalysts were elucidated by X-ray diffraction. All reduced catalysts shows diffraction peaks corresponding to reflections of metallic Cu and ZnO phases (Fig. 8). Small peak corresponding to CuO was also observed in the CZ and CZ-Al-0.66-Ga-0.33 samples. No other diffraction peaks corresponding to phases containing Ga or Al were detected. Both particle size and micro strain of metallic Cu in reduced CZ-Al-x-Ga-y catalysts were calculated from the broadening of the Cu 111 peak (Table 6). The copper particle size in reduced CZ reference was much higher than in the case of the CZ-Al-x-Ga-y. The reduced catalysts with different Ga loading show similar development of crystalline copper domains without significant differences in its size (around 7.5 nm, similar to the typical size in commercial methanol synthesis catalysts [34]). Investigations on Cu-ZnO catalysts have suggested that defects and lattice strain in the Cu particles affect the intrinsic activity of the Cu surfaces [3]. To obtain qualitative information about defects and lattice strain in the Cu particles, the stacking fault was calculated from XRD profiles of reduced catalysts (Table 6). It is observed similar stacking fault in the Cu particles of CZ-Al-x-Ga-y catalysts indicating similarity in defects and lattice of their metallic Cu particles.

Fig. 8. XRD patterns of reduced catalysts: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (3) CZ-Al-0-Ga-1 (■ ZnO, ○ CuO).

TEM analysis gave further insights into the nanostructure of CZ-Al-x-Ga-y reduced catalysts. The representative TEM micrographs (Fig. 9) show that there are not significant differences in the nano-structuration of copper and ZnO among the CZ-Al-x-Ga-y reduced catalysts. The dark spots that appear in the TEM micrographs are caused by the superposition of several layers catalysts particles which generate darker areas with less defined edges. All reduced catalysts show roundish copper metallic particles distributed over small ZnO aggregates which act as spacers of the metallic particles with some of the copper particles epitaxially covered with ZnO species (arrows in Fig. 9). Metallic copper particle sizes determined by TEM (6–8 nm, Table 6) were similar to the crystalline particle size determined

by XRD indicating that the copper particles were mainly mono-crystalline. No other visible segregated phases containing Ga were detected.

Table 6. Copper crystalline domain size (XRD)^a, particle size (TEM)^b and copper surface area (N₂O chemisorption) of reduced catalysts.

	Cu Crystalline domain size ^a (nm)	Cu crystalline stacking fault ^a	Cu particle size ^b (nm)	N ₂ O chemisorption capacity (μmol/g _{cat})	Cu surface area N ₂ O (m ² /g _{cat})
CZ	> 15		--	123	10.1
CZ-Al-1-Ga-0	7.5	0.033	6	239	19.6
CZ-Al-0.66-Ga-0.33	7.3	0.034	6.8	245	20.1
CZ-Al-0.5-Ga-0.5	7.5	0.033	6	184	15.1
CZ-Al-0-Ga-1	7.8	0.035	7.3	203	16.6

The chemisorption with N₂O assuming the stoichiometry Cu/N₂O = 2 is the established method to measure the copper surface area in Cu/ZnO based catalysts and therefore we applied this method as standard to measure the copper surface area in the CZ and CZ-Al-x-Ga reduced catalysts (Table 6). The Cu surface area of the reduced catalysts revealed a maximum (around 20 m²/g) for the samples CZ-Al-1-Ga-0 and CZ-Al-0.66-Ga-0.33. For the catalysts with higher Ga content (CZ-Al-0.5-Ga-0.5 and CZ-Al-0-Ga1) the surface area drops to 15-16 m²/g. The trend in the surface area does not correlate with the size and nanostructure of the metallic copper particles in the reduced catalysts determined by TEM. This fact can be explained with recent findings about the nature of the Cu-ZnO interactions [35] which propose that the established method for the characterization of copper surface area of methanol synthesis catalysts based on N₂O chemisorption does in fact not only describe the copper surface area, but also the oxygen defects which are present at the copper zinc interfaces. This is confirmed by the strong parallel trend observed between N₂O chemisorption capacity (Table 6) and the reducibility of catalysts derived from TPR (Table 4).

Fig. 9. TEM micrographs of reduced catalysts: (a) CZ-Al-1-Ga-0, (b) CZ-Al-0.66-Ga-0.33 (c) CZ-Al-0.5-Ga-0.5 and (d) CZ-Al-0-Ga-1.

3.3. Activity in methanol synthesis

Fig. 10 reports the activity data (CO conversion and methanol productivity) corresponding to the methanol synthesis reaction from syngas over the reduced catalysts. All CZ-Al-x-Ga-y catalysts show syngas conversion (Fig. 10 a) much higher than that obtained with the undoped CZ reference which is in agreement with the known effect of Ga and Al to promote the catalytic performance of Cu/ZnO for methanol synthesis [10,12]. The CZ and CZ-Al-x-Ga-y catalysts show methanol selectivity beyond 99% without DME formation. Among the CZ-Al-x-Ga-y catalysts significant differences in methanol productivity (Fig. 10 b) were observed in function of the Ga concentration in the samples. In this regard the catalysts monosubstituted with Al or Ga show similar methanol productivity (around $810 \mu\text{mol}_{\text{CH}_3\text{OH}}/\text{min g}_{\text{cat}}$) while the catalysts co-substituted with Al and Ga (CZ-Al-0.66-Ga-0.33 and CZ-Al-0.5-Ga-0.5) show higher production rates (around $900 \mu\text{mol}_{\text{CH}_3\text{OH}}/\text{min g}_{\text{cat}}$).

