



Short communication

# Gold nanoparticles onto cerium oxycarbonate as highly efficient catalyst for aerobic allyl alcohol oxidation

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## ARTICLE INFO

## Keywords:

Au nanoparticles  
Cerium oxycarbonate  
Allyl alcohol  
Oxidation  
Air

## ABSTRACT

Au nanoparticles, generated by the metal vapor synthesis technique, were supported onto cerium oxycarbonate monohydrate ( $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$ ) giving  $\text{Au}@(\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O})$ . The obtained heterogeneous catalyst was used in the aerobic allyl alcohol oxidation reaction performed in toluene, showing a notably higher catalytic substrate conversion and isomerization activity compared to Au onto ceria, which is the reference catalyst for this type of catalysis. Results originating from catalytic recycling experiments and PXRD, HRTEM and XPS measurements carried out on recovered  $\text{Au}@(\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O})$ , confirmed the stability of the catalyst under aerobic oxidation reaction conditions and hence its recyclability, without the need of a regeneration step.

## 1. Introduction

Allylic alcohols are challenging substrates in oxidation reactions, since carbon-carbon double bond isomerization, hydrogenation as well as epoxidation reactions might simultaneously occur, notably decreasing thus the chemoselectivity for the desired  $\alpha,\beta$ -unsaturated carbonyl compound. Homogeneous Mn- [1], Cu- [2,3], or Fe-based [4] catalysts have been used to bring about high selectivity in allyl alcohol oxidation reactions towards the carbonyl functionality. Au nanoparticles (NPs), supported onto ceria, have found to be highly promising catalysts for the aerobic allyl alcohol oxidation conducted in apolar solvents or under solventless reaction conditions [5,6]. Brønsted bases, such as inorganic carbonates [7], acetates, borates [8] and mixed metal oxide supports [9,10] notably accelerate in combination with Au the aerobic alcohol oxidation reaction.

Ceria is a well-established inorganic support for a number of metal NPs-based reactions ranging from photocatalytic and water-gas shift reactions to selective alcohol oxidation reactions [11]. In particular, the lattice defects in ceria, leading to the simultaneous presence of  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  centers [12,13] on the support surface, make this support not innocent towards redox-reactions. In fact,  $\text{Ce}^{4+}$  oxidizes in part  $\text{Au}^0$  atoms to  $\text{Au}^+$  on the NPs' surface, decreasing hence the amount of catalytically active  $\text{Au}^0$  centers [5].

Herein we describe the synthesis and application of Au NPs supported onto cerium oxycarbonate monohydrate ( $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$ ) [14–16] for the aerobic allyl alcohol oxidation reaction conducted in toluene.

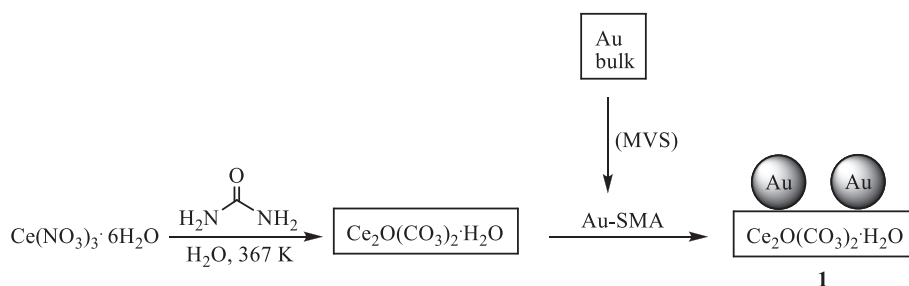
## 2. Results and discussion

The hydrothermal reaction of  $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$  with urea at 90 °C, gave  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  (Scheme 1) as off white powder. The high crystallinity of the latter material and its conversion to  $\text{CeO}_2$  at temperatures > 200 °C is shown by PXRD spectra (Fig. S1) [14–16]. BET measurements carried out on the latter material indicated a very low surface area of 1.123  $\text{m}^2/\text{g}$  (Fig. S2, Table S1) and the absence of a significant microporosity.  $\text{CO}_2$  adsorption was not observed, which is indicating that the bridging oxide groups located on the support surface are not the active Brønsted bases sites [17]. Hence the carbonate oxygen atoms are thus the real Brønsted base sites.

