Ni₅Ga₃ catalysts for CO₂ reduction to methanol: exploring the role of Ga surface oxidation/reductions on catalytic activity

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Abstract

A δ -Ni₅Ga₃/SiO₂ catalyst, which is highly active and stable for thermal CO₂ hydrogenation to methanol, was investigated to understand its surface dynamics during reaction conditions. The catalyst was prepared, tested and characterized using a multitude of techniques, including ex-situ XRD (X-ray Diffraction), TEM (Transmission Electron Microscopy), H₂-TPR (Temperature programmed Reduction), CO chemisorption, along with in-situ ETEM (Environmental Transmission Electron Microscopy), APXPS (Ambient Pressure X-ray Photoelectron Spectroscopy) and HERFD-XAS (High Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy). Upon air exposure Ga migrates from the subsurface region to the surface of the nanoparticles forming a Ga-oxide shell surrounding a metallic core. The oxide shell can be reduced completely only at high temperatures (above 600 °C); the temperature of the reducing activation treatment plays a crucial role on the catalytic activity. HERFD-XAS and APXPS measurements show that an amorphous Ga₂O₃ shell persists during catalysis after low temperature reductions, promoting methanol synthesis.

Keywords

Ni-Ga, intermetallic, methanol synthesis, in-situ characterization, Ga₂O₃, CO₂ utilization

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1 Introduction

Anthropogenic CO₂ production has been linked to serious effects on the globe including climate change, sea level rise, and ocean acidification, among others[1]. CO₂ capture, storage and utilization schemes have been widely proposed as potential solutions to sufficiently lower CO₂ emissions and mitigate these consequences. Converting CO₂ from the atmosphere or from point sources into value added carbon-based products is one such strategy. A number of approaches to CO₂ conversion require the use of a reducing co-reactant such as hydrogen, ideally produced with minimal CO₂ emissions, e.g. renewable hydrogen obtained from wind or solar power, unlike the case in conventional hydrogen production which is a major CO₂ emitter[2, 3]. Developing new processes that can be employed as distributed facilities that utilize renewably produced hydrogen to upgrade CO₂ from point sources could have a substantial impact on lowering global CO₂ emissions. Methanol is a particularly attractive target for sustainable pathways to CO₂ upgrading given its large-scale demand (approx. 10¹¹ kg/yr), a platform chemical readily converted to a broad range of other molecules; arguments for an economy relying heavily on methanol, where methanol also serves as liquid transportation fuel have also been proposed[4, 5]. New catalysts are needed to enable such processes, catalysts with suppressed CO production and high activity at atmospheric pressure.

The current commercial process for methanol synthesis from syngas (CO/CO₂/H₂) involves a Cu/ZnO/Al₂O₃ catalyst operating at temperatures of 513-533 K and pressures in the range 50-100 bar.[6] The Cu/ZnO/Al₂O₃ catalyst used in the commercial process has been optimized for a feed composition consisting largely of CO and H₂, with small amounts of CO₂ (<10%). CO₂ concentration has been found by many researchers to have a marked impact on catalyst performance, with a certain amount being crucial to form H₂O via the reverse water gas shift reaction, that in turn converts CO to CO₂ via the water gas shift reaction to obtain favorable activity towards methanol[7, 8]. However, greater amounts of CO₂ in the feed result in less than optimum methanol yields, deactivation due to increased water production, and conditions favoring the reverse water gas shift reaction, which reduces selectivity to methanol[7-9]. This in large part motivates research into catalysts with improved performance in hydrogenating CO₂-rich feeds to methanol.

In the case of CO₂ hydrogenation, the methanol synthesis reaction (1) competes with reverse water gas shift (2).

Water is produced as byproduct in both reactions and poses a potential deactivation problem at high conversions[9]. In terms of reaction kinetics, the coverage of the methanol intermediate, bidentate formate, poses a restriction on the maximum rate that can be attained due to the high binding energy typically observed on metal surfaces[7].

Catalysts with high activity for CO₂ hydrogenation to methanol and selectivity over the reverse water gas shift reaction need to be developed for large scale CO₂ to methanol schemes. Bimetallic catalysts are attractive because they can allow for catalytic properties to be fine-tuned by modifying the active sites and neighboring atoms and hence modifying the binding strength of reactive intermediates [10-13]. For example, due to the issues

involving CO₂ noted above, copper alone is not an active catalyst for CO₂ hydrogenation to methanol, active only for CO hydrogenation; the bimetallic nature of the Cu-Zn sites in the commercial Cu/ZnO/Al₂O₃ catalyst, however, yields high activities for CO₂ hydrogenation to methanol [7, 14]. The Cu-Zn system is one of many catalyst systems that leverage bimetallic synergies to achieve improved selectivity in methanol synthesis from CO₂; related bimetallics include Pd-Cu[15-18], Ni-Cu[19-21], Ag-Cu[22, 23], Pt-Cu[24], Pd-Ga[25-28], Pd-Zn[18], Pd-In[29-32], and Rh-W[33].

In the work described herein, we focus on a Ni-Ga intermetallic catalyst recently developed using insights from density functional theory (DFT), microkinetic modeling and experimental testing and ex-situ characterization of the intermetallic phase[34]. The Ni₅Ga₃ phase was found to outperform Cu/ZnO/Al₂O₃ in terms of both activity and selectivity towards methanol, while operating at atmospheric pressure[34]. Since the Ni₅Ga₃ bulk phase was found to be the most active and selective composition[34] subsequent work has focused on synthesis and characterization of this active phase[35, 36]. In this work we synthesize Ni₅Ga₃ catalysts for CO₂ hydrogenation to methanol and employ ex-situ and in-situ characterization techniques to understand the redox behavior of Ga, studying its effects on catalytic activity. We investigate changes in Ga oxidation state and surface composition under catalytically relevant conditions using AP-XPS and environmental TEM.