Fig. 10. Catalytic activity in methanol synthesis from syngas: (a) CO conversion and (b) methanol productivity over CZ and CZ-Al-x-Ga-y catalysts: CZ (*) CZ-Al-1-Ga-0 (■), CZ-Al-0.66-Ga-0.33 (●) CZ-Al-0.5-Ga-0.5 (▼) and CZ-Al-0-Ga-1 (◆).

The CZ-Al-x-Ga-y catalysts show a stable behaviour with time-on-stream in contrast with the CZ reference which shows strong deactivation (Fig. 10 a) in agreement with the promoting effect of Al/Ga in the stability of Cu/ZnO catalysts described in the literature [9]. For copper based catalysts sintering and oxidation is often described as one of the main reasons for catalyst deactivation. XRD patterns of the used CZ and CZ-Al-x-Ga-y catalysts are shown in Fig. 11. In all used samples partial copper re-oxidation and segregation of the Cu and Zn phases can be observed. No simple relationship was found in used CZ and CZ-Al-x-Ga-y catalysts between the extent of copper sintering and/or oxidation and their stability indicating that the deactivation mechanisms in the catalysts are much more complicated and can hardly be described as pure sintering/oxidation processes.

The intrinsic activity of CZ-Al-x-Ga-y catalysts calculated by normalizing its activity to the N₂O chemisorption capacity is depicted in Fig. 12. It can be seen that the intrinsic activity is higher for catalysts which contain Ga, reaching the maximum intrinsic activity the sample co-substituted with equal amounts of Al and Ga. The promoting effect of Al and Ga on the Cu/ZnO catalysts is well-known in the literature but an increase in activity observed after Al and Ga incorporation into ZnO structure is a new finding suggesting that some type of cooperation between both elements might exist resulting in an additional promotional effect.

Fig. 11. XRD patterns of used catalysts: (a) CZ, (b) CZ-Al-1-Ga-0, (c) CZ-Al-0.66-Ga-0.33 (d) CZ-Al-0.5-Ga-0.5 and (e) CZ-Al-0-Ga-1 (■ ZnO, ○ CuO).

Fig. 12. Intrinsic activity for methanol synthesis of CZ and CZ-Al-x-Ga-y catalysts.

4. Discussion

The promotional effect of Al and Ga over Cu/ZnO catalysts is not fully understood in the literature and it remains unclear if these ions act as structure promoters (increasing the surface area and the dispersion of the Cu particles) or as electronic promoters (changing the nature of the active site). Behrens et al. [9] and Li et al. [12] propose that the effect of the Al and Ga promoters, in concentration similar to that used in our study, combines both the structural and electronic promotion. In addition to the structural promotion, the electronic promotion is also produced by Al and Ga and is related with the doping of ZnO with these ions which promote the reducibility and contact with copper affecting its intrinsic activity [12]. The XRD of CZ-Al-x-Ga-y precipitates (Fig. 1) show the formation of Zn malachite structures with high degree of insertion of Zn that enables a similar micro-structuration and distribution of the CuO and ZnO species after calcination as the XRD patterns (Fig. 4) and

surface area (Table 3) of calcined precursors showed. On the basis of these results one can expect similar structural promotion effect on all CZ-Al-x-Ga-y catalysts giving rise to a more or less similar exposition of the reduced copper particles. Accordingly the TEM images (Fig. 9) show similar size and nano-structuration of copper and ZnO particles on all reduced CZ-Al-x-Ga-y catalysts. The size and nanostructure of the metallic copper particles determined by TEM do not correlate with the values of copper surface area determined by N₂O chemisorption (Table 6) because the latter, as stated earlier, not only describe the copper surface area but also the oxygen defects which are present at the copper zinc interfaces [35]. Therefore, the differences in CZ-Al-x-Ga-y samples determined by N₂O chemisorption seem to indicate that Ga and Al in CZ-Al-x-Ga-y samples also act as elements which modify, in a different way, the defect chemistry and redox properties of ZnO. The modification of the redox properties of ZnO could be derived from the partial substitution of Zn²⁺ ions by Al³⁺/Ga³⁺ because this kind of substitution is well-known that strongly affect the redox behaviour of ZnO [36]. According to the observations of Behrens et al. [9] the atomic distribution of Al³⁺ and Ga³⁺ ions into the malachite precipitates could facilitate the modification of ZnO by the partial substitution of Zn²⁺ with Al³⁺ or Ga³⁺. In our case the XRD of the CZ-Al-x-Ga-y precipitates suggest the incorporation of Al³⁺/Ga³⁺ ions into the zinc malachite precursors according to the d₂₀₋₁ space values (Table 2) which was slightly higher when Al and Ga were co-loaded respect to the samples loaded with Al or Ga individually. TPR data of CZ-Al-x-Ga-y calcined precursors (Fig. 7) show evident differences in the reducibility of ZnO in contact with CuO which are consistent with the different incorporation of Al³⁺/Ga³⁺ into the malachite structures as previously discussed. There is agreement that the activity of Cu-ZnO catalysts for methanol synthesis is related with the close interaction between metallic Cu and Zn species (Cu dispersion, changes in shape, lattice strain and defects in the Cu particles and SMSI effect). The difference in the activities of CZ-Al-x-Ga-y catalysts normalized by N₂O chemisorption (Fig. 12) point to a different participation of the copper surfaces in combination with the defect sites of ZnO depending on the Al and Ga loading.

