

Surface titration of supported Ni catalysts by O₂-pulse thermal analysis

Marie-Mathilde Millet^[a], Elias Frei^{*[a]}, Gerardo Algara-Siller^[a], Robert Schlögl^[a,b], Andrey Tarasov^{*[a]}

[a] M. M. Millet, Dr. E. Frei, Dr. G. Algara-Siller, Prof. Dr. R. Schlögl, Dr. A. Tarasov
Department of Inorganic Chemistry
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, 14195 Berlin (Germany)

[b] Prof. Dr. R. Schlögl
Max-Planck-Institut für Chemische Energiekonversion
Abteilung Heterogene Reaktionen
Stiftstr. 34-36, 45470 Mülheim an der Ruhr (Germany)

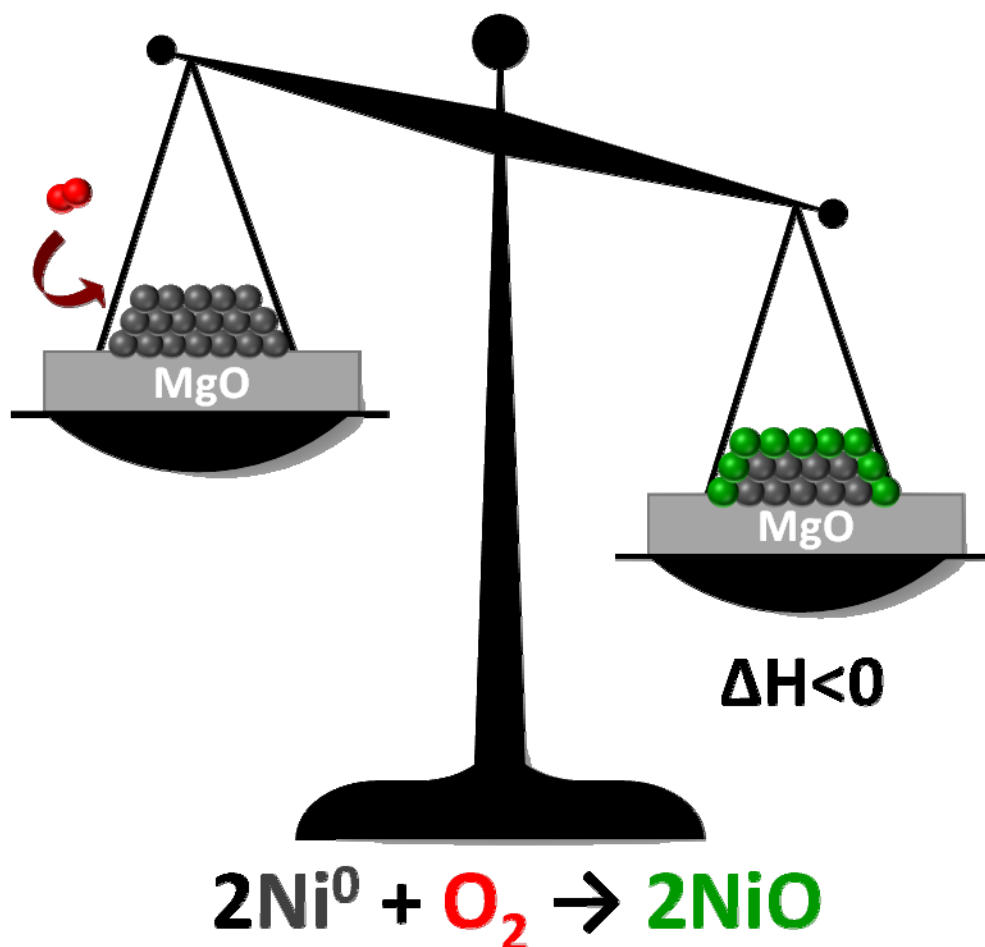
* E-mail: efrei@fhi-berlin.mpg.de
 tarasov@fhi-berlin.mpg.de

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Abstract

A new method for determining the Ni⁰ metal surface area of MgO supported catalysts is proposed. Different series of MgO supported Ni catalysts were prepared and titrated by chemical adsorption of oxygen inside a STA-MS setup. Simultaneous recording of the mass gain upon oxidation, the enthalpy of formation of the oxide and the evolved gas allowed a precise quantification of the metallic Ni surface area. In addition, any uncertainties linked with the complex Ni oxide stoichiometry could be ruled out. A comparison of the newly developed oxygen pulse method with already established techniques using H₂ or N₂O confirmed the applicability of the method and further revealed its surface sensitivity and accuracy with respect to MgO supported Ni catalysts.

Graphical abstract:



1 Introduction

Supported Ni catalysts have been extensively used in various industrial processes. In recent years some of these processes using CO₂, such as its hydrogenation to methane [1, 2], the production of syngas by reverse water-gas shift [3, 4], or the dry reforming of methane [5, 6] have been the focus of a renewed interest. The catalytic properties of these compounds are, as most supported catalysts, highly dependent upon their metal dispersion [7, 8]. Therefore, the design of a simple and reliable method for the determination of metal dispersion remains relevant, especially in the case of Ni.

In the literature, several methods have been described to determine the metallic surface area of supported catalysts; most of them use the chemisorption of various gases such as H₂, CO, N₂O and O₂ [9-12]. Generally, the measuring principle comprises the following steps: (i) adsorption of a probe molecule on the Ni based catalysts, (ii) quantification of the amount of adsorbed molecules and (iii) determination of the amount of surface Ni atoms from the stoichiometry between Ni and the adsorbed gas. Ultimately the number of Ni atoms is calculated and converted into surface area by using the area occupied by one surface atom of Ni [12].

However, since the beginning of the 80s, discrepancies have been constantly observed while using these standard chemisorption techniques for determining the Ni dispersion. These discrepancies have been shown to have different origins such as, the nature of the support [11, 13], the nature of the chemisorbed molecule and its interaction with Ni [14] or an inadequate choice of the testing temperature [12]. One of the difficulties of those characterization methods relies in the precise titration of a single monolayer, and to avoid subsurface uptakes. However, studies have shown that the selective titration of the surface and the suppression of bulk reactions could be achieved for each titration molecule, and could provide reliable data, through the careful selection of the experimental conditions [12, 15, 16].

Therefore, given the difficulties inherent to those techniques, other concepts and surface titration methods were developed with the aim to follow in a different manner the titration process. Due to

its high sensitivity and its three-way measuring principle our focus is dedicated to the pulse thermal analysis.

Classical thermal-analysis has been widely used to investigate solid-gas reactions, offering the possibility of simultaneously monitoring the mass variations and the thermal events related to chemical reactions or physical changes, such as phase crystallization or transformation and thus combining different levels of insights. Various concepts of simultaneous measurements of reaction rates and heat effects on Ni based catalysts were reported in the literature [17, 18], but only few were dealing with gravimetric surface area determination despite the high precision evidenced [16, 19]. The main drawback of the combined use of calorimetric techniques was the difficulty to ensure a reproducible thermal contact between the sample (in the balance holder) and the calorimetric sensor [20].

The potential of thermo-analysis has remarkably increased by modernized construction of the calorimetric cells and coupling with new efficient gas analysis systems. Over the last 20 years, significant progress has been made in the development and application of pulse thermal analysis (Pulse TA[®]) [21-26]. Pulse thermal analysis allows the precise dosing of reacting gas in small quantities into an inert carrier gas stream. Monitoring the variations of the catalyst mass by thermogravimetric analysis (TGA), the reaction enthalpy by differential thermal analysis (DTA) as well as the gas composition by mass spectrometry (MS), facilitates the study of heterogeneous reactions. This type of method also has the advantage of allowing to stop the reaction at any point between the pulses, and to determine its completion when successive pulses no longer lead to any change in the system. Moreover, the use of pulses under flow conditions with short contact time better mimics the reaction environment compared to classical volumetric methods, turning the traditional “bulk” TA into a more surface sensitive method [27, 28].

Using this approach, Feist *et al.* developed a method to probe the surface acid centers of metal fluorides catalysts, leading to a qualitative and semi-quantitative analysis. However the precise

quantification in their study was hindered by desorption phenomena [22]. Following their experience, we put effort to develop a method for the quantification of metallic surface sites.

We report on investigations of solid solutions of NiO and MgO ($\text{Ni}_x\text{Mg}_{1-x}\text{O}$) [29]. The formation of this solid solution, allows the control of the amount of metallic Ni after reduction by changing either the initial Ni concentration or the calcination temperature [30]. The application of the method to the corresponding two series of samples allowed a better understanding of the specificities of the method and a broader confirmation of its relevance. Pulse TA[®] was used to oxidize the surface of metallic Ni, while the amount of oxygen consumed was followed by variation of the samples mass (and by means of mass spectrometry). The enthalpy of formation of the corresponding oxide was measured by differential thermal analysis. Single experiments were chosen to verify certain sources of possible uncertainties, like sub surface oxidation, or O₂ interaction with the support. The aim of this study is to propose a convenient and reliable method to determine the specific Ni surface area of MgO supported catalysts. To the best of our knowledge simultaneous thermal analysis combined with pulse technique has not been previously reported in the literature as a metal surface titration method, and neither was the use of O₂ chemisorption to measure the dispersion of *in-situ* segregated Ni⁰ from $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solutions. Furthermore, the importance and relevance of the O₂-Pulse TA[®] method is discussed in the context of other standard techniques and probe molecules.

2 Experimental

Catalysts preparation

Phase pure $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid-solutions were prepared by co-precipitation of the corresponding metal nitrates with ammonia, as previously reported [31]. The precipitate was dried, and then calcined in a rotating oven [32] under a synthetic air stream with a flow of 100 mL min⁻¹, a rate of 2 °C min⁻¹ and a rotating speed of 2 turns min⁻¹. The samples were calcined up to their respective final temperature and maintained at this temperature for 3 h. Pure MgO was also prepared following the same synthesis route and thermal treatment for comparison.

Following this protocol, two series of samples were prepared, samples with different compositions (0 to 15 at.-% Ni) all calcined at 600 °C, and samples with the same composition (10 at.-% Ni) but calcined at different temperatures [400 , 500 , 600 , 700 and 900 °C]. Samples from the concentration series are named after their Ni content i.e. a sample containing 10 at.-% Ni will be named Ni_10, and the samples from the calcination series are named after their calcination temperature only i.e. Ni_400 (as they all have the same concentration in Ni 10 at.-%).

