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Ligand effects in the stabilization of gold nanoparticles anchored on the surface of graphene: Implications in catalysis



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David Ventura-Espinosa^a, Santiago Martín^{b,c}, Hermenegildo García^{d,*}, Jose A. Mata^{a,*}

^a Institute of Advanced Materials (INAM), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universitat Jaume I, Avda. Sos Baynat s/n, 12006 Castellón, Spain ^b Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza 50009, Spain

^c Departamento de Química Física, Universidad de Zaragoza, Zaragoza 50009, Spain

^d Instituto de Tecnología Química, Consejo Superior de Investigaciones Científicas-Universitat Politècnica de València, Avda. Los Naranjos s/n, 46022 Valencia, Spain

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ABSTRACT

Gold nanoparticles (Au NPs) functionalized with N-heterocyclic carbene (NHC) ligands immobilized onto graphene are obtained via spontaneous decomposition of well-defined gold-NHC complexes by reduced graphene oxide (rGO) without reducing agents. NHC ligands are responsible for the formation of air-stable, crystalline and small (3.0–4-0 nm) Au NPs homogeneously distributed on the surface of graphene. The catalytic properties of three Au NPs functionalized with different ligands were tested in two benchmark reactions (hydration of alkynes and intramolecular hydroamination of alkynes). The results reveal a pronounced ligand effect on the stability of Au NPs on graphene, by acting as a bridge between them. The Au NPs functionalized with a playaromatic group or having a naphthyl tag displayed limited stability and fast deactivation in the first run. On the contrary, the Au NPs functionalized with a NHC ligand containing a pyrenyl handle showed superior catalytic activity and can be recycled at least ten times. The particle size of the Au NPs is preserved after the recycling process indicating a high stability. These results illustrate the use of purposely designed ligands having affinity for both Au NPs and graphene to increase the stability of the hybrid catalyst.

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1. Introduction

Catalytic applications of gold nanoparticles (Au NPs) is a growing research area, since it constitutes a relevant example of the catalytic activity of metal nanoparticles (MNPs) [1–4]. The focus in the field relies on understanding the structure–activity relationship in order to further increase catalytic activity [5]. However, development of efficient catalysts is also directly related to stability and/ or deactivation pathways, two important issues that are barely considered in catalysis research [6–8]. In order to improve the lifetime of a catalyst it is high important to understand the factors that increase stability and the processes that govern deactivation pathways [9,10].

One of the general issues in catalysis by MNPs is the limited stability and the tendency of NPs to coalesce. In order to increase stability of MNPs two main approaches are commonly employed. The first one implies the use of capping agents such as surfactants,

* Corresponding authors.

E-mail addresses: hgarcia@qim.upv.es (H. García), jmata@uji.es (J.A. Mata).

polymers or ligands [11–16] and the second one is the use of supports where the MNPs are stabilized by strong interactions with the material [17]. Supported MNPs are highly active heterogeneous catalysts which have found numerous applications in chemical transformations, including oxidations, reductions and couplings [18–20]. Understanding the metal-support interaction provides the principles to develop more selective and efficient catalysts [21–24]. Stability may represent a bottleneck for the development of efficient catalytic systems. The introduction of ligands on the surface of MNPs provides a tool to control activity and selectivity that combined with the selection of appropriate supports can increase stability [25–29]. Among all the ligands used in the functionalization of MNPs, N-heterocyclic carbene ligands (NHCs) are prominent and have enabled selective transformations [30–32].

We described the benefits in the use of graphene as support to immobilize organometallic complexes by non-covalent interactions [33–35]. Design of ligands containing polyaromatic tags allows strong π interactions with the graphene basal plane that retains under reaction conditions the metal complexes anchored onto the surface of graphene. The metal complexes immobilized onto graphene are efficient catalysts in a variety of transformations, which include oxidations and couplings [36–38]. Decompo-



Abbreviations: NPs, nanoparticles; NHC, N-heterocyclic carbene; rGO, reduced graphene oxide.