Au NPs were generated by the MVS technique [18–20] and supported onto  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  giving  $\text{Au}@(\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O})$  (1) (Scheme 1). This approach has the huge advantage of generating acetone-stabilized Au NPs, which are featured by the metallic state of the surface atoms. The obtained NPs which can be easily dispersed onto solid supports by impregnation at room temperature [18]. 1 was isolated

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Scheme 1. Synthesis of  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  and **1**.

without post-annealing treatments and ICP-OES analysis of it revealed an Au-loading of 0.5 wt%.

IR spectra acquired for  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  and **1** (KBr, transmission mode) (Fig. S3) showed strong absorption bands in the wave number region between 1490 and 1419  $\text{cm}^{-1}$ , which were assigned to the carbonate stretching modes [21]. The broad adsorption band at 3440  $\text{cm}^{-1}$  was indicating the presence of coordinated water molecules [22] and ethanol, originating from the support synthesis.

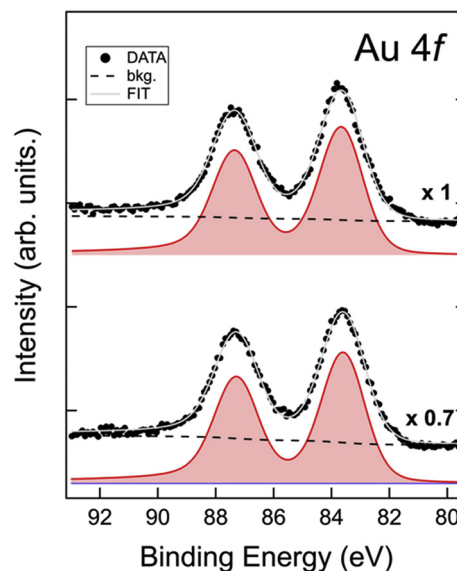
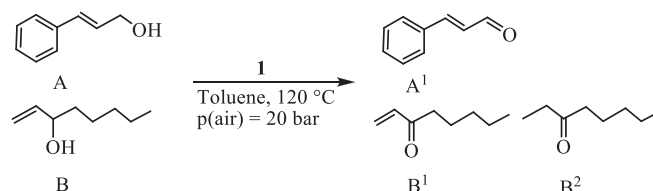
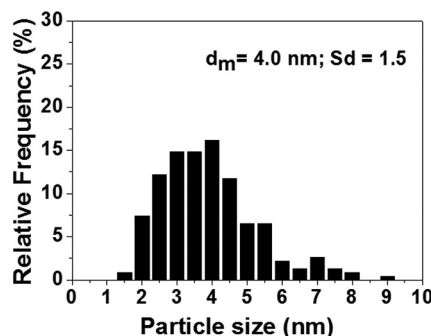
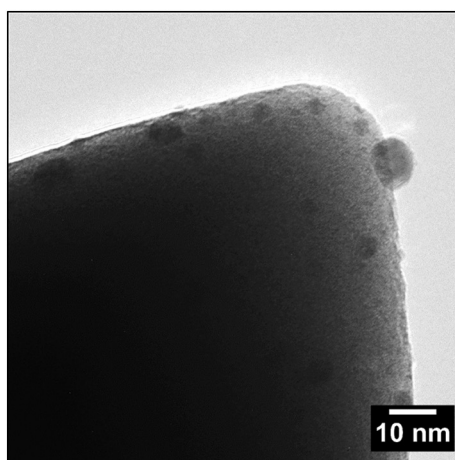
HAADF-STEM micrographs of **1** showed the presence of  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  crystallites of non-regular shape in the size range from 0.5 to 2  $\mu\text{m}$  (Fig. S4), while HRTEM micrographs (Fig. 1) proved the presence of Au NPs' on the support surface characterized by an average size of  $4.0 \pm 1.5$  nm.