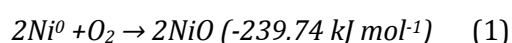
O₂ and N₂O pulse titration

Simultaneous TG-DTA was carried out in a NETZSCH STA 449C Jupiter thermoanalyzer equipped with an SiC oven and an top loading electromagnetic microbalance. Gases used in the experiments were Ar (99.999 %), H₂ (99.999 %), O₂ (99.999 %) and N₂O (99.999 %). The residual oxygen concentration in the carrier gas was determined by decomposition of CuC₂O₄*0.5H₂O in inert flow. Copper oxalate decomposes to elemental copper and any oxygen present will result in formation of copper oxide and cause continues weight gain. The gases were additionally purified on commercial hydrosorb and oxysorb columns. Thus the lowest oxygen background off less then 1ppm was reached. Despite additional gas purification the water contamination in the carrier gas was assessed as 3-5 ppm, which is still quite low as compared with other conventional laboratory flow setups. The catalysts (between 20 and 100 mg of sample as shown Table S1) were placed into corundum crucible (0.2 mL) without lid. The pulses were performed using a 8-port External Volume Sample Injector VICI, with a pulse-loop of 500 µl. To minimize possible over oxidation, the contact time gas-sample was reduced to $\tau < 0.1$ s. All experiments were performed with the total gas flow of 100 mL min⁻¹. The gases evolved were monitored with a quadrupole mass spectrometer (QMS200 Omnistar, Balzers) coupled to simultaneous thermal analysis (STA) via a quartz capillary heated to 140 °C. The experiments were performed with an electron ionization energy of 60 eV and a dwell time per mass of 0.2 s. The DTA sensor was calibrated using usual pure metal standards In, Sn, Pb, Zn, Al and Au, and benzoic acid for the lowest temperatures, (for each reference compound 4 to 5 cycles of melting were performed) giving a calibration factor $a=397.7 \mu\text{V s kJ}^{-1}$. The raw data was evaluated without any further

smoothing or other data treatment. The uncertainty of the enthalpy measurements was evaluated to $\pm 5 \text{ kJ mol}^{-1}$.

The samples were reduced *in-situ* in a 5 %H₂ in Argon atmosphere, with a heating rate of 5 °C min⁻¹ up to 1000 °C and held for one hour. The samples were then purged in Argon for 30 min and cooled down to 40 °C under Argon flow. After mass stabilization, 500 µl of O₂ or N₂O were pulsed over the catalysts with 15 minutes intervals between each pulse, until no signal variation was observed (no mass gain/no exothermic event). The titrations were performed at 40 °C, as Tada *et al.* reported that for Ni catalysts, at such temperatures, only surface oxidation was observed with N₂O [12]. DTA signal, mass changes and gas evolved were monitored during the whole measurement. A final continuous O₂ flow (21 % O₂ in Ar, 100 mL min⁻¹) was also applied after the O₂ pulse series for the sample Ni_400 °C to verify the completion of the oxidation process.

After *in-situ* reduction of the catalysts precursor, metallic Ni is present at the surface of the catalysts. Pure O₂ pulse oxidizes the surface of the metallic Ni, following the reaction:



This oxidation process being very exothermic, it is possible to measure and quantify the heat released at every pulse. At the same time, the oxidation of one atom of Ni corresponds to a mass gain of one atom of oxygen. Knowing the mass gain upon each oxidation and the heat of the reaction, one can determine the enthalpy of reaction for each pulse using the following equation:

$$\Delta H_r = \frac{\Delta H}{\left(\frac{\Delta m}{M_o}\right)} \quad (2)$$

where ΔH_r is the enthalpy of reaction [J mol^{-1}], ΔH the exothermic heat release measured by the DTA sensor [J], Δm the mass gain [g] and M_o the molar mass of atomic oxygen [g mol^{-1}]. The Ni metal surface area was determined using the atom cross-section area of metallic Ni and assuming, as above, a dissociative chemisorption mechanism (Stoichiometric factor $S_f=2$; $2\text{Ni}/\text{O}_2$) [33, 34]:

$$\text{Ni}^0 \text{ s. a.} = \frac{\left(\frac{\Delta m}{M_O}\right) * N_A}{g_{\text{cat}}} * RA \quad (3)$$

where Ni⁰ s.a. is the Ni metallic surface area per gram of catalyst [m² g_{cat}⁻¹], N_A the Avogadro constant (6.022 10²³ mol⁻¹), g_{cat} the mass of catalyst [g] and RA the Ni atomic cross sectional area (6.49 10⁻²⁰ m² atom⁻¹) [35]. The corresponding particle size was calculated using the following equation [36]:

$$\text{MCS} = \frac{F}{(\text{Ni}^0 \text{ s. a.}_{\text{Ni}} * d_{\text{Ni}})} \quad (4)$$

where MCS correspond to the metal particle size [m], F the shape factor (6) assuming spherical particles [37, 38], d_{Ni} the density of metallic Ni (8.908 g cm⁻³) [39] and Ni⁰ s.a._{Ni} the metal surface area per gram of reduced Ni [m² g_{Ni}⁻¹] calculated as:

$$\text{Ni}^0 \text{ s. a.}_{\text{Ni}} = \frac{\left(\frac{\Delta m}{M_O}\right) * N_A}{g_{\text{metal}}} * RA \quad (5)$$

where g_{metal} [g] corresponds to the mass of reduced Nickel upon reduction treatment.

H₂ pulse titration

For the H₂ pulse titration, the method used by Mette *et al.* was reproduced [40]. The samples were reduced according to the reduction protocol described above, in a fixed bed reactor. After the reduction, the temperature was lowered to 40 °C in Argon. A defined volume of H₂ (99.999 %, additionally purified with commercial oxysorb and hydrosorb columns) was introduced by pulse dosing with a volume of 250 μL and monitored with a thermal conductivity detector (TCD). Before the detector, the reactor effluent passed through the molsieve water trap. The pulses were continued until no further uptake was detected. The Ni metal surface area was determined assuming a dissociative chemisorption mechanism of hydrogen (Sf=2; 2Ni/H₂)[41]. The amount of H₂ gas adsorbed was used for the determination of the Ni surface area. The calculation of the Ni⁰ surface area and particle size were performed similarly as for the O₂ titration.

TEM

TEM characterization of the sample was performed as follows: the sample within the reactor was placed after reduction in the glove box to avoid air contact; the powder sample was dry deposited on a TEM grid and then mounted on a vacuum transfer holder (VT-648 GATAN). The holder was opened after 10 min in the air-lock cycle to be then introduced into the column to prevent exposure to air. The characterization of the sample was performed in a FEI TITAN 80-300 with imaging-side aberration corrector operated at 300 kV. Images were taken in STEM mode with a HAADF detector.

3 Results and discussion

3.1 Application to a MgO supported Ni catalyst: Ni_5

After *in-situ* reduction of the Ni_5 sample to metallic Ni, 500 μl of O_2 were pulsed into the DTA-MS chamber, each pulse was monitored by three different techniques as presented Figure 1. The evolved oxygen ($m/z=32$) was measured by mass-spectrometry (Figure 1.A), the heat released at each oxidation was measured by differential thermal-analysis (Figure 1.B) and the mass gain was monitored by thermogravimetry (Figure 1.C).

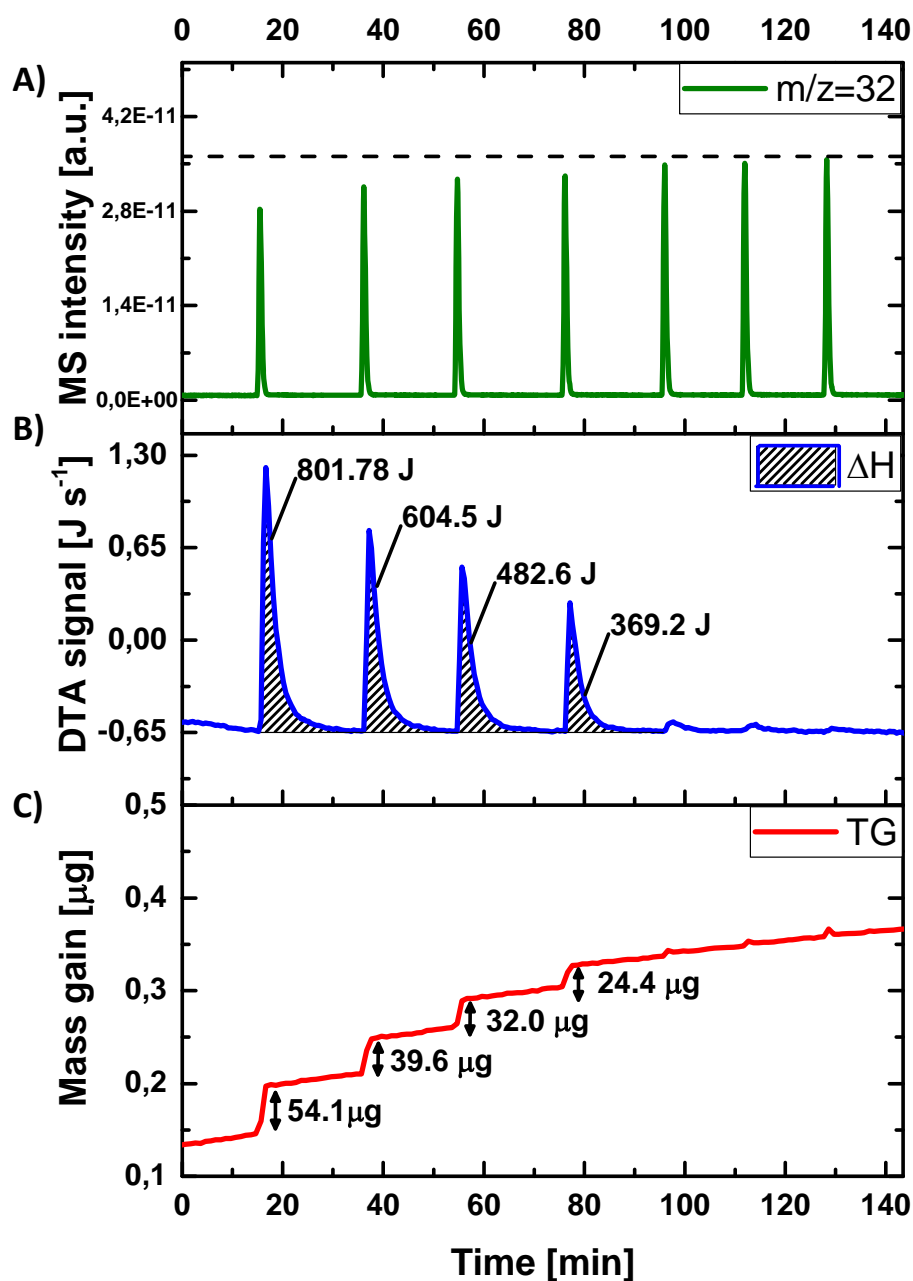


Figure 1. Oxygen pulse experiment on Ni_5 A) Mass-spectrometry signal B) DTA signal C) TG signal.