One key aspect of bimetallic materials for methanol synthesis involves the formation of surface and bulk oxides, an area that has been debated widely for many catalysts, including the commercial Cu-Zn system [37-39]. Regarding the Cu/CeO₂/TiO₂ catalyst, metal/metal oxide synergy is proposed to result in a completely different pathway for CO₂ hydrogenation by stabilizing a carbonate intermediate[40]. For Pd-Ga catalysts, the presence of a Ga₂O₃ phase has been correlated to high methanol synthesis activity[26] whereas in other cases an amorphous gallium oxide phase has been described as an inactive component, thus requiring a reduction treatment to activate the catalyst[28]. A mechanism has also been proposed based on surface science studies where Pd-Ga is suggested to supply dissociated hydrogen to hydrogenate carbonaceous species adsorbed on Ga₂O₃[41]. The role of oxide formation is also unclear in the Pd-In system for CO₂ hydrogenation. In the Pd/In₂O₃ system both Pd-In and In₂O₃ with O-vacancy sites have been suggested to be critical for high activity in methanol synthesis from CO₂[29, 31]. In a different study no correlation was found between surface In₂O₃ concentration and catalytic activity for CO₂ hydrogenation to methanol[30]. Given the recent interest in Ni-Ga as a highly active methanol synthesis catalyst and the potentially complicated effects of oxide formation on catalytic activity, understanding the formation of bimetallic and oxidic sites under relevant methanol synthesis conditions is of great interest for this catalyst.

The nature of the active site for bimetallic catalysts can be investigated through systematic in-situ and operando studies employing spectroscopy and microscopy under conditions that approach and/or reach true reaction conditions. Herein we investigate the Ni-Ga system for CO₂ hydrogenation to methanol and characterize various bimetallic and oxidic phases present upon catalyst reduction/activation as well as during reaction, employing in-situ TEM, AP-XPS, and ex-situ XRD. We observe the formation of a Ga₂O₃ shell on Ni-Ga particles upon air exposure, which can be reduced completely in hydrogen at a temperature of 700°C. The role of the Ga₂O₃ is complex, leading to both a shell formation over the bimetallic particles as well as creating a Ga rich surface. The results

from catalyst evaluation are interpreted using information gathered from in-situ spectroscopy and microscopy.

2 Experimental

2.1 Catalyst synthesis

Powder samples were synthesized according to previously reported procedures[34]. Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Sigma Aldrich) were dissolved in MQ water in order to obtain a Ni/Ga ratio of 5/3 (total metal loading 17 wt %). Once the inorganic precursors were completely dissolved, the sample was synthesized by incipient wetness impregnation using Silica gel (Davison Perkasil SM 660) as the support and subsequently dried at 100°C. With an aim of understanding how different activation processes affect the catalyst and its resulting performance, four types of catalyst activation procedures were employed for the catalyst powders in this study:

- An ex-situ activation treatment that immediately followed impregnation and drying; samples were placed in a tubular furnace under flowing hydrogen at 700 °C for 2 hours (ramp rate: 5 °C/min). This procedure was employed on most catalysts studied herein (as noted below), generally followed by other activation procedures with the exception of catalysts that serve as a baseline. Such samples will be labeled ‘ex-situ(700°C)’. The sample was stored in air at ambient temperature for 2-4 days before further treatments and analysis.
- An ex-situ activation treatment as described above, followed by in-situ activation in an environmental transmission electron microscopy (ETEM) Details on this in-situ activation/reduction step are provided in the microscopy section below.
- An ex-situ activation treatment as described above, followed by in-situ activation in a fixed-bed reactor immediately prior to catalyst studies for CO_2 hydrogenation to methanol or in temperature programmed reduction (TPR) studies. Four distinct temperatures were explored for this in-situ activation (200 °C, 400 °C, and 680 °C), with further details provided below in the catalysis section. Such samples will be labeled ‘ex-situ(700°C)/in-situ(200°C)’, ‘ex-situ(700°C)/in-situ(400°C)’, and ‘ex-situ(700°C)/in-situ(680°C)’.
- Skipping the ex-situ activation treatment after impregnation and drying, in order to investigate the effects of a single, in-situ activation treatment at 680 °C in the fixed-bed reactor immediately prior to CO_2 hydrogenation. Such samples will be labeled ‘in-situ(680°C)’.

All powder catalysts were pressed into pellets, crushed, and sieved to a fraction between 180-300 microns as part of their final preparation and stored in air prior to any in-situ activation/reduction steps involved in the ETEM, TPR, or catalysis studies.

For ambient pressure X-ray photoelectron spectroscopy (APXPS) studies, a thin film of the catalyst was synthesized by modifying a procedure reported previously[42]. Ni and Ga inorganic precursors were dissolved into MQ water (5 ml) and slowly dropcast onto a degenerately doped Si support (n+ Si (100) As-doped 0.001-0.004 Ω cm) held at 120°C in order to obtain a visually homogeneous coating. The sample was subsequently given an ex-situ activation treatment by flowing hydrogen at 700°C for 30 minutes in a tubular furnace. The sample then underwent an in-situ activation step, with details provided in the spectroscopy section below.

2.2 Catalytic Testing

CO₂ hydrogenation experiments were carried out in a glass-lined stainless steel tubular fixed-bed reactor (BenchCAT 4000HP, Altamira Instruments). Ultra high purity (UHP) hydrogen with a 2% Argon internal standard, UHP carbon dioxide, and UHP Nitrogen (Airgas) were used as reactant gases and purge gas respectively. Prior to all CO₂ hydrogenation experiments involving powder catalysts, the samples were pre-treated with an activation step, flowing hydrogen (30 sccm) at 1 atmosphere pressure for 1 hour at 200 °C, 400 °C, or 680 °C.

For the temperature survey 0.20 grams of catalyst were loaded into the tubular reactor. CO₂ hydrogenation steps were conducted with 40 sccm of a 3:1 CO₂:H₂ mixture at 1 bar and the designated temperatures (GHSV = 8000 hr⁻¹).

For the stability tests 0.10 grams of catalyst were used. CO₂ hydrogenation steps were conducted with 20 sccm of a 3:1 CO₂:H₂ mixture at 250°C and 5 bar (GHSV = 7500 hr⁻¹).

The product stream was analyzed by GC-MS (Agilent 7890B & 5977A).