Functionalized MNPs

Fig. 1. Model representation of Au NPs adsorbed onto graphene due to the simultaneous interaction of the ligand with both Au NPs and graphene.

sition of organometallic species under reducing conditions promotes the formation of MNPs immobilized onto graphene. Studies on the catalytic activity of palladium and gold nanoparticles functionalized with ligands supported onto graphene reveal the importance of the support in the stability of the MNPs. Herein we now report that ligands can increase the stability of Au NPs on graphene by simultaneous interaction with both MNPs and graphene. The synthesis of Au NPs anchored onto graphene is performed by decomposition of well-defined gold complexes bearing different NHC ligands. Preparation of three NHC ligands containing different polyaromatic tags conclusively establishes their role in holding together the Au NPs onto graphene (Fig. 1). The selection of the NHC ligand determines the stability of Au NPs onto graphene and, therefore, their catalytic activity. The Au NPs derived from the NHC ligand containing a pyrenyl handle shows better catalytic properties in terms of activity and recyclability.

2. Experimental section

Detailed synthetic procedures for ligands containing different polyaromatic groups and Au-NHC complexes are included in the supporting information (SI).

2.1. Synthesis of hybrid materials α , β or γ -NPs-rGO.

A suspension of 470 mg of rGO in 350 mL of CH_2Cl_2 in a round bottom flask was immersed in an ultrasounds bath for 30 min. In a

Schlenk flask and under the protection of light, complex **1**, **2** or **3** (0.107 mmol) and silver triflate (0.117 mmol) were dissolved in 8 mL of dry CH₂Cl₂ and the mixture was stirred at room temperature for 15 min (Fig. 2). Then the reaction was filtered through a long pad of celite. The solvent was reduced in the rotatory evaporator until ca. 5 mL. Then, this mixture was added to the suspension of rGO in CH₂Cl₂ and was stirred at the selected temperature for 72 h. The black solid was isolated by filtration and washed with 200 mL of CH₂Cl₂ affording the hybrid material **Au-NPs-rGO**. The hybrid material was characterized by HRTEM and XPS (see S6-S7), and the exact amount of gold was determined by ICP-MS analysis. The results accounted for a 0.013 mg Au/100 mg rGO of gold in the hybrid material α -NPs-rGO, 0.016 mg Au/100 mg rGO of gold in γ -NPs-rGO.

2.2. General procedure for the hydration of alkynes.

In a Pyrex[®] tube and under air, 4-octyne (1 eq.), water (2 eq.), catalyst and methanol (alkyne concentration 0.15 M) were mixed. The reaction was stirred at 50 °C in an oil bath. Conversion of alkyne into the corresponding ketone was monitored by GC-FID using anisole as an internal standard. When the reaction was completed the solvent was removed and the yield of isolated product analyzed by ¹H and ¹³C NMR. Recycling experiments were carried out under the same reaction conditions for all runs without catalyst regeneration. After completion of each run, the reaction mixture was allowed to reach room temperature and the solid catalyst was isolated by decantation. The remaining solid was washed thoroughly with MeOH (4 \times 5 mL), dried and reused in the following run.

2.3. General procedure for the cyclisation of 2-alkynil anilines.

In a Pyrex[®] tube and under air, 2-(phenylethynyl)aniline (1 eq.) water (2 eq.), catalyst and toluene (substrate concentration 0.0625 M) were mixed. The reaction was stirred at 50 °C in an oil bath. Conversion of substrate was monitored by GC-FID using anisole as an internal standard. When the reaction was completed the solvent was removed and the yield of isolated product analyzed by ¹H and ¹³C NMR. Recycling experiments were carried out under the same reaction conditions as described before. After completion of each run, the reaction mixture was allowed to reach room temperature and the catalyst was isolated by decantation. The remaining solid was washed thoroughly with MeOH, dried and reused in the following run.



Fig. 2. Bottom-up approach for the synthesis of Au NPs capped with NHC ligands attached to graphene: a) NHC-Au-X complexes (Dipp = 2,6-diisopropylphenyl), b) ORTEP structure from single crystal X-ray diffraction of complex 2 (hydrogen atoms omitted for clarity) and c) reaction scheme for synthesis and deposition of Au NPs.