O₂ was pulsed 7 times onto the reduced sample and changes were observed up to the fourth pulse for all signals, while the three last pulses caused only negligible changes in the system.

Mass gains (O₂ uptakes) became smaller with each pulse, as the amount of metallic Ni, still oxidizable, decreased. After the fourth pulse of O₂ no further mass uptake was observed as all the metallic Ni on the surface of the catalyst was oxidized. The same phenomenon was observed for the heat release, which also decreased as the O₂ uptake decreased until an abrupt loss of the heat signal indicating surface saturation. Interestingly, according to previous literature, the DTA peaks have the typical form of chemisorption [22]. Finally, at each pulse, a peak in the m/z=32 signal was observed. The intensity of the peaks increased with each pulse, as the consumption of oxygen decreased. After the fourth pulse of O₂ the intensity of the peaks remained constant in agreement with the other signals. With ongoing O₂ pulses, very small heat releases were observed that could possibly indicate a consecutive subsurface oxidation. Due to the very low intensity of the signals, the evolved heat could not be precisely quantified and its contribution was not taken into account.

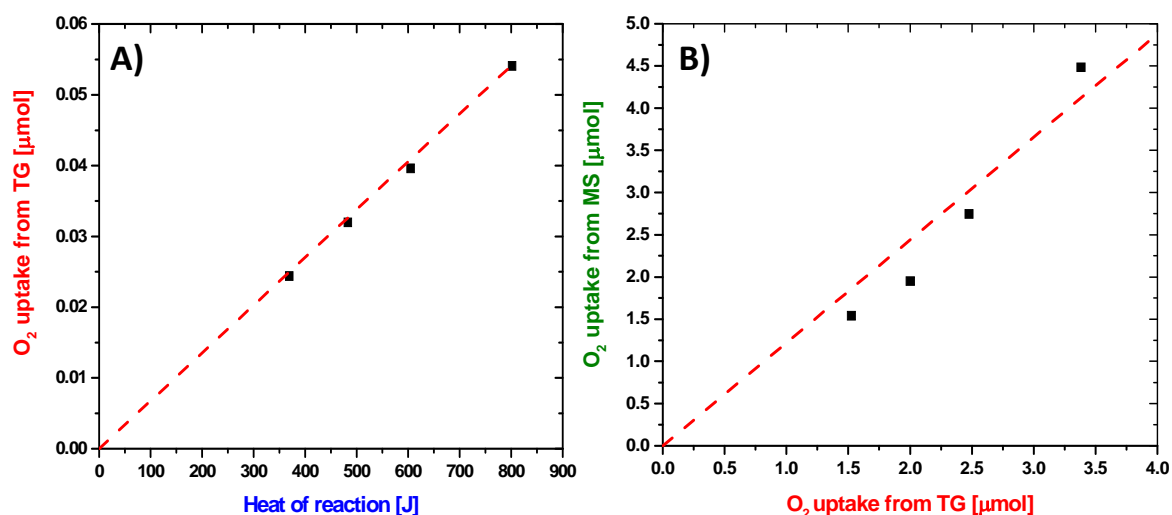


Figure 2. Multi-signal correlation. A) TG signal correlation to DTA signal B) MS signal correlation to the TG signal of Ni_5.

The quantitative evaluation of the measured changes provides three different sets of information, relating mutually well to each other as shown in Figure 2A and B. Linear correlations were observed between the amount of consumed O₂ from TG and the DTA signal and of the O₂ uptake from MS with

the mass gain. However, the uncertainty associated with the MS data is visible, as the points slightly diverge from the linear function passing through zero. Indeed, the calculation of the O₂ uptake by mass spectrometry uses the average area of a 500 μL O₂ pulse (empty cell), the peak area of the O₂ pulse (with catalyst) and a calibration factor (converting areas to moles), while the evaluation of the TG/DTA data relies on a direct reading of the results without further data transformation. As such, MS signal analysis has only been used in a qualitative manner.

In order to avoid a contribution of the slightly drifting mass gain signal in Figure 1C (see detailed explanation), each peak was analyzed as a single event, and the mass gain were measured independently.

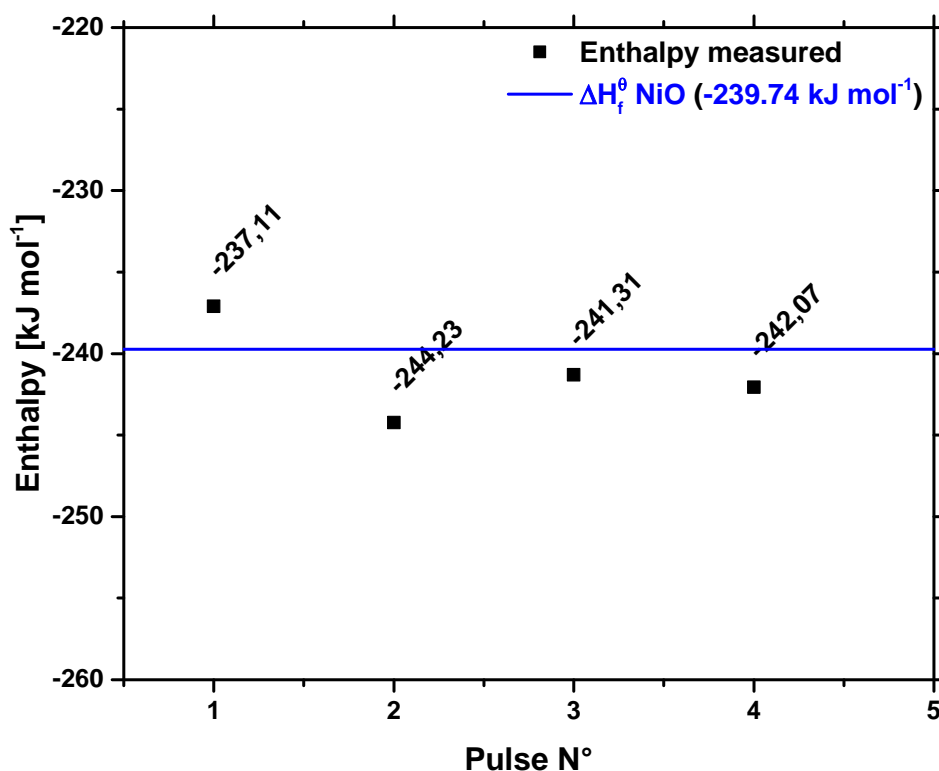


Figure 3. Calculated enthalpy for each O₂ pulse on Ni₅, compared with the theoretical enthalpy of formation of NiO (-239.74 kJ mol⁻¹).

For each pulse, the heat release was measured, and the enthalpy of each oxidation reaction was calculated. The reaction enthalpies varied between -237.1 and -244.2 kJ mol⁻¹, which is in very good agreement with the standard enthalpy of formation of Ni oxide obtained by combustion calorimetry (239.74 ± 0.42 kJ mol⁻¹, Boyle *et al.*, 1954 [42]) as illustrated in Figure 3. These values are also in line

with the calculated standard enthalpy of formation of NiO by the third law method ($-240.28 \text{ kJ mol}^{-1}$, Holmes *et al.*, 1986 [43]). The fact that the measured heat release remained the same for every successive pulse showed that the same reaction took place, and that the same kinds of Ni species were titrated.

In order to verify the absence of any adsorption of O_2 by the MgO support, pure MgO was titrated following the same procedure (Figure 4). At high magnification of the mass gain signal we can observe a temporary “peak” without any remaining mass gain. This phenomenon corresponds to a buoyancy effect recorded by the microbalance. As the density of O_2 is lower than the one of the carrier gas (Argon) the observed mass gain is positive [22]. Since the experiment did not show any mass uptake or heat evolution (DTA signal) the adsorption of oxygen atoms by the MgO support, or the sample holder, is neglected for the applied Ni surface area calculation.

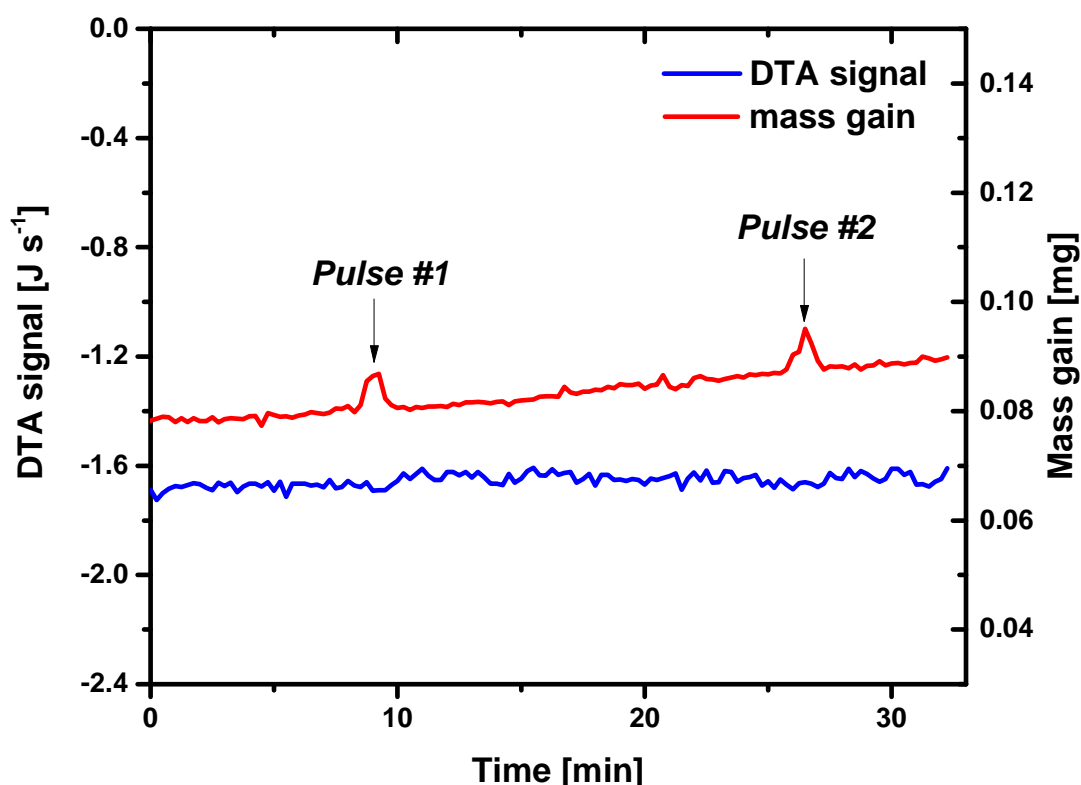


Figure 4. Oxygen pulse experiment on pure MgO [blue curve: DTA signal; red curve: mass gain].