2.3 Catalyst Characterization

Two types of transmission electron microscopy (TEM) instruments were used to characterize the catalysts. For ex-situ TEM studies, where catalysts were imaged before and after testing, an FEI Tecnai G2 F20 X-TWIN operating at 200 kV accelerating voltage was employed. TEM samples were prepared in air by dispersing the catalyst powder in methanol and dropping onto lacey carbon grids. ETEM (Environmental Transmission Electron Microscopy) data were collected at EMSL-PNNL using environmental aberration corrected FEI Titan 80-300 Environmental Transmission Electron Microscope. The instrument is equipped with CEOS aberration corrector, which allows for sub-angstrom imaging. The images were recorded using Gatan's UltraScan 1000 CCD camera. The Ni₅Ga₃/SiO₂ sample were activated in a tubular furnace at 700 °C in H₂ prior to loading to Protochips Aduro's MEMS based heating chips, and imaging at 400°C and 700°C under H₂ atmosphere (2 torr).

X-ray diffraction (XRD) was collected on a PANalytical X'Pert Pro diffractometer using Cu K α radiation.

CO chemisorption and temperature programmed reduction (TPR) data were collected using a custom analytical reactor (BenchCAT 1000RHP, Altamira Instruments). Prior to CO pulsed chemisorption, samples were reduced under identical conditions to the catalytic testing. 10% CO/He was then pulsed over the sample at 25 °C until saturation. TPR measurements were collected under a 30 sccm flow of 10% H₂/Ar.

The APXPS data were collected on BL 11.0.2 at ALS (Advanced Light Source) using a pass energy of 20 eV. After the ex-situ activation at 700°C, the sample was mounted on the high temperature in-situ heater present at BL 11.0.2 and heated (10°C/min) to either 650°C or 400°C under H₂ (10 torr) for activation. After 30 minutes the sample was cooled down to 200°C decreasing the H₂ pressure to 2.5 torr and XPS data were collected. The data were collected at different incident photon energies and the Ni 3p and Ga 3d region intensities were used for depth profile analysis after normalization for inelastic mean free

paths (IMFPs) and photoemission cross sections[43, 44]. Fit of the high resolution regions were performed using the CasaXPS software, utilizing a Shirley background. An asymmetric curve shape was used for metallic peaks, after optimizing the line shape on the sample reduced at high temperature; a convolution of Lorentzian and Gaussian line shapes were used for oxidized species. The peak area ratio of the Ga 3d_{3/2} and 3d_{5/2} doublet was constrained to 2:3 and the same FWHM used during the fit was employed for all Ga lines. The adventitious carbon signal was used for calibration of binding energies with a value of 284.8 eV.

HERFD-XAS data at Ga K-edge (10367 eV) were collected on BL 6-2 at SSRL (Stanford Synchrotron Radiation Lightsource) using 2 Si(100) crystals for Ga K α emission line with an energy resolution of 2.17 eV on the elastic peak at 9.2525 keV using a Si(111) mono crystal. The in-situ measurement was performed replicating the same conditions of the catalytic tests by means of an in-situ/operando set-up composed by a gas manifold, a Be tube reactor and a heater as previously described[31, 45].

3 Results

3.1 Catalytic tests

We evaluated the effect of four different activation conditions on the catalytic activity for CO₂ reduction to methanol at atmospheric pressure, Figure 1. One objective of the present work is to understand the effects of catalyst exposure to air, recognizing that after formation of the desired Ni₅Ga₃ phase via ex-situ activation at 700 °C, air exposure would likely re-oxidize the surface and have an effect on the bimetallic nanoparticle's bulk structure, surface structure, and hence catalytic performance. After ex-situ activation at 700 °C, 3 Ni₅Ga₃ samples were tested in a fixed-bed reactor after receiving an additional in-situ activation at 200 °C, 400 °C and 680 °C, respectively. A fourth sibling sample was also tested after skipping the ex-situ activation (700°C) and receiving only the in-situ activation at 680 °C. Figure 1 shows the activity (a) and selectivity (b) towards methanol at a pressure of 1 bar in the fixed-bed reactor operating at 200 °C, 250 °C and 300 °C, as a function of the four different activation treatments.

All CO₂ hydrogenation experiments revealed methanol (MeOH) and CO as the main products, accounting for more than 98.5% of the total selectivity. The remaining 1.5% was predominantly methane and dimethyl ether. At a reaction temperature of 200°C, clear trends in catalytic performance are observed for the samples prepared with four different activation treatments. The ex-situ(700°C)/in-situ(200°C) sample shows poor performance for methanol synthesis, exhibiting an activity of approx. 2.95 mol_{MeOH}/(m²·hr) and a CO/methanol ratio of 8. The other three samples, ex-situ(700°C)/in-situ(400°C), ex-situ(700°C)/in-situ(680°C), and in-situ(680°C), all show substantially higher activity and selectivity for methanol, approximately 11.5-16.5 mol_{MeOH}/(m²·hr) and 1-1.5 CO/methanol ratio in each case, with the in-situ(680°C) sample being the least active of the three. These findings indicate that modification of the catalyst surface takes place upon air exposure and a catalytically more active phase is created as a result.

The trends among the four samples are similar at a higher reaction temperature of 250 °C, albeit with each sample showing higher activity and lower selectivity than it had at 200 °C. The ex-situ(700°C)/in-situ(200°C) sample again shows poor performance for methanol synthesis, its activity reaching only 4.3 μ mol_{MeOH}/(m²·hr) while reverse water