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Fig. 3. TEM characterization of gold nanoparticles supported onto graphene. First column: Dark field STEM micrographs. Second column: HRTEM micrographs. Third column: Size distribution histograms of Au NPs and fourth column: XPS analysis of the core-level peaks (eV) for the Au4f region.

3. Results and discussion

3.1. Synthesis and characterization of Au-NPs-rGO.

Three NHC ligands having different handles were tested for their properties on reinforcing the anchoring of Au NPs onto the surface of graphene, namely α , β or γ -NPs-rGO. The hybrid materials are composed of graphene that acts as a carbonaceous 2D support and Au NPs capped with the NHC ligands. The synthetic procedure corresponds to a bottom-up approach starting from well-defined organometallic Au(I) complexes, which allows a better control of the nature and composition of Au NPs (Fig. 2) [39]. First, Au(I) complexes containing NHCs ligands with different polvaromatic tags were prepared from imidazolium salts using gold chloride (or bromide) and K₂CO₃ (Complexes **1**, **2** and **3**) [40,41]. Au(I) complexes containing NHCs ligands have been widely used in homogeneous catalysis and represent a convenient starting point for the preparation of Au NPs [42-44]. Previous to the formation of Au NPs, NHC-Au-X complexes were converted into the corresponding triflate (OTf) derivatives using a silver salt. The presence of a labile triflate ligand induces spontaneously the formation of Au NPs in the presence of reduced graphene oxide (rGO) by the organometallic approach as we have previously observed [45]. The NHC-Au-OTf complexes decompose in the presence of rGO resulting in the formation of Au NPs on the surface of graphene. These Au NPs are covered by NHC ligands (vide infra) which can or cannot also interact strongly with rGO, providing stability and control the interaction with substrates that may result in selective catalysis [46–48]. The preparation of the Au NPs requires long times but the process is carried out under mild conditions which preserve the inherent properties of the support and the capping ligands (Fig. 2).

Microscopic characterization by HRTEM of the gold hybrid materials confirmed the presence of spherical Au NPs (Fig. 3). Dark field TEM micrographs facilitates evaluation of the shape, size and position of Au NPs on the surface of graphene. We have observed that spherical Au NPs are homogeneously distributed all over the graphene surface and not only located at the edges or wrinkles. The particle size histogram reveals a size distribution with an average diameter of 3.35 ± 1.7 nm (n = 296) for **α-NPs-rGO**, 4.83 ± 1. 6 nm (n = 120) for β -NPs-rGO and 3.05 ± 1.0 nm (n = 467) for γ -NPs-rGO (Fig. 3). HRTEM micrographs shows the expected interplanar distances for the crystalline Au NPs in the three hybrid materials. The morphological analysis reveals that the remote functionalization using different tags at the NHC ligands does not play an important role on the shape, size and crystallinity of the formed Au NPs. We also assessed the effect of temperature in the formation of Au NPs by decomposing complex 3 in the presence of rGO at 25 and 45 °C. The results reveal that in the range of temperature studied, this parameter does not affect the morphology of the NPs indicating that the growth and dispersion of Au-NPs is predominantly controlled by the interaction with the NHC ligands and graphene surface. We have previously observed that graphene plays an important role in the formation of MNPs. For instance, the synthesis of PdNPs without graphene using molecular hydrogen produces cylindrical particles, while in contrast, in the presence of graphene the shape of the NPs is spherical [49].

X-ray photoelectron spectrometry (XPS) is a characterization technique that provides valuable information about the elemental composition and oxidation states of the elements located on the surface (Fig. 3). The survey XPS spectrum of the three hybrid materials [α , β or γ -NPs-rGO] is dominated, as expected, by the presence of two intense peaks attributed to the oxygen and carbon from the rGO used as a support. In addition, the presence of fluor, nitrogen,