As mentioned above, Figure 1C and 4 show a slight drift in the mass signal. To validate the accuracy of this method to titrate metallic surfaces, it is important to verify that this phenomenon was not caused by the progressive oxidation of the metallic Ni due to oxygen traces in the gas flow. The

presence of this drift on metal free samples (Figure 4) as well as the absence of an increase in its slope with increasing metallic surface area (Figure S1), clearly indicated that this effect was not linked to any oxidation event and as such did not interfere with the interpretation of the data. Thus, this small mass drift could be explained by the fact, that after high temperature treatment the sample slowly adsorbed traces of moisture from the gas stream.

3.2 Titration of two different samples series by O₂ Pulse TA

To validate the consistency of this method, the protocol described above was applied to two series of MgO supported Ni catalysts (see details in experimental part). Figure 5A shows the determined Ni surface areas of a Ni loading series. With increasing Ni content, the available Ni surface area increased in a linear fashion. This is in line with the expected amount of reducible Ni species correlating with its loading and confirms the homogeneous character of the synthesized samples.

A)

B)

C)

D)

Figure 5. Ni⁰ surface area (Ni⁰ s.a.) of each sample for A) the concentration series and B) the calcination series of Ni₁₀.

Measured enthalpy for each sample (calculated as the average of the enthalpy of all pulses) and compared with the enthalpy of formation of NiO (-239.74 kJ mol⁻¹) for C) the concentration series and D) the calcination series.

As second series, catalysts calcined at different temperature were analyzed (Figure 5B). It is known that the calcination conditions strongly affect the properties of the Ni_xMg_{1-x}O solid solution [30, 40]. The higher the applied calcination temperature, the lower is the measured Ni surface area. This is in agreement with the decreasing reducibility of the Ni species with increasing calcination temperatures (Table S2) [44, 45]. The Ni surface areas are constantly decreasing between 400 and 600 °C and abruptly between 600 and 700 °C, while no change was observed between 700 and 900 °C.

The enthalpy of formation was measured for all pulses of each of the 10 catalysts (Figure S2+S3). The average enthalpy for every catalyst was calculated and plotted in Figure 5C (concentration series) and D (calcination series). The enthalpies shown are expressed in kJ mol⁻¹ and as such correspond to the global heat signal normalized by the amount of recorded oxygen uptake. It remained constant irrespective of the Ni content or the calcination temperature. The calculated values show only minor deviations compared to the standard enthalpy of formation of NiO, confirming the high accuracy and the applicability of the O₂ pulse method for titrating the Ni surface area.

3.3 Qualitative validation: comparison with established method

While the concentration series showed a linear evolution of the Ni⁰ specific surface area with the Ni content, as it could be expected, the calcination series presented a much more peculiar profile, and was used to confirm the validity of the method. Consequently, the calcination series was analyzed using the classical and already established H₂ pulse chemisorption [5].

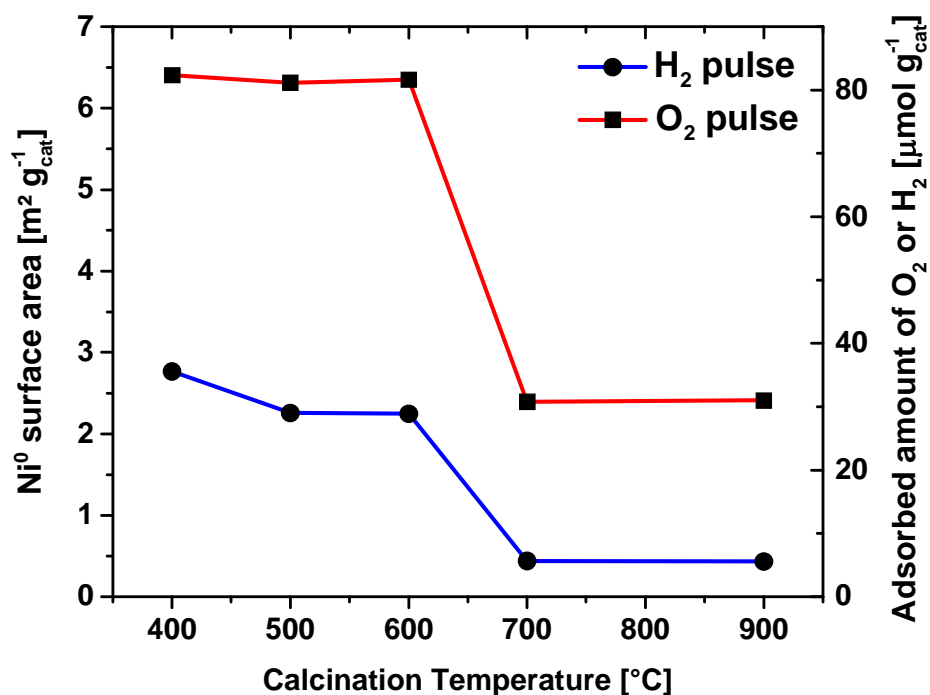


Figure 6. Specific Ni surface area, and amount of adsorbed probe molecule for the Ni₁₀ calcination series [blue curve: determined by H₂ pulse titration; red curve: determined by O₂ pulse STA-MS titration]

The two titration methods revealed the same distinct profile for the Ni⁰ surface area (Figure 6): from 400 to 600 °C high values, slightly decreasing with increasing calcination temperature, from 600 to 700 °C an abrupt decrease and between 700 and 900 °C respectively, almost no evolution of the Ni⁰ surface area. Although O₂ titration gave larger Ni surface areas, the similarity of the profiles confirms first of all the relevance of the newly developed O₂ pulse method for qualitative analysis.

3.4 Quantitative validation: subsurface oxidation?

For a quantitative assessment, the consistently higher surface area values observed using the O₂ pulse titration method required further investigation (~factor of 2 to 5, compared to the H₂ titration method as reported in the literature [11, 13]).

This discrepancy could be explained by an incomplete H₂ pulsed titration, consequently underestimating the available Ni surface area. It was shown in the literature by temperature desorption experiments (H₂ TPD) on metallic Ni surfaces [15, 46, 47] that the H₂ desorption regime starts far below room temperature [46, 48]. So, it is very likely that H₂ pulses and adsorption at 40 °C, respectively, lead only to a partial titration of the Ni⁰ sites.

However, this does not exclude the possibility of an overestimation of the values obtained by O₂ pulse, due to a sublayer or even bulk oxidation. For this purpose, reference measurements with N₂O as milder oxidizing molecule were conducted (all other experimental parameters were kept constant). N₂O is a widely used titration molecule for metallic surface area determination and is commonly accepted as less reactive than oxygen towards Ni [18]. It is an established method for the titration of copper surfaces [27, 49, 50] and was also applied to other metals such as Platinum [51], Silver [52], Cobalt [53] and more recently for Ni catalysts at temperatures ranging from 50 to 100 °C [12, 18]. In our study the titration temperature did not exceed 40 °C to prevent bulk oxidation [12]. Each molecule of N₂O adsorbed on the metallic surface results in the chemisorption of an oxygen atom, accompanied by the production of gaseous N₂. Furthermore, Hinrichsen *et al.* showed that the pulsing of N₂O for copper surface titration is in excellent agreement with Reactive Frontal chromatography (N₂O RFC) in flow [27].

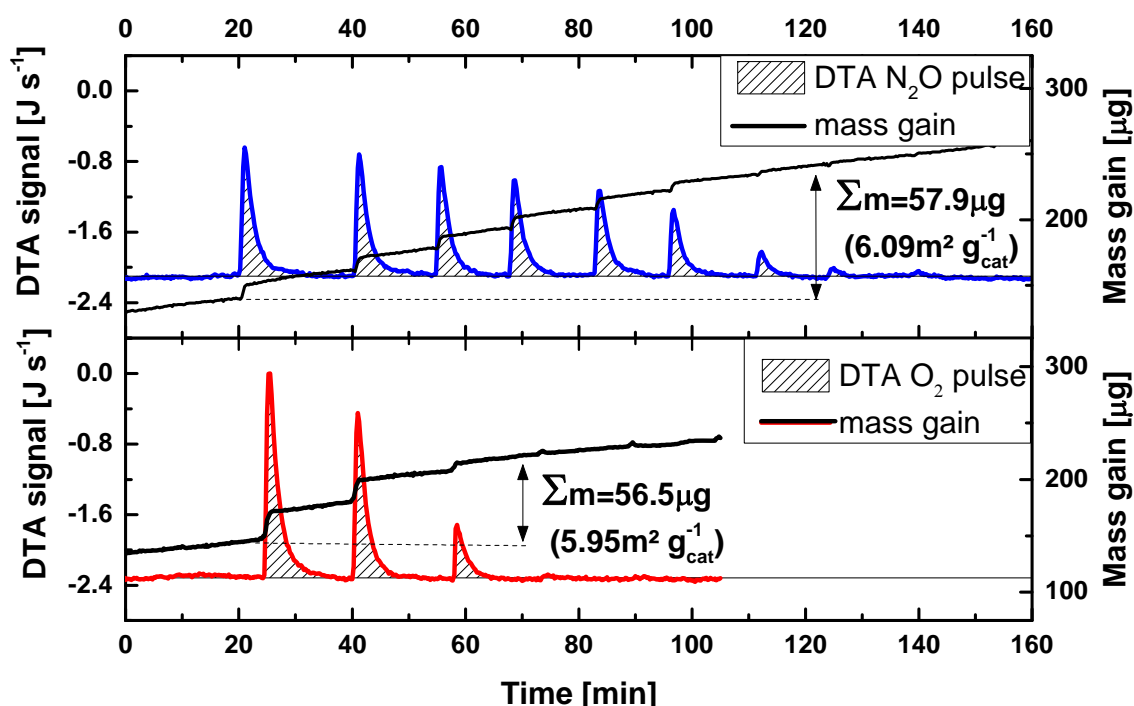


Figure 7. Pulse STA-MS titration of Ni₄₀₀ [blue curve: by N₂O pulse; red curve: by O₂ pulse].

In contrast to classical Reactive Frontal Chromatography (RFC) techniques, only the mass uptake and the enthalpy were taken into consideration. The Ni₄₀₀ sample (23.2 mg) was analyzed by O₂ pulse titration, and then a fresh sample of Ni₄₀₀ (23.2 mg) was analyzed by N₂O titration (Figure 7). Each

experiment was performed on the fresh sample to avoid sintering, which could influence the result of the titration. In comparison to the O₂ titration, to reach a surface saturation with N₂O as oxidizing agent, a higher number of pulses is needed (7 vs 3 pulses) and a smaller mass uptake at each pulse is gained. The final mass uptake was essentially the same for the two titration methods (57.9 μg for N₂O vs. 56.5 μg for O₂) and a variation of only 2.3 % was observed for the final Ni⁰ surface area (6.09 m² g_{cat}⁻¹ for N₂O vs 5.95 m² g_{cat}⁻¹ for O₂).