gas shift (rWGS) increases considerably ($\text{CO}/\text{methanol}=20$). The other three samples, ex-situ(700°C)/in-situ(400°C), ex-situ(700°C)/in-situ(680°C), and in-situ(680°C), all show substantially higher activity for methanol production, $32.3 \mu\text{mol}_{\text{MeOH}}/(\text{m}^2 \cdot \text{hr})$, $29.6 \mu\text{mol}_{\text{MeOH}}/(\text{m}^2 \cdot \text{hr})$ and $26.4 \mu\text{mol}_{\text{MeOH}}/(\text{m}^2 \cdot \text{hr})$, respectively, with a moderate increase of rWGS. At a reaction temperature of 300°C , all samples showed marked decreases in both activity and methanol selectivity compared to their performance at either 200°C or 250°C . While ex-situ(700°C)/in-situ(400°C), ex-situ(700°C)/in-situ(680°C) show comparable activity of $5 \mu\text{mol}_{\text{MeOH}}/(\text{m}^2 \cdot \text{hr})$, in-situ(680°C) maintain a higher activity due to lower rWGS activity at high temperature. In comparing the catalysts' performance (Table 1) to that previously reported for bimetallic Ni_5Ga_3 on silica, we observe our methanol activity trend shift towards higher temperature, indicating a possible enrichment of Ga at the catalyst surface for our catalyst system[34, 35]. Indeed, previous studies reported a methanol activity at 250°C of $0.06 \text{ mol}_{\text{MeOH}}/(\text{mol}_{\text{active metal}} \cdot \text{hr})$ and $0.025 \text{ mol}_{\text{MeOH}}/(\text{mol}_{\text{active metal}} \cdot \text{hr})$ for $\text{Ni}_5\text{Ga}_3/\text{SiO}_2$ and $\text{CuZnO}/\text{Al}_2\text{O}_3$, respectively, whereas $\text{GaPd}_2/\text{SiO}_2$ showed better activity compared to Ni-based systems, with $72 \mu\text{mol}_{\text{MeOH}}/\text{m}^2/\text{h}$ [46].

Ultimately, the data reported in Figure 1 show that the catalytic performance of the Ni-Ga catalyst strongly depends on activation conditions. The investigations described further below aim to understand the catalyst trends in activity and selectivity.

Figure 1. Activity (a) and selectivity (b) for CO_2 reduction to methanol at 1 bar ($\text{H}_2/\text{CO}_2=3/1$) for air-exposed and in-situ activated $\text{Ni}_5\text{Ga}_3/\text{SiO}_2$. Ex-situ(700°C) sample activated in-situ at 200°C (★), 400°C (▲) and 680°C (●) and in-situ activated sample (in-situ(680°C)) (■).

We investigated the effects of pretreatment conditions on accessible surface Ni sites using CO chemisorption. For the PdGa system, it is well known that CO adsorbs preferentially on exposed Pd rather than on Ga (or Ga_2O_3) sites and the same is true for Ni on Ni-Ga systems[47, 48]; thus we decided to use the same approach to quantify the exposed Ni sites. Despite identical nanoparticles diameters, and therefore specific geometric surface area, a considerable difference in CO chemisorption was detected for all samples (Table 1). Not surprisingly, the highest CO uptakes were measured on catalysts that had undergone the highest temperature in-situ activation treatments, ex-situ(700°C)/in-situ(680°C) and in-situ(680°C), with CO uptakes of 47.3 and $83.2 \mu\text{mol}/\text{g}_{\text{cat}}$, respectively. This finding indicates the presence of a more Ni-rich surface upon increase of in-situ activation temperature after air exposure and in particular after direct in-situ activation.

Notably, the presence of segregated Ni can be excluded as the activity towards methane remains negligible for all catalysts. The ex-situ(700°C)/in-situ(680°C) sample exhibited a lower CO uptake than the in-situ(680°C) sample, despite the additional ex-situ pre-treatment, suggesting that the surface becomes Ga-enriched upon air exposure due to the oxophilic nature of Ga (*vide infra*). Exposure to air after the ex-situ treatment has a pronounced effect, as clearly demonstrated by the CO uptake measurements of the ex-situ(700°C)/in-situ(200°C) and ex-situ(700°C)/in-situ(400°C) samples at 6.1 and 26.5 $\mu\text{mol/g}_{\text{cat}}$, respectively, far below the values for samples receiving in-situ treatments at higher temperatures.

What is notable is that higher CO uptake does not correspond to increased activity and suggests that interplay between surface site accessibility, reducibility of Ga_2O_3 surface layer (*vide infra*) and nature of Ni-Ga sites determines the activity of the final Ni-Ga catalysts. The nature of the surface site is influenced by air-exposure and in-situ activation temperature. Specific activity of the catalysts calculated based on geometric surface area reveal that a highly reduced surface is not the most active (Table 1). In fact, the high specific activity of the ex-situ(700°C)/in-situ(400°C) and ex-situ(700°C)/in-situ(680°C) samples suggest that air exposure creates a Ga enriched surface which promotes specific activity.

Activation	Particles diameter (nm)	^a Specific Activity ($\mu\text{mol}_{\text{MeOH}}/\text{m}^2/\text{h}$)	Activity ($\text{mol}_{\text{MeOH}}/\text{mol}_{\text{Ni+Ga}}/\text{h}$)	CO uptake ($\mu\text{mol}_{\text{CO}}/\text{g}_{\text{cat}}$)
ex-situ(700°C)/in-situ(200°C)	6.9±2.9	4.30	0.020	6.1
ex-situ(700°C)/in-situ(400°C)	6.5±3.0	32.3	0.150	26.5
ex-situ(700°C)/in-situ(680°C)	6.8±2.7	29.6	0.141	47.3
in-situ(680°C)	6.8±2.6	26.4	0.129	83.2

Table 1. Activity and specific activity at 250°C, as well as number weighted-average particle diameter and CO uptake for different activation conditions.^a Defined as activity per geometric area derived from the value of a surface-weighted average diameter evaluated by TEM (spherical particles)[49].

3.2 Catalyst characterization

To begin probing the catalyst phases present before and after catalysis, ex-situ x-ray diffraction was conducted. The XRD pattern (Figure 2) of the as-synthesized sample, ex-situ(700°C), primarily showed a bulk $\delta\text{-Ni}_5\text{Ga}_3$ phase. In a previous study this phase has been associated with the highest activity for CO_2 hydrogenation to methanol at atmospheric pressure; the post-run XRD analysis showed the emergence of an $\alpha\text{-Ni}_3\text{Ga}$ phase as well [34]. This is consistent with the post-run XRD analysis of the higher-performing samples in our study – ex-situ(700°C)/in-situ(400°C), ex-situ(700°C)/in-situ(680°C), and in-situ(680°C) – as they showed that during catalysis a mixture of Ni_5Ga_3 and Ni_3Ga had formed. A previous work investigating Ni/Ga intermetallic nanoparticles for methanol synthesis found that in-situ activation alone, in hydrogen and above 600°C,

could in some cases form a mixed phase of 80% Ni_5Ga_3 and 20 % Ni_3Ga [35]. In our case, the mixed phase was only observed after catalytic evaluation for CO_2 hydrogenation. In order to account for a nominal overall Ni/Ga stoichiometry of 5/3, the formation of a Ni_3Ga phase necessitates the formation of either a Ga rich phase (e.g. NiGa) or gallium oxide (e.g. Ga_2O_3), though neither was detectable by XRD indicating phases that may be amorphous, of low crystallinity, and/or are crystalline with very small nano-scale dimensions.

