## Supporting Information: The role of hydrogen during Pt-Ga nanocatalyst formation

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#### 1. Ga K edge XANES quantitative peak fitting analysis

The procedure of Nishi et al.<sup>1</sup> was followed for peak fitting analysis of the Ga K edge XANES signals. To fit a single contribution, an arctangent function was used for modeling the continuum absorption in combination with a Gaussian function to model the white line. The inflection point of the arctangent function is implemented at the same value as the inflection point of the Gaussian curve. The ratio between the height of the arctangent function and the peak area (or intensity) of the Gaussian curve is kept constant. Notably, the width of the arctangent function was always fixed to 1 eV.

Fitting of the Ga K edge XANES spectrum of the initial non-reduced Pt/Mg(Ga)(Al)O<sub>x</sub> sample (Figure 2.a) was done by modeling of the two single contributions of the spectrum, namely Ga<sup>3+</sup>(t) and Ga<sup>3+</sup>(o) (in total by 2 arctangents and 2 Gaussians). The energy position of the coupled Gaussian and arctangent functions, as well as their amplitude and Gaussian widths were estimated by minimizing the sum of squared residuals, after implementation of suitable initial guesses. The resulting energy positions of these Gaussians and arctangents for the Ga<sup>3+</sup>(t) and Ga<sup>3+</sup>(o) contributions were fixed during further peak fitting analysis of the reduced Ga K edge XANES spectra of H<sub>2</sub> reduced Pt/Mg(Ga)(Al)O<sub>x</sub> (Figure 2.b) and Pt/Mg(Al)O<sub>x</sub> + Mg(Ga)(Al)O<sub>x</sub> catalysts (Figure 2.c).

Next, the Ga K edge XANES spectrum of H<sub>2</sub> reduced Pt/Mg(Al)O<sub>x</sub> + Mg(Ga)(Al)O<sub>x</sub> (Figure 2.c) was modeled by adding a third Gaussian and arctangent function, besides the ones of Ga<sup>3+</sup>(t) and Ga<sup>3+</sup>(o). Finally, a fourth contribution was added to the fitting model for H<sub>2</sub> reduced Pt/Mg(Ga)(Al)O<sub>x</sub>. Because of its small contribution in the H<sub>2</sub> reduced Pt/Mg(Ga)(Al)O<sub>x</sub> signal, the arctangent function was left out during analysis, and only a Gaussian was used to fit the Ga<sup>0</sup> contribution. The resulting fits and single contributions are shown in Figure 2.

#### 2. Ga K edge EXAFS modeling of Pt/Mg(Ga)(Al)O<sub>x</sub> before H<sub>2</sub> TPR.

XAS data reduction and analysis were executed with Athena and Artemis, part of the Demeter 0.9.13 software package.<sup>2</sup> Background subtraction, normalization,  $\chi(k)$  isolation and Fourier transformation were performed using the methodology of Koningsberger et al..<sup>3</sup> The FEFF 6.0 code<sup>4</sup> was used to calculate the phase shifts and backscattering amplitude function of Pt-O. The Levenberg-Marquardt algorithm was applied for non-linear least-squares minimization of the objective function in order to estimate the implemented structural parameters. This minimization was carried out by IFEFFIT software<sup>2</sup> through multiple shell fitting in R-space using multiple k-weightings.

The Fourier transformed Ga K edge EXAFS signal of Pt/Mg(Ga)(Al)O<sub>x</sub> before H<sub>2</sub> TPR shows an intense peak ~1.4 Å (non-corrected R-space), characteristic of Ga-O bonds. Fourier transformed EXAFS modeling of this oxygen contribution with a single Ga-O shell results in convergence between the model and the experimental signal ( $\Delta k = 3.5 - 13.3 \text{ Å}^{-1}$ ,  $\Delta R = 1 - 2 \text{ Å}$ ). The estimated Ga-O coordination number N<sub>Ga-O</sub> amounts to 4.7 ± 0.8 and therefore indicates that Mg(Ga)(Al)O<sub>x</sub> contains both tetrahedral and octahedral oxygen coordinated Ga<sup>3+</sup> cations. More quantitatively, ~ 60 % of the Ga<sup>3+</sup> cations is tetrahedral whereas the remaining 40 % is of the octahedral type (0.6 × 4 + 0.4 × 6 ≈ 4.7). These EXAFS modeling results fully correspond with quantitative XANES peak fitting analysis, showing that 60 % Ga<sup>3+</sup>(t) and 40 % Ga<sup>3+</sup>(o) is present for Pt/Mg(Ga)(Al)O<sub>x</sub> before H<sub>2</sub> TPR (Figure 2.a, Supporting Information 1). The estimated structural parameters resulting from EXAFS modeling are shown in Supporting Table 1.