The intrinsic activities of the CZ-Al-x-Ga-y catalysts co-loaded with Al and Ga show different values depending on the Ga/Al ratio (Fig. 12). The sample with lower Ga/Al ratio, CuZn-Al-0.66-Ga-0.33, shows an intrinsic activity similar to that expected from the combination of the activity of the individual Al and Ga promoters. However the sample co-loaded with equal Ga and Al amount (CuZn-Al-0.5-Ga-0.5) shows a marked improvement in the intrinsic activity respect to the individual Al and Ga promoters which indicates changes in the type of the Cu-ZnO contacts producing sites of higher activity. Although the exact origin and nature of this improvement is nontrivial from results presented here, the special reducibility behaviour observed in the CuZn-Al-0.5-Ga-0.5 catalyst, indicative of a different speciation of the CuO in contact with ZnO, may be helpful to rationalize the activity behavior of this sample.

The TPR profile of the CuZn-Al-0.5-Ga-0.5 with two overlapped reduction peaks (Fig. 7) implies the existence of different CuO species in contact with ZnO with different

degree of cross-substitution $\text{Zn}^{2+}/\text{Al}^{3+}/\text{Ga}^{3+}$ than that obtained in the rest of the samples of the series. This fact seems to be linked to the increase of the insertion of the Ga^{3+} into the malachite structure observed in the precipitates of the co-promoted sample respect to the monopromoted counterparts. The precise implication of these species in the observed improvement of the intrinsic activity is not easy to find because the high complexity of the ternary system $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ but we can hypothesize changes in ZnO defects with the substitution $\text{Zn}^{2+}/\text{Al}^{3+}/\text{Ga}^{3+}$ achieved in the sample co-loaded with equal Ga and Al amount which leads to a different surface contact between Cu and reduced ZnO which translates in sites with higher activity for methanol synthesis. In this respect it would be interesting to quantify these defects according to the methodology established by Fitchl et al [37] by combining H_2 -TPD and N_2O -RFC measurements but it was not available for this study. Although we have not been able to quantify the changes in the ZnO defects, their variation, evidenced by the special reducibility behavior of the sample co-loaded with equal amount of Ga and Al in comparison with its Cu surface area by N_2O and Cu particle size by TEM, is a reasonable hypothesis which as mentioned above should be corroborated with additional characterization to quantify the ZnO defects.

5. Conclusions

The modification of the structure and activity of Cu/ZnO catalysts with the co-modification with Al and Ga (CZ-Al-x-Ga-y, $x/y = 1/0, 0.66/0.33, 0.50/0.50$ and $0/1$) was investigated. The influence of co-loading was studied in all stage of synthesis of catalysts: precipitate, calcined precursors and reduced catalysts. Characterization of precipitates shows that co-modification with Al^{3+} and Ga^{3+} slightly increases the insertion of Ga into malachite precipitates respect to the monosubstituted counterparts. The CZ-Al-x-Ga-y samples show similar micro-structuration and distribution of the CuO and ZnO species after calcination but the TPR data show evident differences in the reducibility of ZnO species in contact with CuO related with differences in the partial substitution of Zn^{2+} by $\text{Al}^{3+}/\text{Ga}^{3+}$ after the calcination of the precursors. The intrinsic activities of CZ-Al-x-Ga-y catalysts normalized by N_2O chemisorption capacity point to a different participation of the copper surfaces in combination with the defect sites of ZnO depending on the Al and Ga loading. The sample with lower Ga/Al ratio, CuZn-Al-0.66-Ga-0.33, shows an intrinsic activity similar to that expected from the combination of the activity of the individual Al and Ga promoters, however the sample co-modified with equal Ga and Al amount, CuZn-Al-0.5-Ga-0.5, shows a marked improvement in the intrinsic activity respect to the individual Al and Ga promoters. The improvement in activity was hypothesized to be related with changes in the ZnO defects with the substitution $\text{Zn}^{2+}/\text{Al}^{3+}/\text{Ga}^{3+}$ achieved with the sample co-loaded with equal Ga and Al amount, which leads a different surface contact between Cu and reduced ZnO which translates in sites with higher activity for methanol synthesis.

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