sulphur and gold confirms the presence of NHC ligands and triflate anions (OTf) on the surface of Au NPs (see SI for the highresolution spectra and assignment of these elements). The highresolution spectrum of Au(4f) region for α -NPs-rGO shows two doublet peaks, due to the spin-orbit splitting effect $(4f_{7/2}$ and $4f_{5/2}$) at binding energies of 88.7 and 85.0 eV attributed to Au(I) [50,51] and at 88.0 and 84.3 eV attributed to Au(0) [52,53] (Fig. 3d). Analysis of the corresponding areas associated with each signal in the convoluted spectrum shows an area ratio of 2:1 for the peaks attributed to Au(0) respect to the peaks attributed to Au(I). In the case of the hybrid material containing a naphthalene group (**β-NPs-rGO**), the two doublet peaks appear at the same binding energies than that for **α-NPs-rGO**, confirming the presence of Au(I) and Au(0), albeit in this case the relative area ratio is inverted with Au(I) being the prevalent (Fig. 3h). Surprisingly, in the case of γ -**NPs-rGO** only a doublet peak at the binding energies corresponding to Au(I) is observed without detecting the presence of Au(0) (Fig. 3i). This last result is in agreement with the findings of Toste and Somorjai who reported that XPS of Au NPs functionalized with chiral-NHC ligands showed only the presence of Au(I). A further study using EXAFS revealed a major contribution Au(0) [48]. In our case, the differences in the XPS analysis are ascribed to a ligand effect. The three hybrid materials have the same Au environment but different remote ligand functionalization and in the case of the bulkier polyaromatic group (pyrenyl) only Au(I) is observed.

3.2. Ligand effects in the catalytic hydration of alkynes.

The evaluation of ligand effect in the stabilization of Au NPs was assessed in hydration and intramolecular hydroamination of alkynes. Gold is an efficient catalysts in the hydration of alkynes for a variety of different substrates at low catalysts loadings and under mild reaction conditions [54–56]. We chose 4-octyne as a model substrate. In all cases the catalytic reactions were carried out under the same conditions and using a low catalyst loading ([Au] 0.05 mol%). The activity and stability of the three hybrid materials was evaluated by monitoring the reaction progress by gas chromatography and by reusing the hybrid materials (Fig. 4). After each run, the catalysts is removed from the solution by decantation, washed with MeOH and dried with pentane. The results in the first run using α -NPs-rGO show full conversion in the hydration of 4-octyne in less than 100 min at 50 °C. In the second run an important decrease in activity was observed, but still full conversion was achieved in 200 min. The activity decrease is more pronounced in run 3, where less than 50% conversion was achieved in 500 min (Fig. 4a). These results indicate that in the case of the hybrid material α -NPs-rGO deactivation in the first run occurs in a significant extent. Similar results were obtained using β-NPs-rGO as catalyst. Thus, there was a considerable catalyst deactivation from run 1 to run 2, but the decrease in activity was even more important in run 3, where only 50% conversion could be achieved in 500 min (Fig. 4b). Therefore, the catalytic behaviour of α -NPs-rGO and β -NPs-rGO is similar and characterized by a high activity in the first run at low catalyst loadings and a notable deactivation in the second and third runs.

Completely different behavior was observed for γ -NPs-rGO. In terms of activity, γ -NPs-rGO is even a better catalyst than α -NPs-rGO or β -NPs-rGO, a fact that can be attributed to the major amount of Au(I) as observed by XPS. Using γ -NPs-rGO full conversion of 4-octyne was achieved in 60 min. The γ -NPs-rGO material could be recycled up to ten times (Fig. 4c) indicating its high stability. The results show that from run 1 to run 3 the activity is maintained according to the similar apparent rate constants and the coincidence in the reaction-time profiles (Fig. 4c inset). Then, there is a gradual catalyst deactivation from run 4 to run 8, but still full



Fig. 4. Performance of **Au-NPs-rGO** as catalysts in hydration of alkynes. Reaction conditions: 4-octyne (0.2 mmol), catalyst loading (0.05 mol% based on Au), MeOH (1.4 mL) as solvent, H₂O (2 Eq, 7.2 μ L) at 50 °C. Conversion determined by GC/FID and using 1,3,5-trimethoxybenzene as an internal standard.

conversions were obtained in less than 150 min. In runs 9 and 10, there is a considerable catalyst deactivation but still full conversion is achieved in 300 min. The differences in the activity and stability using the three catalytic systems indicates a pronounced effect of the ligand in the stabilization of the Au NPs on the surface of graphene.