Figure 2. XRD analysis of $\text{Ni}_5\text{Ga}_3/\text{SiO}_2$ catalysts for different activation conditions.

Temperature programmed reduction (TPR) was performed on the ex-situ(700°C) sample to understand changes occurring during in-situ activation. Results of TPR analysis on the ex-situ(700°C) sample are shown in Figure 3. We qualitatively analyzed the TPR results at first comparing the data with literature. Hydrogen consumption above 200°C with three main maxima at 250°C, 370°C and 620°C revealed that oxidized species had clearly formed on the catalyst upon exposure to air after the 700°C ex-situ activation treatment. Since XRD did not reveal any Ni oxide or Ga oxide crystallites for this sample, we conclude that the oxidized species must be forming either a thin layer on the nanoparticles surface or segregating onto the support in ensembles not detectable by XRD[50]. The first reduction peak at 250°C likely arises from the reduction of Ni^{2+} species, as had been previously reported for NiO/Ni structures [51]. The second peak at 370°C might arise from a convolution of the reduction of residual oxidized nickel[52] and oxidized gallium. The reduction of well-dispersed, supported Ga species was previously reported to occur at 600°C[53], however the presence of a second metal active for hydrogen (e.g. Ni) can facilitate the process and lead to a decrease in the temperature required for Ga reduction[54]. Reduction of segregated Ga_2O_3 was not evident in our TPR analysis, as Ga_2O_3 supported on SiO_2 is reported to require reduction temperatures above 650°C[55].

We finally quantitatively analyzed the reduction profile. The analysis, performed by Gaussian curve-fitting of the H₂-TPR profile, shows the presence of 4 main peaks centered at 247°C, 368°C, 398°C and 607°C (Table 2).

Peak	Center (°C)	Area (%)	H ₂ consumption (μmol/g _{cat})	Species
I	247	34	342	NiO (close to M ⁰)
II	368	5	51	NiO
III	398	49	488	Ga ₂ O ₃ (close to M ⁰)
IV	607	12	119	Ga ₂ O ₃

Table 2. H₂-TPR: Curve fitting results.

The two main broad peaks, I and III, that account for most of the hydrogen consumption (83%), can be assigned to the reduction of oxidized Ni (peak I) and oxidized Ga (peak III) in proximity of a reduced metal [51]. As mentioned above, the metallic surface in fact helps the reduction of NiO and Ga₂O₃ through a hydrogen spillover mechanism, lowering the reduction temperature compared to oxide-supported NiO (400°C) and Ga₂O₃ (>650°C). Peaks II and IV represent respectively the reduction of a small fraction of silica-supported NiO and well-dispersed oxidized Ga species that are not assisted by this spillover mechanism [52, 53]. These findings corroborate our AP-XPS and HERFD-XAS results (*vide infra*) that show at 400°C a complete reduction of NiO while maintaining a fraction of oxidized Ga. According to the TPR fitting, higher temperatures are needed for a complete reduction of the oxidized Ga species. Air-exposure of the catalysts does not fully oxidize the Ni and Ga intermetallic, as the total amount of H₂ consumed during TPR accounts for the oxidation of only ca. 1/3 of the total metal loading, based on the following reduction reactions for NiO and Ga₂O₃, respectively:

- 1) NiO + H₂ → Ni + H₂O
- 2) Ga₂O₃ + 3H₂ → 2Ga + 3H₂O

More specifically, the TPR data quantitatively show that 23% of the total Ni atoms and 40% of the total Ga atoms are oxidized upon air-exposure at room temperature. This indeed reflects the higher oxophilicity of Ga that favors its preferential segregation towards the surface when the catalyst is exposed to air. The segregation of Ni and Ga oxides on the surface leaves behind a Ni rich subsurface region where the Ni⁰/Ga⁰ ratio is 3.2, consistent with the presence of the Ni₃Ga phase revealed by XRD. Reduction at 200°C does not significantly affect the fraction of Ga₂O₃ present and is not sufficient for a complete reduction of NiO. When the sample is reduced at 400°C, however, Ni is fully reduced to metal while a fraction of oxidized Ga is still present at the surface. Finally, the higher temperature treatment promotes the complete reduction of the remaining Ga₂O₃ leading to a Ga enriched metallic surface. In conclusion the TPR analysis supports the presence of residual oxidized Ga for the sample ex-situ(700°C)/in-situ(400°C) that is completely reduced only above 600°C (ex-situ(700°C)/in-situ(680°C)).

Figure 3. H₂-TPR analysis of Ni₅Ga₃/SiO₂ catalyst reduced ex-situ in H₂ at 700°C and exposed to air prior the analysis. Data: solid black line; Fit Envelop: dashed red line; Gaussian Peaks: dashed grey lines.

Figure 4 shows TEM analysis (Fig. 4A) of the as-synthesized ex-situ(700°C) sample, particle size distributions of the sample before and after reaction (Fig. 4B), as well as direct ETEM information on the ex-situ(700°C) sample's structural evolution during reduction after a series of treatments in hydrogen (Fig 4c-e). Initially, the as-synthesized ex-situ(700°C) sample showed the presence of a shell surrounding the bimetallic nanoparticles. The difference in contrast between the shell and the core is an indication of surface oxidation as the sample had been exposed to air after the ex-situ reduction treatment. Efforts to remove the oxide shell by exposing the sample to a reducing atmosphere in the ETEM, 2 Torr H₂ at room temperature or H₂ at 400 °C, proved to be insufficient, Fig. 4c and 4d, respectively. In both cases, a shell of thickness of 1-2 nm surrounding a core is clearly visible. These results are consistent with related, previous work on metallic Pd-Ga nanoparticles that changed markedly upon air exposure as HRTEM evidenced an amorphous Ga₂O₃ layer encapsulating a Pd rich core[41]. A similar native oxide-shell was also observed in a prior work by HRTEM for Ni and Ni/Cr nanoparticles upon exposure to air and for the bimetallic nanoparticles the native oxide was enriched with the most oxophilic metal[56].