Supporting Table 1: Ga-O coordination number  $N_{Ga-O}$ , interatomic distance  $R_{Ga-O}$ , Debye-Waller disorder factor  $\sigma^2_{Ga-O}$ , as well as the edge energy shift  $\Delta E_0$ .

N <sub>Ga-O</sub> [-]	$4.7 \pm 0.8$
$\Delta E_0 [eV]$	$7.7 \pm 2.3$
R <sub>Ga-O</sub> [Å]	$1.88\pm0.02$
$\sigma^{2}_{\text{Ga-O}} \left[ 10^{-3} \times \text{\AA}^{2} \right]$	$9.3 \pm 2.5$



Supporting Figure 1: (black full line) magnitude and (black dotted line) imaginary part of the Fourier transformed Ga K edge EXAFS signal of  $Pt/Mg(Ga)(Al)O_x$  before the start of  $H_2$  TPR; (red full line) magnitude and (red dotted line) imaginary part of the Ga-O shell model fit.

# 3. Possible Ga-H bond formation and Ga coordination change and their influence on the Ga K edge XANES edge

Two additional causes, namely a coordination change around Ga (octa- to tetrahedral) and Ga-H bond formation, could equally induce negative shifts in the XANES edge energy besides Ga oxidation state decrease. However, in the present case, the observed changes in the XANES signal can be attributed to true changes in the Ga oxidation state, as explained below.

1. **Ga-H bond formation.**  $Ga_2O_3$  heterolytically dissociates  $H_2$  molecules on Ga-O bonds, resulting in the formation of Ga-H and Ga-OH surface bonds (reversible endothermic process).<sup>5</sup> The Mg(Ga)(Al)O<sub>x</sub> surface therefore also displays Ga-H bonds under  $H_2$  atmosphere at 650 °C. Indeed, TAP experiments show high H coverages on the Mg(Ga)(Al)O<sub>x</sub> surface during  $H_2$  pulse-response experiments compared to Mg(Al)O<sub>x</sub> (Figure 3.b).

Although Ga-H bonds occur on Mg(Ga)(Al)O<sub>x</sub> (both supported by literature and TAP), the Ga K edge XANES spectra upon H<sub>2</sub> treatment of Mg(Ga)(Al)O<sub>x</sub> supports at 650 °C do not show significant changes (Figure 1.a). This shows that Ga-H bond formation does not induce substantial changes in the Ga K edge XANES spectrum, and therefore it cannot be the cause of the observed white line shifts for Pt/Mg(Al)O<sub>x</sub> + Mg(Ga)(Al)O<sub>x</sub>, Pt/Mg(Ga)(Al)O<sub>x</sub> (Figure 1.b-c).

Ga coordination. All Ga K edge XANES white line features in Figure 1.a-c show double peak features for the three cases investigated, i.e. Mg(Ga)(Al)O<sub>x</sub>, Pt/Mg(Al)O<sub>x</sub> + Mg(Ga)(Al)O<sub>x</sub>, Pt/Mg(Ga)(Al)O<sub>x</sub>. As proven by Nishi et al.<sup>1</sup>, the first peak above the edge corresponds to tetrahedrally coordinated Ga (Ga(t)), whereas the second peak at higher energy originates from octahedral Ga (Ga(o)).

As shown below (Section 3), the edge energy of the Ga K edge XANES spectrum of  $Mg(Ga)(Al)O_x$  fully coincides with the one of a tetrahedrally coordinated  $Ga^{+3}$  reference. If the observed Ga K edge shift would be a consequence of a change in  $Ga^{3+}$  coordination (Ga(o) to Ga(t), or vice versa), the edge

would shift in between the pure  $Ga^{3+}(t)$  and  $Ga^{3+}(o)$  edge positions – as the total signal is a linear combination of the  $Ga^{3+}(t)$  and  $Ga^{3+}(o)$  fractions. However, the observed Ga edges of Pt/Mg(Al)O<sub>x</sub> + Mg(Ga)(Al)O<sub>x</sub> and Pt/Mg(Ga)(Al)O<sub>x</sub> (Figure 1.b-c) are shifting – during H<sub>2</sub> TPR – to values below the one of a pure  $Ga^{3+}(t)$  reference, implying that a coordination change is not the underlying cause of the observations.