3.3. Characterization of Au NPs after the hydration of alkynes.

In order to clear up the differences in activity/stability and understand deactivation pathways of Au NPs, the hybrid materials after the recycling experiments were characterized by HRTEM microscopy, XPS and ICP/MS (Fig. 5). First, we focused on the morphological assessment of the support in the three hybrid materials. The HRTEM images before and after the recycling experiments show similar properties for the graphene, indicating that the support is not altered under the conditions of hydration of alkynes, even in the case of the material γ -NPs-rGO after ten consecutive runs. Regarding the presence of Au NPs, it is important to note that



Fig. 5. Characterization of Au NPs supported onto graphene after recycling. First column: Dark field TEM micrographs. Second column: HRTEM micrograph showing the crystallinity and same morphology for Au NPs after recycling and third column: XPS analysis of the core-level peaks (eV) for the Au4f region.

few Au NPs could be observed in the case of α -NPs-rGO after three catalytic runs (Fig. 5a). The scarce number of Au NPs in α -NPs-rGO explains the sharp drop of activity in this material from run 2 to run 3 (Fig. 4a). On the contrary, the number of Au NPs is still abundant in the case of γ -NPs-rGO even after ten runs (Fig. 5g). TEM characterization suggests that the role of NHC ligands consist in attaching Au NPs to the surface of the support and in consequence increasing stability under catalytic conditions, particularly important in the case of γ -NPs-rGO containing a pyrenyl tag. Additionally, high magnification HRTEM micrographs confirm the same morphology for Au NPs after recycling and that the shape (spherical) and size (ca. 3.5 nm) of Au NPs in the three hybrid materials is preserved after the recycling experiments. In the case of hybrid material β -NPs-rGO the shape and size is preserved after three runs but in γ -NPs-rGO the morphology is preserved even after ten catalytic runs (Fig. 5h).

The XPS characterization after recycling confirms a similar nature and composition of the three hybrid materials. The survey XPS spectrum of the hybrid materials **Au-NPs-rGO** is again dominated by two intense peaks corresponding to the carbon and oxygen of the support. The presence of fluor, nitrogen, sulfur and gold, which confirm the nature and composition of the Au NPs is also observed. The relative intensity of the peaks corresponding to Au decreases vs. the peaks assigned to the support compared to the as prepared hybrid material. This effect is more pronounced in the case of α -NPs-rGO as can be deduced also, for example, from the low signal/noise ratio of the core-level peak for the Au4f region (Fig. 5c). On the contrary, in the case of γ -NPs-rGO the noise signal is lower revealing a greater amount of gold. Although XPS may only provide a semiquantitative analysis, gold loading was confirmed by ICP/MS (see discussion below). These results point towards a potential deactivation of the hybrid material α -NPs-rGO caused by leaching. The XPS oxidation state analysis of gold after recycling reveals that the core-level peaks of Au4f appear at the same binding energy indicating a similar nature of the Au NPs in the three hybrid materials.

Finally, the remaining amount of gold in the three hybrid materials after recycling was analysed by ICP/MS. Gold content in used α -NPs-rGO could not be detected by ICP/MS, indicating that all the Au NPs are lost by leaching in only three catalytic runs. The gold amount in β -NPs-rGO is 54 wt% of the initial content implying a fast deactivation by leaching in only three runs. The remaining gold in γ -NPs-rGO is 65 wt% of the initial content after ten catalytic runs. The characterization techniques employed give important information about the hybrid materials after recycling under catalytic conditions. The results clearly support a deactivation pathway caused by leaching and negligible Ostwald effects. The hybrid material γ -NPs-rGO containing a pyrenyl group that favours a strong interaction with the graphene resulted in a better performing catalysts derived from the higher stability and the diminished Au leaching.