In-situ reduction of the ex-situ(700°C) Ni-Ga sample at 2 Torr H₂ at 700°C in the ETEM, however, led to a complete disappearance of the shell (Fig. 4e). It is worth noting that the thickness of the oxide shell in the catalyst after activation in pure hydrogen at 1 bar may differ from what is observed during ETEM and APXPS analysis due to the low hydrogen pressure in the in-situ analysis. In the present work no significant change in dispersion was revealed during the in-situ ETEM analysis of NiGa catalysts. Ex-situ TEM analysis shows an identical particle diameter of 6.8 nm for all the samples (Table 1; figure 4B) evidencing how the pretreatment conditions do not influence the dispersion of the active phase and negligible sintering occurs during the test.

Figure 4. TEM (A) and ETEM (C,D,E) images. (A) ex-situ(700°C) Particle size distribution for all catalysts (B). Conditions ETEM : (C) RT (D) 400°C 2 torr H₂; (E) 700°C 2 torr H₂.

In order to further probe the surface of the NiGa catalysts, a model NiGa bimetallic film was studied in presence of H₂ using APXPS. After ex-situ activation at 700°C, XRD confirmed the formation of δ -Ni₅Ga₃ (Fig.SI2), similar to that observed for the nanoparticulate version of the catalyst. The film was then in-situ activated at 400°C and 650°C under H₂ (2.5 torr). The analysis of the 2p_{3/2} region and 3d region for Ga under the H₂ atmosphere revealed substantial differences in the oxidation state that strongly depend on the temperature of the in-situ reduction and proximity to the surface. Figure 5a reveals a substantial amount of Ga₂O₃ (Ga 2p_{3/2} region, peak at 1117.6 eV) on the surface of the sample activated in-situ at 400°C, along with metallic Ga (peak at 1117.0 eV)[26]. These features are consistent with measurements in the Ga 3d region (Fig. 5b), with a doublet typical for metallic Ga, 18.6 eV (3d_{5/2}) and 19.1 eV (3d_{3/2}), [26], and a broader shoulder typical for Ga₂O₃ at 20.2 eV (3d_{5/2}) and 20.6 eV (3d_{3/2}). A small peak at 23 eV for O 2s is also visible[54]. By varying the photon energy from hv=275 eV to hv=850 eV, it is possible to obtain a depth profile of the two observed oxidation states of Ga. Qualitatively the intensity of the Ga₂O₃ doublet substantially decreases from the surface (hv=275 eV; IMFP=0.8 nm) towards the subsurface/bulk of the film (hv=850 eV; IMFP=1.7nm) where a metallic Ga phase is predominant.

Figure 5. Ga 2p_{3/2} (A) and Ga 3d at 200°C after reduction at 400°C (B) and 650°C (C) in H₂ (2.5 torr). Blue line: Ga⁰; green line: Ga₂O₃; red line: fit; black dots: data. Ga 2p_{3/2} measured at photon energy 1290 eV. Ga 3d measured at photon energy 275 eV, 500 eV and 850 eV.

The enrichment of Ga₂O₃ at the surface of the film can be quantified using the APXPS data (Table 3). The measurements in the Ga 2p_{3/2} region reflect an inelastic mean free path (IMFP) of 0.6 nm, similar to the IMFP of 0.8 nm for the Ga 3d region at hv=275 eV; in this surface region the Ga is measured at 52% and 51% metallic, respectively. At higher photon energies reflecting an IMFP of 1.1 (hv=500 eV) and 1.7 nm (hv=850 eV), the metallic Ga reaches 61% and 73%, respectively. The results of the in-situ depth profile analysis clearly show an increase in the amount of Ga⁰ for deeper regions of the film.

Photon Energy (eV)	IMFP ^a (nm)	Ga ⁰ (%)	Ni/Ga
1290	0.6	52 ^b	N/A
275	0.8	51 ^c ; 41 ^d	0.66
500	1.1	61 ^c	0.89
850	1.7	73 ^c	1.51

Table 3. XPS quantitative fit results for Ga in H₂ (2.5 torr) at 400°C. a) for Ga₂O₃; b) fit of Ga 2p_{3/2} region; c) fit of 3d region. d) Upon exposure to CO₂/H₂ (1:3) at 2.5 torr at 200°C.

Upon reduction at 650°C in H₂, the sample is reduced substantially. At all depths and Ga lines, measurements show > 90% metallic Ga. The small % of oxidized Ga could arise from particularly reactive, undercoordinated sites at the surface.

Photon Energy (eV)	IMFP ^a (nm)	Ga ⁰ (%)	Ni/Ga
1290	0.7	95 ^b	N/A
275	0.9	96 ^c	0.66
500	1.3	93 ^c	1.13
850	2.0	95 ^c	1.91

Table 4: XPS quantitative fit results for Ga in H₂ (2.5 torr) at 650°C. a) for Ga⁰; b) fit of Ga 2p_{3/2} region; c) fit of 3d region.

The nickel oxidation state was monitored by means of the Ni 2p_{3/2} region (Fig SI3). The extent of reduction to metallic Nickel was 90% at 400°C and complete at 650°C, where an asymmetric peak with a tail towards higher BE with maximum at 852.6 eV is visible. Curve fitting reveals satellite peaks at 855.8 eV and 859.3, typical for metallic Ni[57]. Interestingly, XPS Ni 2p_{3/2} data for NiGa intermetallic phases do not show a strong dependence on the composition and are comparable to metallic Ni [58, 59], confirming our assignments.