For these two reasons, the observed decreasing XANES edge energies are not related to changes in Ga coordination (Ga(o)  $\rightarrow$  Ga(t)) or Ga-H bond formation, but rather to changes in the oxidation state of the Ga species in the support. Indeed, the reduction of metal oxides generally results in an edge shift towards lower photon energies. The full reduction of Ga<sup>3+</sup> into metallic Ga<sup>0</sup> is accompanied by a total shift of – 5 eV.<sup>6</sup> For this reason, partial reduction of Ga<sup>+3</sup> surface centers into Ga<sup>+6</sup> results in a shift of the Ga XANES edge to lower energies, as observed in Figure 1.b-c.

#### 4. Ga K edge XANES reference spectra.

Supporting Figure 2 (left) shows the Ga K edge XANES signal of a bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reference, containing 50 % Ga<sup>3+</sup>(t) and 50 % Ga<sup>3+</sup>(o).<sup>1</sup> Supporting Figure 2 (right) shows the Ga K edge XANES spectra of (1) Mg(Ga)(Al)O<sub>x</sub> mixed oxide (blue), (2) amorphous Ga<sub>2</sub>O<sub>3</sub> inside a ZSM-5 zeolite (red), (3) Ga<sub>2</sub>O<sub>3</sub> inside a ZSM-5 zeolite which was treated by H<sub>2</sub> TPR to 650 °C (green). The edges of Mg(Ga)(Al)O<sub>x</sub> and Ga<sub>2</sub>O<sub>3</sub> in the zeolite are situated at the same photon energies, showing that Ga is in a 3+ oxidation state for non-reduced Mg(Ga)(Al)O<sub>x</sub>. The reduction treatment of Ga<sub>2</sub>O<sub>3</sub> in the zeolite induces a negative shift (~ – 5 eV) in the Ga K edge XANES signal as a result of metallic Ga formation.



Supporting Figure 2: (left) bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> reference containing 50 % Ga<sup>3+</sup>(t) and 50 % Ga<sup>3+</sup>(o), obtained by Nishi et al.<sup>1</sup>; (right) Ga K edge XANES spectra of Mg(Ga)(Al)O<sub>x</sub> mixed oxide (blue), amorphous Ga<sub>2</sub>O<sub>3</sub> inside a ZSM-5 zeolite (red) Ga<sub>2</sub>O<sub>3</sub> inside a ZSM-5 zeolite which was treated by a H<sub>2</sub> TPR to 650 °C (green).

### 5. Temporal Analysis of Products (TAP) experiments

#### Experimental details

Material	Zone 1 (SiO <sub>2</sub> ), mm	Zone 2, (sample), mm	Zone 3 (SiO <sub>2</sub> ), mm	°33	Sample mass, mg	T, ℃	** $D_{ref} \cdot 10^2$ , m <sup>2</sup> /s	<sup>**</sup> $N_p \cdot 10^8$ , mol/pulse
SiO <sub>2</sub>	57.5	-	-	0.5	-	650	1.20	4.35
Mg(Al)O <sub>x</sub>	32.9	1.5	23.1	0.5	8.8	650	1.32	4.32
Mg(Al,Ga)O <sub>x</sub>	33	1.1	23.5	0.5	7.1	650	1.30	5.67
5%Pt/Mg(Al)O <sub>x</sub>	33.5	1.0	23.0	0.5	8.6	650	1.31	5.59

#### Supporting Table 2: Experimental details

\* characteristic value for 250<d<500 μ particles</p>
\*\*estimated by regression from He response

#### Data analysis

The flow rates of  $H_2$  and He exiting from the reactor were measured with a calibrated QMS with millisecond time resolution. Quantitative observations of  $H_2$  behavior in heterogeneous media of catalytic materials often face experimental challenges due to the exceptional mobility and light mass of H atoms and  $H_2$  molecules. In the state-of-the-art TAP-3 instrument employed in this study,  $H_2$  transport through the catalyst bed and within the catalytic particles could be very accurately quantified (time-resolved and high S/N ratio) based on the transport of an internal inert standard, in this case He.