Using simultaneous mass spectrometry, the formation of N₂ as a product of the N₂O decomposition was observed. Unfortunately, the N₂O conversion was only partial, due to the geometry of the cell and N₂⁺ (m/z=28) correspond to a natural fragment of N₂O⁺ (m/z=44). To observe the N₂ formation relative to the N₂O decomposition, it is necessary to subtract to the N₂⁺ peak area obtained upon titration the average peak area of the N₂⁺ fragment of a N₂O pulse in the empty cell (in the manuscript named as “Differential peak area”). The same trends are obtained for the mass gain and for the N₂ production as shown Figure 8A and B. During the first seven pulses, a progressive oxidation is observed (continuous decrease of the mass gain and the N₂ formation), followed by surface saturation (pulse 8 to 12). The measured enthalpy of reaction at each pulse (Figure 8C) is in very good agreement with the calculated value for the reaction of Ni⁰ oxidation by N₂O:



Thus for this system, we ruled out the possible adsorption of N₂ and N₂O recently mentioned in the literature [15].

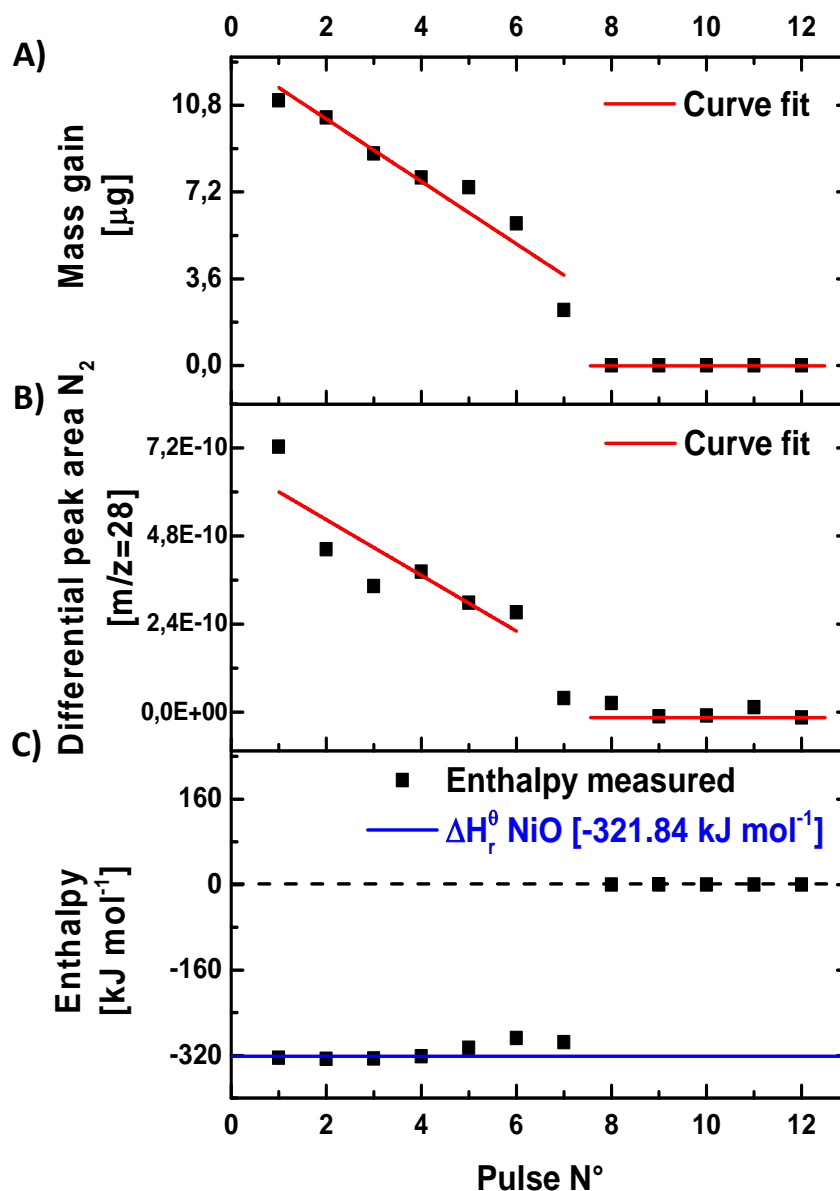


Figure 8. A) Mass gain B) Differential peak area N₂ C) Enthalpy of reaction upon each pulse on a fresh Ni₄₀₀ sample.

The depth of the oxidation process was also verified by further oxidizing the sample. After a completed O₂ pulse titration, the sample was exposed to a flow of 21 % O₂ in Ar for 30 min. This resulted in a large exothermic peak, corresponding to a deeper oxidation of the metal particles, which were not accessed by the O₂ pulses. While switching back to an Ar flow, a large mass uptake took place during the O₂ flow treatment due to the subsurface oxidation mentioned above. This procedure was repeated, and no further exothermic event was visible since the accessible metallic Ni has already been oxidized during the first O₂ treatment.

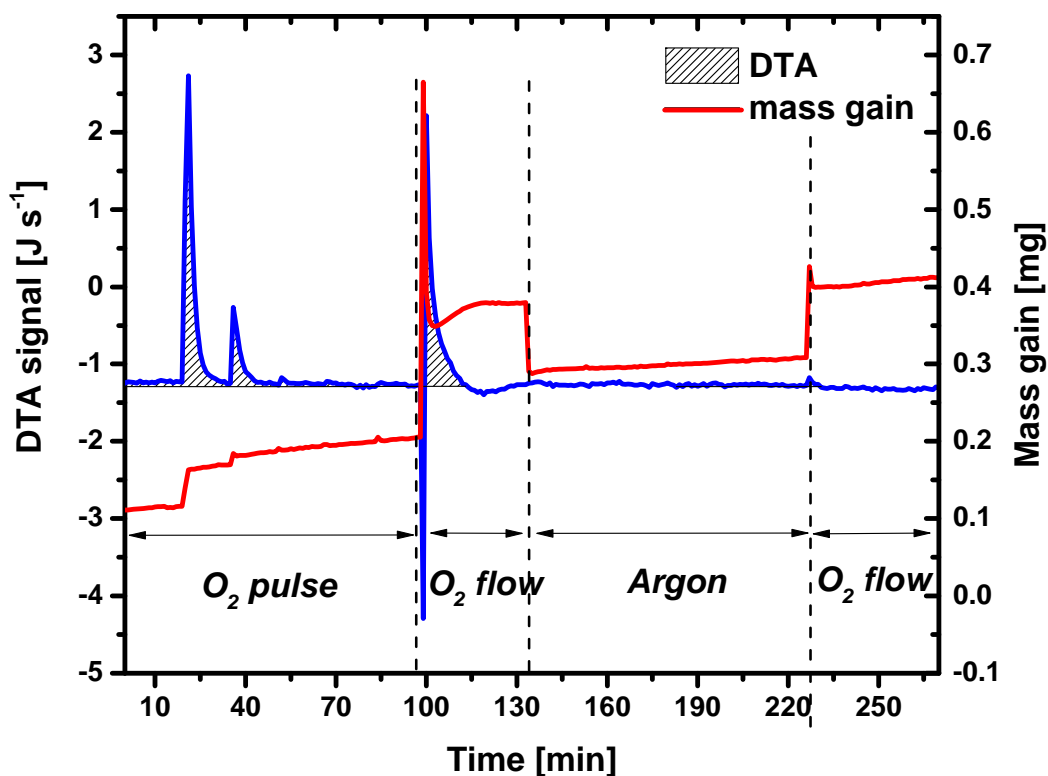


Figure 9. Oxygen Pulse experiment on Ni₄₀₀ °C followed by pure oxygen flow testing.

As mentioned earlier, due to a slight drift of the mass signal it is important to take into consideration the sharp mass increase at each pulse as opposed to the global mass gain. The ongoing drift even after the complete oxidation of the catalyst directly evidences that this process is not related to any oxidation event, and does not disturb the measurement. Comparing the amount of Ni atoms titrated with the total amount of Ni reduced, the metal dispersion never exceeded 12 %, confirming the incomplete oxidation of the Ni particles.

In the literature, there is a fair degree of disagreement concerning the experimental conditions of the N₂O chemisorption for Ni⁰ s.a. determination, regarding whether or not subsurface oxidation takes place. However, the accordance of the mean particle size with the one determined by electron microscopy is considered as a consistent descriptor, relying on an independent and direct measurement (as opposed to the O/Ni_s stoichiometry which usually relies on comparison with H₂ TPD measurements, with its intrinsic large sources of uncertainty). The inconsistencies in the use of O/Ni_s as a descriptor are largely documented in the literature, and it was observed that a change of the

support (SiO_2 , Al_2O_3 , TiO_2) was enough to induce large discrepancies [11, 13]. To our knowledge none of those studies involved the use of MgO as a support.