The Ni/Ga ratio was monitored changing the photon energy (275 eV, 500 eV and 850 eV) in order to perform a depth profile study following the ratio of the normalized intensity of Ni 3p and Ga 3d photoemission peaks. The results are presented in Figure 6 and Table 3 and 4. A Ni/Ga ratio of 0.66, lower than the nominal 1.67 ratio, was observed with a photon energy of 275 eV both for low and high temperature activations, indicating the presence of a Ga-rich surface in both cases. It is important to point out that although the surface Ni/Ga ratio is similar for both activation temperatures, the oxidation state of the Ga differs significantly. This difference can be explained by the presence of segregated Ga oxide at the surface that reduces completely to metallic gallium only at high temperature. In the subsurface region, differences in Ga concentration are observed that are related to the different inelastic mean free path due to the changes in the composition at the surface (Ga₂O₃ vs Ga). In particular for a photon energy of 850 eV, i.e. the maximum sampling depth of this study, Ni/Ga ratios of 1.9 and 1.5 were measured at 650°C and 400°C, respectively. A clear trend in the increase in Ni/Ga ratio with sample depth confirms the formation of a Ni-rich subsurface region in both cases. The fact that the subsurface Ni/Ga ratio for the 650°C sample is higher than the nominal value for pure Ni₅Ga₃ supports the presence of a Ni-rich subsurface region of few nanometers. Since XRD confirms the presence of δ -Ni₅Ga₃ in the bulk of the sample, that implies a Ga segregation towards the surface region upon exposure to air; the formation of Ga₂O₃ leaves behind a Ni-rich subsurface region. It is common for intermetallic compounds where one component shows high oxophilicity to undergo this segregation process upon exposure to air or oxygen[59-61]. Our XPS analysis finally shows that at low temperature under H₂ a complete reduction of the Ga₂O₃ surface layer is not achieved. High temperatures are required to achieve nearly complete reduction of Ga, with a Ga-rich surface layer persisting at the surface.

Figure 6 Ni/Ga ratio obtained from in-situ depth profile analysis. White bar: reduction at 400°C; grey bar: reduction at 650°C in 2.5 torr of H₂. Dashed line represents the nominal Ni/Ga ratio for Ni₅Ga₃.

3.3 Characterization of NiGa catalyst during operational conditions

Metallic nanoparticles are prone to changes under reactive gas atmosphere, especially under relevant conditions[35, 62]. In order to assess the oxidation state of Ga under true reaction conditions, we conducted High Energy Resolution Fluorescence Detected – X-ray Absorption Spectroscopy (HERFD-XAS) Ga K-edge measurements during reduction at 400°C (1bar flowing H₂) and methanol synthesis (1 bar CO₂:H₂=1:3) of the sample reduced ex-situ at 700°C and subsequently exposed to air. It is clear from Figure 7 that after reduction at 400°C the Ga is substantially in the reduced form, as indicated by the clear shift of the on-set towards lower energy compared to Ga₂O₃ (Figure 7A). However, when we focus our attention on the first derivative plot (Figure 7B), a major maximum at 10369.7 eV, typical for metallic Ga, along with a small contribution at 10375.5 eV show also the presence of a minor fraction of oxidized Ga in the catalyst even under these reducing conditions[63]. This confirms that despite the difference in H₂ pressure compared to the in-situ characterization using AP-XPS and environmental TEM, the results are consistent, i.e. a small fraction of Ga is still oxidized after reduction treatments.

Figure 7. HERFD-XAS at Ga K-edge. A) Normalized XANES. B) Normalized first derivative of the XANES region.

Upon switching exposure of the reduced sample from pure H₂ to CO₂/H₂ (1:3; 1 bar) at 200°C, a slight shift toward higher energy of the Ga⁰ peak occurs (Figure 7B), due to an increase in the oxidation state of Ga. This trend becomes more evident when the temperature is further increased to 250 °C. The peak related to Ga³⁺ remains present within this range of temperatures (Figure 7B), indicating a persisting oxidized Ga, however further interpretation is complicated by the broadness of this feature in the spectra. As shown in Figure 1, increasing reaction temperature causes a substantial gain in methanol activity, consequently with a higher production of water that is well known to promote the surface oxidation of intermetallic particles[64].

Indeed, the analysis of the AP-XPS data also reveals the oxidation of Ga under CO₂/H₂ (1:3; 2 mbar) at 200°C with a decrease of the surface metallic Ga fraction from 51% to 41% (Table 3). Collectively, this has led to a complete picture of the morphology of the bimetallic nanoparticles under reducing activation treatments and under methanol synthesis reaction conditions. A bulk sensitive technique (i.e. HERFD-XAS) under true reaction conditions shows the presence of oxidized Ga, while the lower-pressure surface sensitive measurements obtained by AP-XPS and environmental electron microscopy reveal that the oxidized Ga is located at the surface. It was found that 1 bar of H₂ at 400°C is not sufficient to completely reduce the surface oxidized Ga formed after air-exposure of the sample, and that the fraction of surface oxidized Ga actually increases during CO₂ hydrogenation. The evidence shown here for the presence of oxidized Ga during CO₂ hydrogenation conditions supports findings from previous reports regarding the important role played by gallium oxide in catalyzing transformations of CO₂.[65-69]

4 Discussion

DFT calculations and experiments on NiGa bimetallic catalysts for CO₂ reduction to methanol at atmospheric pressure have identified the Ni₅Ga₃ phase as the most active intermetallic composition[34]. This catalyst was found to outperform a Cu-Zn-Al₂O₃ catalyst due to a more efficient interaction between the two metals deriving from the intermetallic nature of active sites, compared to a surface alloy as in Cu-Zn. The higher methanol formation rate for the Ni-Ga is derived from the inhibition of the rWGS reaction, and the thermodynamically more favorable conditions for methanol synthesis in the absence of large quantities of water. It was postulated that two distinct surface sites are

responsible for different reactivity towards CO₂ hydrogenation: Ni-rich sites facilitate rWGS and methanation, while Ga-rich sites promote methanol synthesis. Ni₅Ga₃ represents an improved balance between surface bimetallic sites and tolerance to CO and C poisoning[34].