To calibrate the sensitivities of the QMS towards He and H<sub>2</sub>, a series of 1000 H<sub>2</sub>/He (1:1) pulses was injected into the microreactor packed with SiO<sub>2</sub> from a fixed ( $V_f = 6.8$  ml) feed volume which was kept at 75°C. The pressure drop in the feed volume was measured as 11.7 kPa. The sensitivities of He and H<sub>2</sub> were calculated based on the recorded responses as  $5.8 \cdot 10^6$  and  $14.0 \cdot 10^6$  V/mol, respectively. The following formula based on the ideal gas law was used:

 $c_{f}^{i} = \frac{m_{0}^{i} \cdot 1000 \cdot R \cdot T}{\Delta P \cdot 0.5 \cdot V_{f}}$ , where R = 8.314, J/mol/k is the universal gas constant and m<sub>0</sub>, V is the average area under the response curve.

To quantify the transport of gases through the microreactor packing, the reference effective diffusion coefficient was estimated for each experiment from the He response using a standard 1D Knudsen model.<sup>7</sup> The reference effective diffusion coefficient is defined as diffusion coefficient of a reference gas, in this case He, measured at room temperature (298.15 K). The diffusion coefficient at any temperature (T) and for any gas with molecular mass (M) can then be calculated using this reference according to

$$D_{i}(T) = D_{ref}(T_{ref}) \sqrt{\frac{T}{T_{ref}}} \sqrt{\frac{M_{ref}}{M_{i}}}.$$

Simultaneously, the total pulse intensity was also estimated from He response using the He QMS sensitivity. Estimated reference diffusion coefficients and pulse intensities are listed for all samples in Table 1. To illustrate the quality of the fit, Supporting Figure 3.a depicts an experimental and fitted H<sub>2</sub> responses over 5%Pt/Mg(Al)O<sub>x</sub> sample. The obtained estimates were used to scale the exit-flow rate curves presented in Figure 3.a. Furthermore, they were used to simulate how the H<sub>2</sub> response would look like in the absence of chemical reactions (diffusion-only). Supporting Figure 3.b depicts simulated diffusion-only and experimental responses for He and H<sub>2</sub> pulsed over the 5%Pt/Mg(Al)O<sub>x</sub> sample.



Supporting Figure 3: (a) Regression of the experimental He response; (b) simulation of the diffusion-only  $H_2$  response based on the estimated diffusion coefficient of He.

From the difference between the simulated diffusion-only and the actual experimental (diffusion + reaction) response of  $H_2$ , the rate of  $H_2$  consumption by the sample can be reconstructed with no additional kinetic assumptions using the Y-Procedure. The reconstructed adsorption rates for all investigated samples are plotted in Supporting Figure 4. The rate reaches the peak very early during the pulse, when adsorption dominates desorption. Then, the rate decreases and becomes negative, when desorption begins to dominate. In the tail of the curve, the rate very slowly approaches zero from below as a result of slow desorption. These rates were subsequently integrated in time and normalized by the catalyst mass and the BET surface area to yield the surface coverage presented in Figure 3.b:

$$\theta_{\rm H}(t) = \int_{0}^{t} \frac{2R_{\rm H_2}(t')}{m_{\rm cat} \cdot {\rm BET}} dt'$$

It should be noted that the 0.1 s lag before the pulse, which is clearly visible in Supporting Figure 3, was cut out in Supporting Figure 4 for proper time integration of the rates.



Supporting Figure 4. Adsorption rates of  $H_2$  over different materials reconstructed via the Y-Procedure from the difference between experimental and diffusion-only  $H_2$  response.

## 6. XANES during H<sub>2</sub> TPR to 750 °C on a physical mixture of Pt/Mg(Al)O<sub>x</sub> and Mg(Ga)(Al)O<sub>x</sub>.

The XANES profiles depicted in Supporting Figure 5 are recorded during H<sub>2</sub>/He TPR treatment from 650 °C to 750 °C on a physical mixture of Pt/Mg(Al)O<sub>x</sub> and Mg(Ga)(Al)O<sub>x</sub>. Below 650 °C, no Pt-Ga alloying is observed (Figure 1.e) due to the limited mobility of partially reduced Ga species on Mg(Ga)(Al)O<sub>x</sub>. However, thermal activation from 650 °C to 750 °C in H<sub>2</sub>/He environment results in a significant Pt L<sub>III</sub> XANES edge shift and white line decrease, characteristic for Pt-Ga alloying. This strongly suggests that partially reduced Ga species gain mobility upon temperature increase and migrate to Pt to form Pt-Ga nano-alloys.



Supporting Figure 5: Pt L<sub>III</sub> edge XANES spectra recorded during H<sub>2</sub>/He TPR from 650 °C to 750 °C of a physical mixture of Pt/Mg(Al)O<sub>x</sub> + Mg(Ga)(Al)O<sub>x</sub>.

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