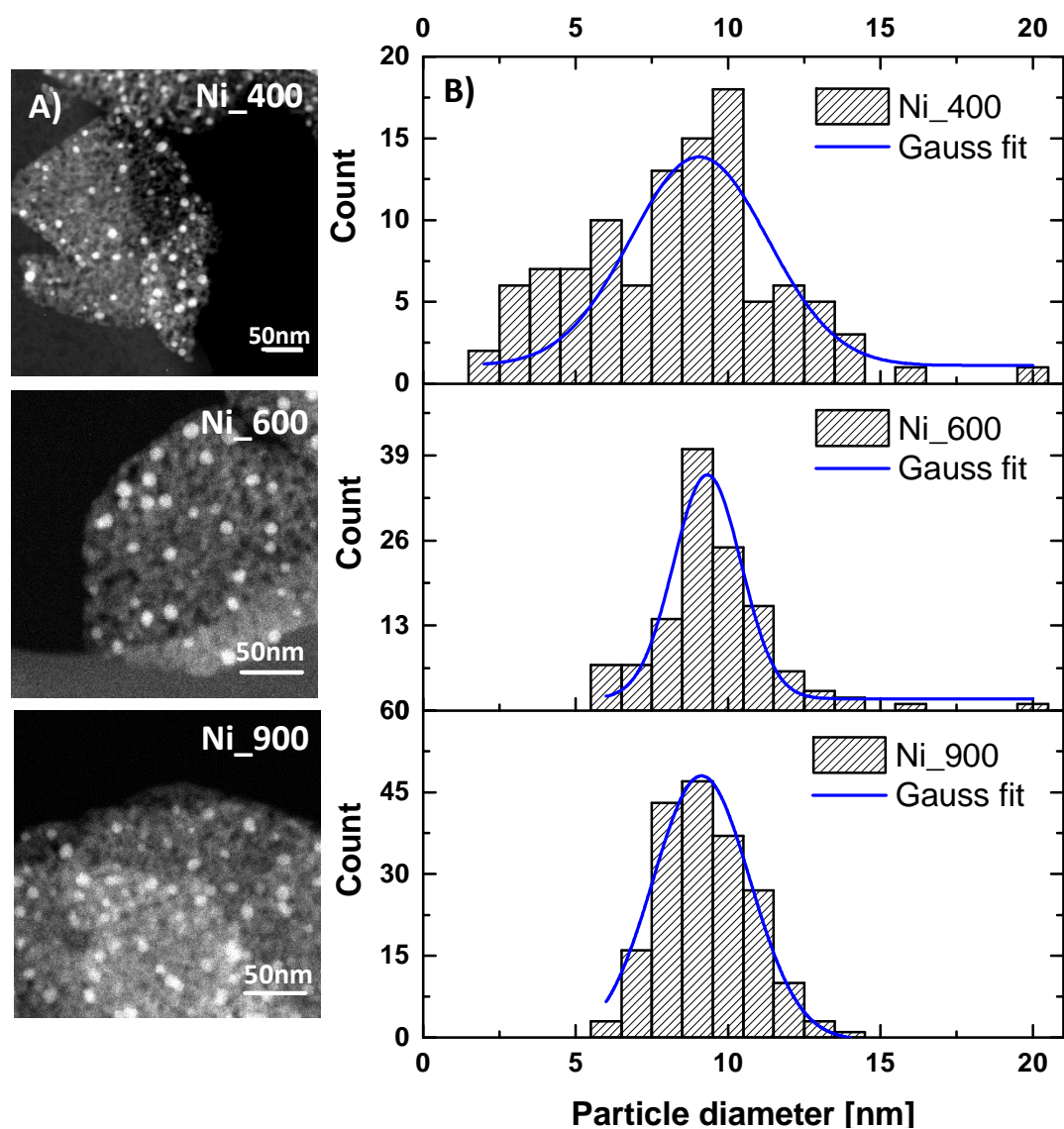


Figure 10. A) HAADF Image of Ni₄₀₀, Ni₆₀₀ and Ni₉₀₀ after reduction B) particle size distributions of the three samples

	Sample	H ₂ pulse	O ₂ pulse	TEM* (from Gauss fit)	TEM* (maximum count)
Particle Size [nm]	Ni10_400	24.8	10.6	9	10
	Ni10_600	24.8	8.6	9.3	9
	Ni10_900	46.6	8.4	9.1	9

*Calculated on more than 110 particles

Table 1. Summary table of the different mean particle size obtained by different techniques.

As a consequence, electron microscopy was used as complementary analysis method. The estimated particle size (from O₂ titration) is in good agreement with the TEM observations as shown Figure 10 and Table 1 (an exemplary calculation is provided in the supporting information).

3.5 Other probe molecules and techniques

H₂ as a probe molecule

H₂ titration, which is extensively used for numerous metals, shows some challenges in precisely quantifying the adsorbed H₂ when applied to metallic Ni. Ewald *et al.* recently published a thorough investigation of H₂ interaction with Ni, underlining the complexity of the system and the variability of the results obtained, depending on the adsorption and pre-treatment conditions [15]. An overestimation is critical, as H₂ tend to dissolve into the subsurface of the metallic Ni particles [54, 55]. Furthermore, choosing arbitrarily the H₂:Ni stoichiometric factor or hydrogen activation and spillover phenomena (that can occur on the support) can also distort the results [15, 56]. In that context, MgO may exhibit such effects as experimental and theoretical studies have shown that MgO has the ability to undergo direct adsorption and dissociation of H₂ [57]. Besides, it could diffuse into the subsurface layers and into the bulk sites [58-61]. This could only happen on surface defects with a radical character and able to bind (radical) H atoms (after activation at high temperatures) [62, 63]. The H₂ spillover is believed not to occur on MgO, which is an unreducible oxide [64]. Indeed, to observe spillover on a support, the binding energy of the support with hydrogen should be equivalent to the binding energy of the Metal-H bond. This value has to be larger than 218 kJ mol⁻¹ (one-half the dissociation energy of H₂ [65]) which is not the case for H-MgO [62]. However, the literature still diverge on this topic, as hydrogen spillover has been proposed to occur on MgO in the case study of supported copper catalyst [66]. Finally, an underestimation of desorbed H₂ can occur, as seen earlier, as simple room temperature adsorption techniques can lead to uncomplete Ni⁰ surface titrations.

CO as a probe molecule.

Titration of the metallic Ni with CO shows two main inconvenients: the formation of Ni(CO)₄ and the complex stoichiometry of the CO adsorption on metallic Ni. Ni(CO)₄ is a volatile compound that need proper disposal because of its high toxicity, and that disturbs proper titration by removing Ni atoms from the surface of the catalysts. This phenomenon only allows the titration of Ni⁰ species by CO at low temperature to avoid the *tetra*-carbonyl formation. Furthermore, the stoichiometry of CO adsorption on metallic Ni adds to the complexity of the task, making any titration method useless without spectroscopic is demanding, making any titration method useless without spectroscopic quantification of the linear/bridging adsorption ratio [9, 67, 68].

3.6 O₂ Pulse TA[®] advantages

Compared to these methods, oxidative pulse titration for Ni/MgO system proposed in this article present several advantages. It appeared safer, easier and more reliable. The use of O₂ suppresses H₂ direct dissociation, or spillover related issues and do not necessitate complementary spectroscopic analysis for data interpretation. Nevertheless, one could argue that the O₂ titration proposed in this article could lead to the formation of Ni₂O₃ (“black oxide”) and not to NiO (“green oxide”) [69], and that the different stoichiometry of the oxide could lead to difficulties for the metallic surface area determination. Due to the differential thermal analysis this hypothesis was rejected, as the standard enthalpy of formation of Ni₂O₃ largely differs from the one of NiO [70] ($\Delta H_{f, NiO}^0 = -239.74 \text{ kJ mol}^{-1}$ [42], $\Delta H_{f, Ni_2O_3}^0 = -489.5 \text{ kJ mol}^{-1}$ [71]). Furthermore, the STA-MS setup allows to work under flow conditions as opposed to vacuum, which facilitate the drawings of correlation with catalytic data (in our case with the methanation of CO₂ as will be shown in a separated manuscript).

The question that remains concerns its applicability to all sorts of supports. This depends on the ability of the support to adsorb or react with oxygen, which could disturb the Ni titration signals. Such adsorptions or reactions were linked to the presence of oxygen vacancies on the support after high temperature treatment and have to be minimized [72]. In this respect, MgO as a support is very convenient since O₂ titration on pure MgO after pre-treatment up to 1000 °C in H₂ did not show any mass uptake.

Conclusions

A new simple method to determine Ni⁰ surface areas of MgO supported catalysts is proposed. This method which is based on Pulse TA[®] of oxygen, was efficiently applied to Ni⁰/MgO systems. Pulse TA[®] was used to oxidize the surface metallic Ni. The amount of oxygen consumed was determined through the mass variation (but also observable by mass spectrometry) and the enthalpy of formation of the corresponding oxide was measured by differential thermal analysis, to gain insight on the stoichiometry of the formed oxide.

The relevance and accuracy of the method was evidenced in comparison to classical titration methods (H₂ pulse) and different probe molecules (N₂O). Furthermore, it allows the use of adequate stoichiometric factor (based on experimental data) instead of an arbitrary determination. The application of the method to two series of MgO supported Ni samples allows a better understanding of the specificities of the method and a broader confirmation of its relevance. This method is very fast compared to other classical method and does not necessitate the construction of a dedicated adsorption setup, as it merely requires a conventional STA-MS instrument with a pulse unit. The quality of the measurements could be improved, by using stronger gas purification systems (to remove traces of moisture), and less porous and hydrophilic materials for the reactor inner wall. In addition, as this study was limited to Ni⁰/MgO catalysts, we are currently working on applying and establishing this new method to other catalytic systems.

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References

- [1] T. Van Herwijnen, H. Van Doesburg, W.A. De Jong, Kinetics of the methanation of CO and CO₂ on a nickel catalyst, *Journal of Catalysis*, 28 (1973) 391-402.
- [2] Y. Li, G. Lu, J. Ma, Highly active and stable nano NiO–MgO catalyst encapsulated by silica with a core–shell structure for CO₂ methanation, *RSC Adv.*, 4 (2014) 17420-17428.
- [3] F.-m. Sun, C.-f. Yan, Z.-d. Wang, C.-q. Guo, S.-l. Huang, Ni/Ce–Zr–O catalyst for high CO₂ conversion during reverse water gas shift reaction (RWGS), *International Journal of Hydrogen Energy*, 40 (2015) 15985-15993.
- [4] L. Wang, S. Zhang, Y. Liu, Reverse water gas shift reaction over Co-precipitated Ni-CeO₂ catalysts, *Journal of Rare Earths*, 26 (2008) 66-70.
- [5] K. Mette, S. Kühn, H. Düdder, K. Kähler, A. Tarasov, M. Muhler, M. Behrens, Stable Performance of Ni Catalysts in the Dry Reforming of Methane at High Temperatures for the Efficient Conversion of CO₂ into Syngas, *ChemCatChem*, 6 (2014) 100-104.
- [6] K. Mette, S. Kühn, A. Tarasov, H. Düdder, K. Kähler, M. Muhler, R. Schlögl, M. Behrens, Redox dynamics of Ni catalysts in CO₂ reforming of methane, *Catalysis Today*, 242, Part A (2015) 101-110.
- [7] M. Chareonpanich, N. Teabpinyok, S. Kaewtaweesub, Effect of Nickel Particle Size on Dry Reforming Temperature, *WCECS 2008*, (2008).
- [8] G. Garbarino, P. Riani, L. Magistri, G. Busca, A study of the methanation of carbon dioxide on Ni/Al₂O₃ catalysts at atmospheric pressure, *International Journal of Hydrogen Energy*, 39 (2014) 11557-11565.
- [9] C.H. Bartholomew, R.B. Pannell, The stoichiometry of hydrogen and carbon monoxide chemisorption on alumina- and silica-supported nickel, *Journal of Catalysis*, 65 (1980) 390-401.
- [10] R. Geyer, J. Hunold, M. Keck, P. Kraak, A. Pachulski, R. Schödel, Methods for Determining the Metal Crystallite Size of Ni Supported Catalysts, *Chemie Ingenieur Technik*, 84 (2012) 160-164.
- [11] C. Hoang-Van, Y. Kachaya, S.J. Teichner, Y. Arnaud, J.A. Dalmon, Characterization of nickel catalysts by chemisorption techniques, x-ray diffraction and magnetic measurements, *Applied Catalysis*, 46 (1989) 281-296.
- [12] S. Tada, M. Yokoyama, R. Kikuchi, T. Haneda, H. Kameyama, N₂O Pulse Titration of Ni/ α -Al₂O₃ Catalysts: A New Technique Applicable to Nickel Surface-Area Determination of Nickel-Based Catalysts, *J. Phys. Chem. C*, 117 (2013) 14652-14658.
- [13] J.S. Smith, P.A. Thrower, M.A. Vannice, Characterization of NiTiO₂ catalysts by TEM, X-ray diffraction, and chemisorption techniques, *Journal of Catalysis*, 68 (1981) 270-285.
- [14] J.M. Criado, Influence of particle size on the stoichiometry of chemisorption of oxygen on supported nickel catalysts, *Reaction Kinetics and Catalysis Letters*, 8 (1978) 143-147.
- [15] S. Ewald, S. Standl, O. Hinrichsen, Characterization of nickel catalysts with transient methods, *Applied Catalysis A: General*, 549 (2018) 93-101.
- [16] Y.-S. Ho, C.-T. Yeh, Microgravimetric study on the interaction of nickel powders with nitrous oxide and dioxygen, *Journal of Molecular Catalysis*, 59 (1990) 53-59.
- [17] J.T. Richardson, H. Friedrich, R.N. McGill, Pulsed thermo kinetic (PTK) measurements, *Journal of Catalysis*, 37 (1975) 1-7.
- [18] J. Zieliński, Reaction of nitrous oxide with a nickel surface, *Applied Catalysis*, 35 (1987) 1-12.
- [19] G. Lohrengel, M. Baerns, Determination of the metallic surface area of nickel and its dispersion on a silica support by means of a microbalance, *Applied Catalysis*, 1 (1981) 3-7.
- [20] P.C. Gravelle, Calorimetry in Adsorption and Heterogeneous Catalysis Studies, *Catalysis Reviews*, 16 (1977) 37-110.
- [21] M. Feist, R. König, S. Bäßler, E. Kemnitz, Adsorption properties of various forms of aluminium trifluoride investigated by PulseTA[®], *Thermochimica Acta*, 498 (2010) 100-105.
- [22] M. Feist, K. Teinz, S.R. Manuel, E. Kemnitz, Characterization of surfacial basic sites of sol gel-prepared alkaline earth fluorides by means of PulseTA[®], *Thermochimica Acta*, 524 (2011) 170-178.