The XPS spectra acquired for as-synthesized **1** showed for Au 4f the presence of only  $\text{Au}^0$  on the NPs' surface (i.e. binding energy (BE) (Au 4f<sub>7/2</sub>) = 83.6 eV ( $\text{Au}^0$ )) (Fig. 2, upper trace) [23], while the pattern observed for the Ce 3d BEs (Fig. S5, upper trace) is characteristic for the presence of only  $\text{Ce}^{3+}$  [24,25].

The O 1s XPS spectra of **1** and of  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  (Fig. S6) exhibited a BE of 530.2 eV, which was assigned to bridging oxide units, while the BE of 531.6 eV was ascribed to the presence of carbonate oxygen atoms [26]. The O 1s XPS peak characterized by a BE of 532.9 eV was assigned to the C–O group of adsorbed ethanol [27], which originated from support synthesis.

Catalyst **1** (100 mg), characterized by a Au content of 0.5 wt%, contained 2.538  $\mu\text{mol}$  of Au atoms of which 0.989  $\mu\text{mol}$  were surface Au atoms (i.e. Au dispersion of 39%). This latter catalyst was tested in the aerobic oxidation of selected allyl alcohols (i.e. cinnamyl alcohol (A) and 1-octen-3-ol (B)) (Scheme 2), applying a substrate to catalyst molar ratio of 5792. Results obtained from catalytic reactions in terms of surface atom-related TOF ( $\text{h}^{-1}$ ) and chemoselectivity are compiled in Table 1 and the reaction products obtained are shown in Scheme 2.

A blank reaction carried out with  $\text{Ce}_2\text{O}(\text{CO}_3)_2\cdot\text{H}_2\text{O}$  in the presence

Fig. 2. Au 4f XPS spectra of as-synthesized **1** (upper trace) and of recovered **1** (lower trace) acquired with an energy resolution of  $\sim 0.8$  eV.Scheme 2. Aerobic allyl alcohol oxidation reactions catalyzed by **1** in toluene.Fig. 1. Representative HRTEM micrograph and histogram for **1**.

**Table 1**  
Aerobic allyl alcohol oxidation in toluene by catalyst 1.<sup>a</sup>

Entry	t(h)	Substrate	Conv. (%) / [TOF (h <sup>-1</sup> )] <sup>b</sup>	Selectivity (%) <sup>c</sup>		
				A <sup>1</sup>	B <sup>1</sup>	B <sup>2</sup>
1 <sup>d</sup>	5	A	2 [n.d.]	100		
2	5	A	23 [698]	100		
3	20	A	85 [627]	100		
4 <sup>e</sup>	20	A	75 [617]	100		
5 <sup>f</sup>	20	A	70 [n.d.]	100		
6 <sup>d</sup>	5	B	3 [n.d.]		100	
7	5	B	47 [1380]		82	18
8 <sup>e</sup>	5	B	45 [1338]		81	19
9 <sup>f</sup>	5	B	43 [n.d.]		80	20
10	20	B	100 [n.d.]		79	21
11 <sup>g</sup>	20	B	100 [n.d.]		4	93

<sup>a</sup> Catalytic condition: 1 (100 mg, Au (2.54 μmol)), substrate (14.7 mmol), toluene (50 mL), T (120 °C), p(air) = (20 bar at 120 °C).

<sup>b</sup> Surface atom-related TOF (h<sup>-1</sup>) defined as mmol (converted substrate) / [mmol (Au NPs' surface atoms) × t(h)]

<sup>c</sup> Selectivity (%) defined as mmol(product) / Σmmol(products) × 100.

<sup>d</sup> Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (100 mg) instead of 1.

<sup>e</sup> First recycling.

<sup>f</sup> Third recycling.

<sup>g</sup> Under N<sub>2</sub>-atmosphere. Octan-3-ol (3%) was obtained.

of substrate A (Table 1, entry 1), confirmed a negligible substrate conversion of ca. 2%, which indicates the need of Au to catalyze the oxidation reaction.

Catalyst 1 converted substrate A into the α,β-unsaturated carbonyl compound A<sup>1</sup> with a chemoselectivity of 100% (Table 1).