Our characterization of the Ni₅Ga₃ catalyst shows that the main effect observed upon air exposure of the catalyst after activation ex-situ at 700°C was the formation of a Ga₂O₃ shell encapsulating alloyed metallic-core nanoparticles. Surprisingly, the presence of a fraction of Ga₂O₃ at the nanoparticle surface is not always detrimental for the catalyst performance. An improvement in activity for methanol synthesis was observed for Ni₅Ga₃ intermetallic nanoparticles after exposure to air and subsequent in-situ activation in hydrogen at a temperature of 400°C and above. This effect is attributed to an increase in the amount of Ga on the surface, as evidenced by our APXPS, HERFD-XAS and CO chemisorption experiments. Evidently, the change in the surface composition of the Ni₅Ga₃ nanoparticles resulted in the formation of bimetallic Ga-rich sites active and stable for methanol synthesis. In bimetallic particles or films, the partial segregation upon air exposure into a native surface oxide layer of one of the components is not uncommon. In the case of Pd-Ga intermetallic catalysts for selective hydrogenation of acetylene a compact Ga₂O₃ layer formed during synthesis blocks Pd and an increase of catalytic activity was obtained only after removal of this layer by chemical etching[47]. Also in our case the formation of a thick Ga₂O₃ shell hinders the catalytic activity, as evidenced by poor catalyst performance after in-situ activation at only 200°C. According to the CO uptake experiments in this case, only a small number of Ni sites are accessible to reactants. HERFD-XAS, TPR and CO chemisorption results indicate that a temperature of at least 400°C is necessary to promote extended reduction of the oxide-shell and therefore expose a considerable number of reduced Ni sites. For activations at 400°C and above, the order of the activity ex-situ(700°C)/in-situ(400°C) $\cong$ ex-situ(700°C)/in-situ(680°C) > in-situ(680°C) correlates, interestingly, inversely with the amount of Ni on the surface. The sample with the greatest amount of Ga₂O₃ at the surface, based on CO chemisorption, TPR, ETEM, AP-XPS and HERFD-XAS, shows the highest surface activity and, on the contrary, the sample with the most accessible surface Ni sites presents the lowest activity. The sample reduced in-situ at 680°C after exposure to air shows a slightly lower activity compared to that activated in-situ at 400 °C. This trend highlights how Ga at the surface plays a role in methanol synthesis and more specifically, how the presence of a small fraction of amorphous Ga₂O₃ in contact with reduced Ni-Ga sites is beneficial. Indeed, the fraction of surface oxidized Ga increases during catalysis for the sample ex-situ(700°C)/in-situ(400°C) according to AP-XPS and HERFD-XAS analysis.

A large fraction of Ni becomes metallic between 350°C and 400 °C and promotes the reduction of the surrounding Ga₂O₃, likely by a hydrogen spill-over mechanism. This way Ni-Ga sites start to form at the interface of very well dispersed amorphous Ga₂O₃ (or GaO_x) on the surface of the nanoparticles that might be responsible for the high activity achieved by this sample considering that the surface is still partially covered by oxidized Ga during catalysis, as revealed by HERFD-XAS. Gallium oxide has widely demonstrated ability in activating CO₂ and to be an efficient promoter for methanol synthesis from CO₂ hydrogenation[25, 41, 60, 61, 65, 68, 70]. A general observation is that Ga₂O₃ activity for CO₂ transformation is greatly enhanced when it is coupled with a metal able to activate hydrogen[66, 67] . The presence of a metal able to activate hydrogen also helps to increase

the number of oxygen vacancies in Ga_2O_3 that can facilitate CO_2 adsorption and activation [71, 72]. According to DFT calculations, while CO_2 adsorption on beta- $\text{Ga}_2\text{O}_3(100)$ is slightly endothermic, the presence of oxygen vacancies promotes the adsorption and activation of CO_2 [73]. In the case of Ni-Ga, a synergistic effect between the oxide and the intermetallic phase is also observed.

A higher reduction temperature of the air-exposed sample favors the complete reduction of the amorphous Ga_2O_3 leading to the formation of surface Ga-enriched bimetallic sites highly active for methanol. Unexpectedly, a higher degree of surface sites reduction did not result in an increase in activity. In fact, despite the incomplete reduction of Ga_2O_3 leading to half the amount of adsorbed CO for the catalyst reduced at 400°C compared to activation at 680°C , a similar specific activity was detected for the two. Notably, the minimal presence of the $\text{Ga}_2\text{O}_3/\text{Ni-Ga}$ interface is responsible for the slight activity decrease for the ex-situ(700°C)/in-situ(680°C) sample, as it is not completely compensated by a higher fraction of reduced Ni-Ga sites at the surface. The in-situ(680°C) sample shows the most Ni-rich surface of the series and therefore the lowest activity. Its fast deactivation at 250°C within the first hour on stream also correlates well with the presence of Ni-rich sites easily poisoned and deactivated by C deposition and CO adsorption [34]. On the contrary, greater amounts of Ga on the surface improve the stability of the air-exposed samples.

5 Conclusions

$\delta\text{-Ni}_5\text{Ga}_3/\text{SiO}_2$ is a highly active and stable catalyst for CO_2 hydrogenation to methanol. The effect of surface oxidation/reductions on catalytic performance was investigated by reconciling results from in-situ and ex-situ characterization techniques with catalytic test results. APXPS, ETEM, HERFD-XAS, H_2 -TPR, CO chemisorption, XRD revealed the presence of an amorphous Ga_2O_3 shell surrounding an alloyed, metallic core that forms for catalysts exposed to air. For instance, for samples activated ex-situ at 700°C , exposed to air, then re-activated in-situ at 400°C prior to catalytic testing, the activity for methanol synthesis is higher than that observed for catalyst samples activated in-situ at higher temperatures, or for catalysts directly activated without air exposure, even though the latter samples are reduced to their metallic forms to a much greater extent. This indicates that the presence of amorphous Ga_2O_3 at the surface of the metallic nanoparticles plays a role in methanol synthesis, likely in promoting CO_2 activation, rather than hindering the reduction of CO_2 as expected if inactive. In fact, a surface oxidized Ni_5Ga_3 is more active for methanol synthesis than a fully reduced Ni_5Ga_3 catalyst thanks to a surface enrichment with gallium and a synergetic effect with remaining Ga_2O_3 . The present study also proves the importance of characterizing catalysts via in-situ and operando experiments when ascribing catalytic activity to different species that exist within the catalyst only during catalysis. In conclusion, the systematic characterization and testing of Ni-Ga catalysts in the present work have identified the synergy between Ga_2O_3 and NiGa_3 intermetallic compound for CO_2 hydrogenation to methanol, that may be exploited further to fine tune catalytic activity by means of controlled oxidation treatments.

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