3.4. Ligand effects in the catalytic hydroamination of alkynes.

The catalytic properties of **Au-NPs-rGO** in the intramolecular hydroamination exhibited similar trends as in the hydration of alkynes (Fig. 6). The three Au-NPs-rGO are efficient catalysts in intramolecular hydroamination affording quantitative yields of indol in short reaction times (less than 100 min) at low temperatures (50 °C) and using a low catalyst loading of 0.05 Au mol%. The materials **α-NPs-rGO** and **β-NPs-rGO** could be reused four runs with only a gradual decrease in activity. This deactivation was more pronounced in run 5 as reflected in the corresponding temporal reaction profiles (Fig. 6a, 6d). The behaviour of the hybrid material γ -NPs-rGO was significantly different. In this case, the catalyst was reused up to six times without significant deactivation. Then, there was a gradual deactivation but still full conversion was achieved in the tenth run (Fig. 6g). Microscopic characterization by STEM of the spent catalysts after recycling experiments confirmed the spherical shape of Au NPs and provided a visual indication of the amount of particles remaining in the hybrid material. For instance, images of α -NPs-rGO (Fig. 6b) showed a small amount of particles after run 5. On the contrary, the number of Au NPs in γ -NPs-rGO (Fig. 6h) is higher even after ten catalytic runs. These results revealed a first hint that leaching should be the main deactivation pathway in α -NPs-rGO, but not in the case of γ -NPs-rGO. These results were confirmed by ICP/MS of the used catalytic materials. In the case of α -NPs-rGO the remaining gold

after 5 runs is 28% of the initial amount and in γ -NPs-rGO the remaining gold is more than 70% after 10 runs. These results are in agreement to Au leaching as the prevalent deactivation pathway. Notably, as we have previously observed in the case of hydration of alkynes, the morphology of Au NPs is preserved after ten runs in the intramolecular hydroamination (Fig. 6i). The XPS analvsis of α -NPs-rGO reveals a low amount of gold meanwhile the XPS spectrum of γ -NPs-rGO confirms a similar elemental composition and at the same binding energies for the spent catalyst in comparison to the fresh sample. The catalytic results in the intramolecular hydroamination indicate a clear difference between the three hybrid materials in terms of stability depending on the nature of the NHC ligand. The material containing a pyrenyl group (γ -NPs**rGO**) is more efficient as a consequence of a stronger interaction with graphene that again avoids deactivation by leaching. Thus, we have observed in two benchmark reactions, the importance of ligand design in order to obtain more efficient catalytic systems based on avoiding deactivation caused by leaching.

4. Conclusions

We have assessed the ligand influence in the catalytic properties of Au NPs immobilized onto graphene. For this purpose, three types of Au NPs containing different NHC ligands have been synthesized by decomposition of well-defined Au(I)–NHC complexes.



Fig. 6. Catalytic properties of Au-NPs-rGO in intramolecular hydroamination of alkynes. Reaction conditions: substrate (0.2 mmol), catalyst loading (0.05 mol% based on Au), toluene (2 mL) as solvent, at 50 °C. Conversion determined by GC/FID and using 1, 3, 5-trimethoxybenzene as an internal standard. Characterization of Au NPs supported onto graphene after recycling. Dark field TEM and HRTEM micrographs.

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The ligands contain different functionalities at a remote position based on polyaromatic groups that permit π -stacking interactions with the graphene support of different strength. The synthetic procedure of Au NPs allows the formation of similar NPs that are crystalline and small in size (3.0 - 4.0 nm) independently of the ligand used. The catalytic properties of the three Au NPs types immobilized onto graphene revealed important ligand effects in hydration of alkynes and intramolecular hydroamination. The Au NPs functionalized with an NHC ligand containing a pyrenyl as polyaromatic group showed superior stability versus the Au NPs functionalized with a naphthyl or lacking of a polyaromatic group. The presence of a pyrenyl handle allows a stronger interaction with graphene increasing the stability of Au NPs. We have observed that Au NPs are deactivated by leaching from the support and not by Ostwald ripening effects. It is important to note that the Au NPs functionalized with a pyrenyl group preserved their morphology even after ten catalytic runs. We believe that these results clearly evidence the possible contribution of the ligand in the development of efficient catalytic materials by attaching simultaneously to the Au NPs and to the surface of graphene, diminishing leaching and increasing catalyst stability. This unexplored role of ligands may inspire other research groups in the development of efficient catalysts.

Author contributions

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.12.027.

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