Under comparable catalytic conditions (i.e. cinnamyl alcohol, toluene, 120 °C), Au@CeO<sub>2</sub>, which is the most promising heterogeneous catalysts for selective aerobic allyl alcohol oxidation reactions in organic solvents, showed a chemoselectivity for cinnamylaldehyde of 99% but a lower substrate conversion compared to catalyst 1 (i.e. 538 h<sup>-1</sup> vs 698 h<sup>-1</sup>) which might be due to the fact that Au@CeO<sub>2</sub> exhibits a notable fraction of oxidized Au atoms (i.e. Au<sup>+</sup> is not the active form of the catalyst) on the NPs' surface [6]. Pd@apatite showed a low chemoselectivity of only 63% for cinnamaldehyde along with a catalytic activity (i.e. TOF of 402 h<sup>-1</sup>) that is inferior to those obtained for 1 and Au@CeO<sub>2</sub> [6]. Au NPs in the size range 6–9 nm and located onto the ternary mixed-oxide support Cu<sub>5</sub>Mg<sub>1</sub>Al<sub>2</sub>O<sub>x</sub> were shown to be suitable for 1-phenylethanol oxidation, whereas its activity for the cinnamyl alcohol oxidation was low (TOF of 243 h<sup>-1</sup>) while the chemoselectivity for cinnamyl alcohol was of 99%, which is typical for Au-based catalysts [9]. Au onto mixed GaAl-oxide has been tested only at 80 °C applying a substrate to catalyst molar ratio of 200. As a result, a TOF value of only 76 h<sup>-1</sup> was obtained [10]

Catalyst 1 showed for substrate B a higher conversion compared to A, at the expense of chemoselectivity for the unsaturated carbonyl compound B<sup>1</sup>. In fact, a notable percentage of the saturated carbonyl compound B<sup>2</sup> was obtained (Table 1, entries 7–10). A blank reaction conducted with Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O in the presence of B gave B<sup>1</sup> with 3% yield as the only organic product (Table 1, entry 6). This experimental result confirmed the need of Au to catalyze the allyl alcohol isomerization reaction. The selectivity for B<sup>2</sup> was further increased to 93% by conducting the catalytic reaction in the absence of air (i.e. under nitrogen atmosphere) (Table 1, entry 11). Under the latter experimental condition octan-3-ol (3%) was obtained which indicates that B was acting to some extent as hydrogen acceptor under anaerobic experimental conditions.

Recycling experiments with 1 in the presence of substrates A and B were carried out, showing only a small activity drop in terms of surface-related TOF values (Table 1). Most importantly, the chemoselectivity of the catalytic reactions remained almost identical (Table 1, entries 4/5 vs 3 and 8/9 vs 7). In addition, recycling experiments were conducted

without the need of a catalyst reactivation step (i.e. washing the recovered catalyst with base), which is indicating that substrate over-oxidation to carboxylates, which strongly coordinate surface Au atoms and contribute hence to catalyst deactivation, did not occur with 1 [28,29]. 1 was recovered by centrifugation and decantation of the catalytic solution, followed by washing the solid catalyst with toluene and drying at 50 °C in vacuum. In order to estimate the amount of leached Au in solution, the reaction suspension was filtered at 80 °C and the obtained clear solution analyzed by ICP-OES. As a result, a Au content of 25 ppb was found in solution which corresponds to a Au leaching of 0.25%.

PXRD (Fig. S7), Ce 3d (Fig. S5, lower trace) and O 1 s-XPS (Fig. S6, lower trace) spectra of recovered 1 proved the stability of the support material under the chosen catalytic reaction conditions oxidation. In addition, an intense peak in the O 1 s spectrum centered at a BE of 532.9 eV, was assigned to the alcohol functional group of adsorbed cinnamyl alcohol, proving hence the strong interaction between the substrate and surface carbonate groups [30].