- [23] M. Maciejewski, A. Baiker, Chapter 4 - Pulse Thermal Analysis, in: M.E.B. Gallagher, K. Patrick (Eds.) Handbook of Thermal Analysis and Calorimetry, Elsevier Science B.V.2008, pp. 93-132.
- [24] M. Maciejewski, C.A. Müller, R. Tschan, W.D. Emmerich, A. Baiker, Novel pulse thermal analysis method and its potential for investigating gas-solid reactions, *Thermochimica Acta*, 295 (1997) 167-182.
- [25] F. Eigenmann, M. Maciejewski, A. Baiker, Gas adsorption studied by pulse thermal analysis, *Thermochimica Acta*, 359 (2000) 131-141.
- [26] M. Maciejewski, A. Baiker, Quantitative calibration of mass spectrometric signals measured in coupled TA-MS system, *Thermochimica Acta*, 295 (1997) 95-105.
- [27] O. Hinrichsen, T. Genger, M. Muhler, Chemisorption of N₂O and H₂ for the Surface Determination of Copper Catalysts, *Chem. Eng. Technol.*, 23 (2000) 956-959.
- [28] X. Xia, R.N. d'Alnoncourt, M. Muhler, Entropy of adsorption of carbon monoxide on energetically heterogeneous surfaces, *J Therm Anal Calorim*, 91 (2008) 167-172.
- [29] A. Kuzmin, N. Mironova, Composition dependence of the lattice parameter in NiMg_{1-cO} solid solutions, *Journal of physics. Condensed matter*, 10 (1998) 7937-7944.
- [30] M. Jafarbegloo, A. Tarlani, A.W. Mesbah, J. Muzart, S. Sahebdehfar, NiO–MgO Solid Solution Prepared by Sol–Gel Method as Precursor for Ni/MgO Methane Dry Reforming Catalyst: Effect of Calcination Temperature on Catalytic Performance, *Catal Lett*, 146 (2016) 238-248.
- [31] M.-M. Millet, G. Algara-Siller, S. Wrabetz, A. Mazheika, F. Girgsdies, D. Teschner, F. Seitz, A. Tarasov, S.V. Levchenko, R. Schlögl, E. Frei, Ni single atom catalyst for CO₂ activation, To be submitted to *ChemCatChem*, (2018).
- [32] T. Cotter, <http://dx.doi.org/10.14279/depositonce-2970>, <http://dx.doi.org/10.14279/depositonce-2970>.
- [33] H. Yang, J.L. Whitten, Dissociative adsorption of H₂ on Ni(111), *The Journal of Chemical Physics*, 98 (1993) 5039-5049.
- [34] A.V. Hamza, R.J. Madix, Dynamics of the dissociative adsorption of hydrogen on nickel(100), *J. Phys. Chem.*, 89 (1985) 5381-5386.
- [35] C.H.B. J.B. Butt, *Catalyst Deactivation*, 1st Edition ed.1991.
- [36] R. Geyer, J. Hunold, M. Keck, P. Kraak, A. Pachulski, R. Schödel, Methods for Determining the Metal Crystallite Size of Ni Supported Catalysts, *Chemie Ingenieur Technik*, 84 (2011) 160-164.
- [37] C. Hoang-Van, Y. Kachaya, S.J. Teichner, Y. Arnaud, J.A. Dalmon, Characterization of nickel catalysts by chemisorption techniques, x-ray diffraction and magnetic measurements: Effects of support, precursor and hydrogen pretreatment, *Applied Catalysis*, 46 (1989) 281-296.
- [38] P.A. Webb, *Introduction to Chemical Adsorption Analytical Techniques | Adsorption | Catalysis*, Scribd.
- [39] N.K. Nakai K., Pulse chemisorption measurement <Metal dispersion measurement>, BEL-CAT Application note, CAT-APP-002 (2003).
- [40] K. Mette, S. Kühl, A. Tarasov, M.G. Willinger, J. Kröhnert, S. Wrabetz, A. Trunschke, M. Scherzer, F. Girgsdies, H. Düdder, K. Kähler, K.F. Ortega, M. Muhler, R. Schlögl, M. Behrens, T. Lunkenbein, High-Temperature Stable Ni Nanoparticles for the Dry Reforming of Methane, *ACS Catal.*, 6 (2016) 7238-7248.
- [41] M. Fadoni, L. Lucarelli, Temperature programmed desorption, reduction, oxidation and flow chemisorption for the characterisation of heterogeneous catalysts. Theoretical aspects, instrumentation and applications, *Studies in Surface Science and Catalysis*, 120 (1999) 177-225.
- [42] B.J. Boyle, E.G. King, K.C. Conway, Heats of Formation of Nickel and Cobalt Oxides (NiO and CoO) of Combustion Calorimetry, *J. Am. Chem. Soc.*, 76 (1954) 3835-3837.
- [43] R.D. Holmes, H.S.C. O'Neill, R.J. Arculus, Standard Gibbs free energy of formation for Cu₂O, NiO, CoO, and Fe₃O₄: High resolution electrochemical measurements using zirconia solid electrolytes from 900–1400 K, *Geochimica et Cosmochimica Acta*, 50 (1986) 2439-2452.
- [44] N. Takezawa, H. Terunuma, M. Shimokawabe, H. Kobayashib, Methanation of carbon dioxide: preparation of Ni/MgO catalysts and their performance, *Applied Catalysis*, 23 (1986) 291-298.

- [45] F. Arena, F. Frusteri, A. Parmaliana, N. Giordano, On the reduction of NiO forms in magnesia supported catalysts, *Reaction Kinetics and Catalysis Letters*, 42 (1990) 121-126.
- [46] L. Znak, J. Zieliński, Interaction of Hydrogen with Unsupported and Supported Nickel, *Langmuir*, 22 (2006) 8758-8763.
- [47] L. Znak, J. Zieliński, Effects of support on hydrogen adsorption/desorption on nickel, *Applied Catalysis A: General*, 334 (2008) 268-276.
- [48] Y. Yao, Z. Yan, L. Chen, Z. Zhou, L. Liu, D.W. Goodman, Nickel Particle Size Effects on Cyclohexane Dehydrogenation: A Combined Reaction Kinetics and Surface Science Study, *Catal Lett*, 142 (2012) 1437-1444.
- [49] G.C. Chinchin, C.M. Hay, H.D. Vandervell, K.C. Waugh, The measurement of copper surface areas by reactive frontal chromatography, *Journal of Catalysis*, 103 (1987) 79-86.
- [50] J. Schumann, M. Eichelbaum, T. Lunkenbein, N. Thomas, M.C. Álvarez Galván, R. Schlögl, M. Behrens, Promoting Strong Metal Support Interaction: Doping ZnO for Enhanced Activity of Cu/ZnO:M (M = Al, Ga, Mg) Catalysts, *ACS Catal.*, 5 (2015) 3260-3270.
- [51] J. Dawody, L. Eurenus, H. Abdulhamid, M. Skoglundh, E. Olsson, E. Fridell, Platinum dispersion measurements for Pt/BaO/Al₂O₃, NO_x storage catalysts, *Applied Catalysis A: General*, 296 (2005) 157-168.
- [52] S.R. Seyedmonir, D.E. Strohmayer, G.L. Geoffroy, M.A. Vannice, H.W. Young, J.W. Linowski, Characterization of supported silver catalysts, *Journal of Catalysis*, 87 (1984) 424-436.
- [53] M. Brainbridge, J.S. Clarkson, B.L. Parnham, J. Tabatabaei, D.V. Tyers, K.C. Waugh, Evidence for support effects in metal oxide supported cobalt catalysts: *Catalysis, Structure & Reactivity: Vol 3, No 3*.
- [54] J. Greeley, M. Mavrikakis, A first-principles study of surface and subsurface H on and in Ni(1 1 1): diffusional properties and coverage-dependent behavior, *Surface Science*, 540 (2003) 215-229.
- [55] B. Bhatia, D.S. Sholl, Chemisorption and diffusion of hydrogen on surface and subsurface sites of flat and stepped nickel surfaces, *The Journal of Chemical Physics*, 122 (2005) 204707.
- [56] S.J. Techner, A.R. Mazabrard, G. Pajonk, G.E.E. Gardes, C. Hoang-Van, Hydrogen spillover in catalytic reactions, *Journal of Colloid and Interface Science*, 58 (1977) 88-99.
- [57] A. Mazheika, S.V. Levchenko, Ni Substitutional Defects in Bulk and at the (001) Surface of MgO from First-Principles Calculations, *J. Phys. Chem. C*, 120 (2016) 26934-26944.
- [58] G. Wu, J. Zhang, Y. Wu, Q. Li, K. Chou, X. Bao, Adsorption and dissociation of hydrogen on MgO surface: A first-principles study, *Journal of Alloys and Compounds*, 480 (2009) 788-793.
- [59] H. Kobayashi, D.R. Salahub, T. Ito, Dissociative Adsorption of Hydrogen Molecule on MgO Surfaces Studied by the Density Functional Method, *J. Phys. Chem.*, 98 (1994) 5487-5492.
- [60] T. Ito, T. Sekino, N. Moriai, T. Tokuda, Hydrogen adsorption on magnesium oxide powders, 77 (1981) 2181-2192.
- [61] H.C. Wu, Y.C. Chang, J.H. Wu, J.H. Lin, I.K. Lin, C.S. Chen, Methanation of CO₂ and reverse water gas shift reactions on Ni/SiO₂ catalysts: the influence of particle size on selectivity and reaction pathway, 5 (2015) 4154-4163.
- [62] R. Prins, Hydrogen Spillover. Facts and Fiction, *Chem. Rev.*, 112 (2012) 2714-2738.
- [63] E.A. Colbourn, W.C. Mackrodt, Theoretical aspects of H₂ and CO chemisorption on MgO surfaces, *Surface Science*, 117 (1982) 571-580.
- [64] R. Prins, V.K. Palfi, M. Reiher, Hydrogen Spillover to Nonreducible Supports, *J. Phys. Chem. C*, 116 (2012) 14274-14283.
- [65] R.B. Levy, M. Boudart, The kinetics and mechanism of spillover, *Journal of Catalysis*, 32 (1974) 304-314.
- [66] R. Shi, F. Wang, X. Mu, Y. Li, X. Huang, W. Shen, MgO-supported Cu nanoparticles for efficient transfer dehydrogenation of primary aliphatic alcohols, *Catalysis Communications*, 11 (2009) 306-309.
- [67] K.I. Hadjiivanov, G.N. Vayssilov, Characterization of oxide surfaces and zeolites by carbon monoxide as an IR probe molecule, in: B.T.A.i. *Catalysis (Ed.)*, Academic Press 2002, pp. 307-511.