The Au 4f XPS spectrum of recovered 1 (Fig. 2, lower trace) confirmed the presence of only Au<sup>0</sup> on the NPs' surface after the aerobic oxidation reaction, while HRTEM (Fig. S8) and representative HAADF-STEM micrographs (Fig. S9) confirmed a slight increase of the mean NPs' size to 4.1 ± 1.3 nm and to 4.7 ± 1.5 nm after a 5 and 20 h reaction time, respectively. As a consequence, the amount of surface Au atoms of recovered 1 was found to be almost identical to that of as-synthesized 1, after a reaction time of 5 h or slightly decreased to 0.889 μmol, which corresponds to a Au dispersion of 35%, after a reaction time of 20 h. Although, a drop of the amount of surface Au atoms (10%) was observed for long reaction times (20h), the catalytic activity, expressed in surface-related TOF, was almost unaltered for the first recycling experiment (Table 1, entry 4 vs 3).

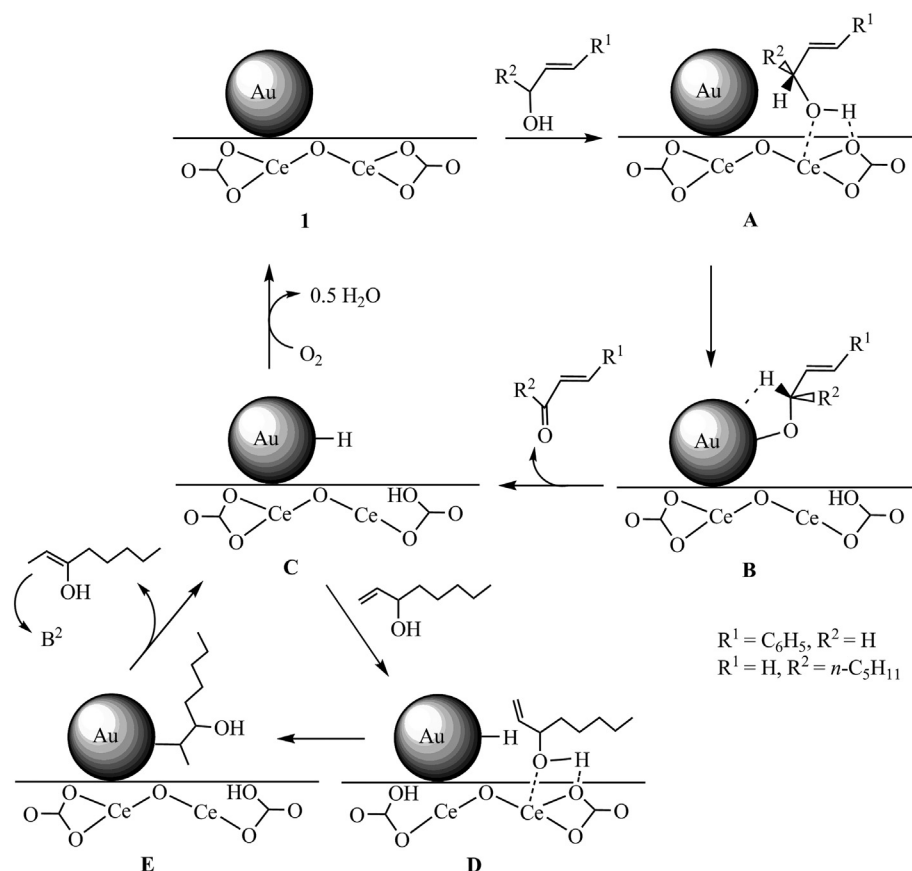
We propose the following catalytic cycles operative for the 1-catalyzed allyl alcohol oxidation reaction (Scheme 3) after combining experimental results obtained from catalytic batch reactions and physical measurements carried out on the recovered catalyst.

The alcohol functional group of the substrate interacts with the surface carbonate units of the catalyst's support (Scheme 3, A). Then deprotonation of the alcohol functional group by carbonate (Brønsted base sites) gave the alcoholate which is coordinated to the Au NPs' surface (Scheme 3, B). Indeed, DFT calculations showed that the alcoholate formation in aerobic alcohol oxidation reactions is significantly favored in the presence of a Brønsted base [31,32]. The rate-determining step (i.e. α-hydrogen abstraction from coordinated alcoholate) leads to the formation of Au hydride species (Scheme 3, C) [5,33,34] and the concomitant release of the corresponding unsaturated carbonyl compound.

Species C reacts either with oxygen giving water [28] and the regenerated catalyst 1, or undergoes an insertion reaction with the C–C double bond (Scheme 3, E) of a sterically less hindered allyl alcohol, such as substrate B, followed by β-hydride elimination, which gives species C and the enolate [35]. The enolate tautomerizes in solution giving B<sup>2</sup>. The isomerization activity of the Au hydride species increases in the absence of oxygen, due to a higher concentration of Au hydride species on the NPs' surface compared to the aerobic experimental reaction condition.

### 3. Conclusions

Au nanoparticles, generated by the metal vapor synthesis technique, were supported onto Ce<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, a crystalline, Ce<sup>3+</sup>-based inorganic material. Au XPs measurements confirmed the presence of only Au atoms in the metallic oxidation state on the NPs' surface. Aerobic allyl alcohol oxidation reactions conducted with the obtained heterogeneous catalyst in toluene showed: (i) A catalytic conversion of allyl alcohols to the unsaturated carbonyl compound (major compound) which is superior to that of Au@CeO<sub>2</sub>, known as reference system for



**Scheme 3.** Proposed catalytic cycles operative for the 1-catalyzed aerobic allyl alcohol oxidation in toluene.

this kind of chemistry. (ii) A partial allyl alcohol isomerization activity to the corresponding saturated carbonyl compound, when the allyl group of the substrate is sterically not hindered, which contrasts results obtained with Au@CeO<sub>2</sub> [6]. The selectivity for the saturated carbonyl compound can be increased to 93% under anaerobic reaction conditions. Recycling experiments, conducted without the need of a catalyst regeneration step, confirmed the stability of the support material, as well as of the catalytically active Au NPs in terms of size (Au dispersion) and oxidation state of the surface atoms even after a prolonged reaction time.

#### Credit author statement

**Werner Oberhauser:** writing of the draft and PXRD measurements; **Claudio Evangelisti:** catalyst preparation, **Marcello Marelli:** TEM measurements; **Vladimiro Dal Santo:** CO<sub>2</sub>-chemisorption experiments, **Cinzia Cepek:** XPS study; **Marco Bellini:** physisorption measurements.

#### Declaration of Competing Interest

There are no conflicts to declare.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2020.105989>.