- [68] J. B. Peri, Infra-red studies of carbon monoxide and hydrocarbons adsorbed on silica-supported nickel, *Discussions of the Faraday Society*, 41 (1966) 121-134.
- [69] N.N. Greenwood, A. Earnshaw, *Chemistry of the elements*, Pergamon Press 1984.
- [70] K. Raznjevic, *Handbook of thermodynamic tables and charts*, Washington, Hemisphere publishing corporation, 1976, 1976.
- [71] D.W. Donald, *The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units*, American Chemical Society and the American Institute of Physics for the National Bureau of Standards ed. 1982.
- [72] E. Castanier, C. Noguera, Oxygen vacancies on MgO(100), *Surface Science*, 364 (1996) 1-16.

SUPPORTING INFORMATION

1. Mass of catalyst used

Catalyst ref.	Mass used (mg)	Sample #
Ni_400	20.9	#21743
Ni_500	20.01	#21808
Ni_600	21.6	#21810
Ni_700	20.1	#21584
Ni_900	23.0	#22304
Ni_3	79.41	#21547
Ni_5	116.99	#21548
Ni_10	108.14	#21549
Ni_15	19.8	#23892

Table S 1. Mass of catalyst used for O₂ titration.

2. Reducibility of the samples (calcination serie)

Sample	Ni_400	Ni_500	Ni_600	Ni_700	Ni_900
Reducibility [%]	74.5	64.2	58.8	19.1	18.1

Table S 2. Reducibility of the calcination series

The reducibility of the samples was determined by temperature programmed reduction using CuO as reference for the quantification.

3. Signal drift intensity

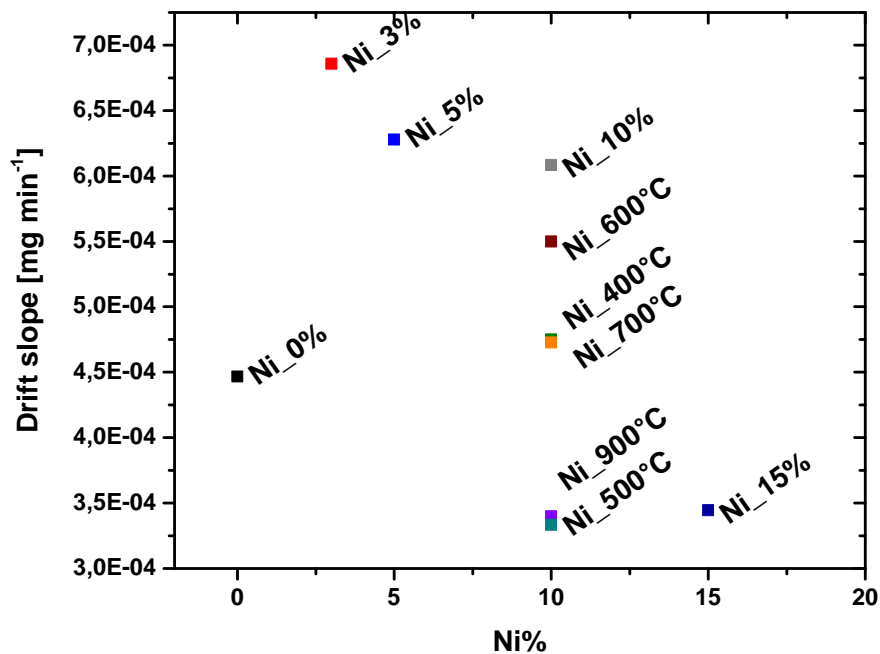
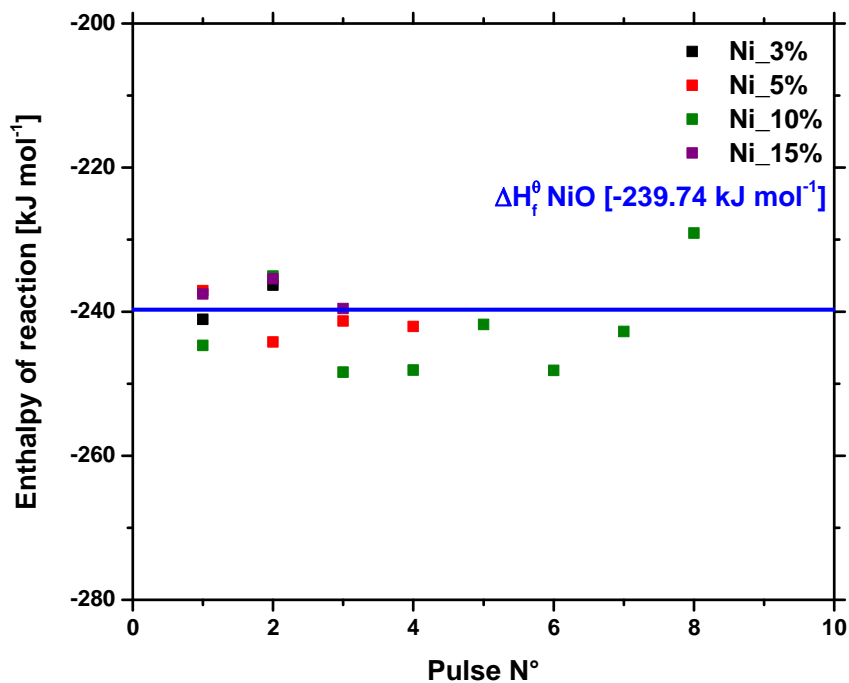


Figure S 1. Representation of the slope of the drift for each sample.

4. Detail of each pulses enthalpy for the two Ni



series

Figure S 2. Enthalpy of each pulse, for the titration of both the concentration and the calcination series.

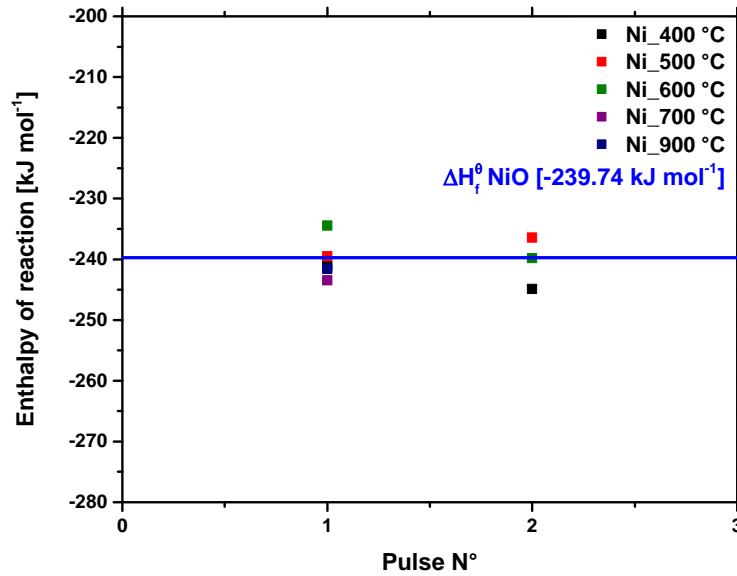


Figure S 3. Enthalpy of each pulse, for the titration of both the concentration and the calcination series.

5. Exemplary calculation of the metal particle size for H₂ pulse titration on Ni 400°C

For the determination of the metal particle size (MCS) the equations (4) and (5) (see experimental part) were used:

$$MCS = \frac{F}{(Ni^0 \text{ s. a.}_{Ni} * d_{Ni})}$$

With $F=6$; $d_{Ni}=8.908 \text{ g cm}^{-3}$, and $Ni^0 \text{ s. a.}_{Ni}$ defined as follows:

$$Ni^0 \text{ s. a.}_{Ni} = \frac{((n_H) * N_A)}{g_{metal}} * RA$$

With $N_A=6.022 \cdot 10^{23} \text{ mol}^{-1}$, $RA=6.49 \cdot 10^{-20} \text{ m}^2 \text{ atom}^{-1}$, and where:

- n_H corresponds to the amount of hydrogen adsorbed on the nickel calculated following the procedure of Mette *et al.* [40]. For the Ni_400°C sample $n_H=7.12 \cdot 10^{-6} \text{ mol}$.
- g_{metal} corresponds to the mass of reduced Nickel upon the reduction treatment. Considering 0.101 g of a 10% atomic concentration of nickel and a reduction grade of 75%, we end up with 10.24 mg of metallic Ni after reduction.

Injecting back in the previous equation, we find:

$$Ni^0 \text{ s. a.}_{Ni} = 27.1 \text{ m}^2 \text{ g}_{Ni}^{-1}$$

$$MCS = 24.6 \text{ nm}$$