#### References

- [1] C.C. Cosner, P.J. Cabrera, K.M. Byrd, A.M.A. Thomas, P. Helquist, *Org. Lett.* 13 (2011) 2071–2073.
- [2] D. Könnig, T. Olbrisch, F.D. Sypaseuth, C.C. Tzschucke, M. Christmann, *Chem. Commun.* 50 (2014) 5014–5016.
- [3] D. Könnig, W. Hiller, M. Christmann, *Org. Lett.* 14 (2012) 5258–5261.
- [4] A.J. Pearson, Y. Kwak, *Tetrahedron Lett.* 46 (2005) 5417–5419.
- [5] A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem. Int. Ed.* 44 (2005) 4066–4069.
- [6] A. Abad, C. Almela, A. Corma, H. García, *Chem. Commun.* (2006) 3178–3180.
- [7] J. Yang, Y. Guan, T. Verhoeven, R. van Santen, C. Li, E.J.M. Hensen, *Green Chem.* 11 (2009) 322–325.
- [8] N. Zheng, G.D. Stucky, *Chem. Commun.* (2007) 3862–3864.
- [9] P. Haider, A. Baiker, *J. Catal.* 248 (2007) 175–187.
- [10] F.-Z. Su, Y.-M. Liu, L.-C. Wang, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem. Int. Ed.* 47 (2008) 334–337.
- [11] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.* 116 (2016) 5987–6041.
- [12] M. Baron, O. Bondarchuk, D. Stacchiola, S. Shaikhtudinov, H.-J. Freund, *J. Phys. Chem. C* 113 (2009) 6042–6049.
- [13] F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, R. Rosei, *Science* 309 (2005) 752–755.
- [14] B. Bakiz, F. Guinneton, J.-P. Dallas, S. Villain, J.-R. Gavarri, *J. Cryst. Growth* 310 (2008) 3055–3061.
- [15] K. Nakagawa, Y. Tezuka, T. Ohshima, M. Katayama, T. Ogata, K.-I. Sotowa, M. Katoh, S. Sugiyama, *Adv. Powder Technol.* 27 (2016) 2128–2135.
- [16] S. Chen, S.-H. Yu, B. Yu, L. Ren, W. Yao, H. Cölfen, *Chem. Eur. J.* 10 (2004) 3050–3058.
- [17] L. Vivier, D. Duprez, *ChemSusChem* 3 (2010) 654–678.
- [18] C. Evangelisti, E. Schiavi, L.A. Aronica, R. Psaro, A. Balerna, G. Martra, *Solvated metal atoms in the preparation of supported gold catalysts*, in: L. Prati, A. Villa (Eds.), *Gold Catalysis: Preparation, Characterization, and Applications*, Pan Stanford Publishing Pte. Ltd., Singapore, 2016, pp. 73–92.
- [19] M. Marelli, C. Evangelisti, M.V. Diamanti, V. Dal Santo, M.P. Pedferri, C.L. Bianchi, L. Schiavi, A. Strini, *ACS Appl. Mater. Interfaces* 8 (2016) 31051–31058.
- [20] L.A. Aronica, E. Schiavi, C. Evangelisti, A.M. Caporusso, P. Salvadori, G. Vitulli, L. Bertinetti, G. Martra, *J. Catal.* 266 (2009) 250–257.
- [21] F.A. Miller, C.H. Wilkins, *Anal. Chem.* 24 (1952) 1253–1294.
- [22] J. Soria, J. Sanz, I. Sobrados, J.M. Coronado, A.J. Maira, M.D. Hernández-Alonso, F. Fresno, *J. Phys. Chem. C* 111 (2007) 10590–10596.
- [23] M.P. Casaletto, A. Longo, A. Martorana, P. Prestianni, A.M. Venezia, *Surf. Interface Anal.* 38 (2006) 215–218.
- [24] E. Bêche, P. Charvin, D. Perarnau, S. Abanades, G. Flamant, *Surf. Interface Anal.* 40 (2008) 264–267.
- [25] J. Matharu, G. Cabailh, R. Lindsay, C.L. Pang, D.C. Grinter, T. Skála, G. Thornton, *Surf. Sci.* 605 (2011) 1062–1066.

- [26] B. Feng, J.Y. Chen, S.K. Qi, L. He, J.Z. Zhao, X.D. Zhang, *Biomaterials* 23 (2002) 173–179.
- [27] Y.L. Khung, S.H. Ngalm, A. Scaccabarozzi, D. Narducci, *Beilstein J. Nanotechnol.* 6 (2015) 19–26.
- [28] A. Abad, A. Corma, H. García, *Chem. Eur. J.* 14 (2008) 212–222.
- [29] W. Oberhauser, A. Lavacchi, F. Vizza, L. Capozzoli, H.M. Lee, *Appl. Catal. A Gen.* 451 (2013) 58–64.
- [30] D.J. Cooke, R.J. Gray, K.K. Sand, S.L.S. Stipp, J.A. Elliot, *Langmuir* 26 (2010) 14520–14529.
- [31] M.S. Ide, R.J. Davis, *Acc. Chem. Res.* 47 (2014) 825–833.
- [32] B.N. Zope, D.D. Hibbitts, M. Neurock, R.J. Davis, *Science* 330 (2010) 74–78.
- [33] I.P. Silverwood, S.M. Rogers, S.K. Callear, S.F. Parker, C.R.A. Catlow, *Chem. Commun.* 52 (2016) 533–536.
- [34] M. Conte, H. Miyamura, S. Kobayashi, V. Chechik, *J. Am. Chem. Soc.* 131 (2009) 7189–7196.
- [35] E. Sadeghmoghaddam, H. Gu, Y.-S. Shon, *ACS Catal.* 2 (2012) 1838–1845.