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Partially oxidized gold nanoparticles: A catalytic base-free system for the aerobic homocoupling of alkynes

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ABSTRACT

The mechanism of alkyne homocoupling over gold nanoparticles and clusters, isolated and supported on CeO_2, has been theoretically investigated by means of periodic DFT calculations. The theoretical study indicates that O_2 dissociation on gold generates basic O atoms able to abstract the proton of the alkyne, and cationic $Au^{\delta+}$ and Au^+ species that decrease the activation barrier for the C—C bond forming step. Kinetic results show that the base-free homocoupling of alkynes is effectively catalyzed by gold nanoparticles supported on different solids, and confirm the theoretical prediction that the dissociation of oxygen on the gold nanoparticle is the controlling step of the global reaction.

1. Introduction

The synthesis of 1,3-diynes, which are important building blocks in fine chemistry, pharmaceuticals and bioactive compounds, has been traditionally carried out via oxidative homocoupling of terminal alkynes. Copper salts assisted by a base, as well as catalytic systems formed by a combination of palladium and copper salts have been extensively used in homogeneous phase [1–4]. The development of heterogeneous catalysts for the homocoupling of alkynes, with the advantages of easy separation and recycling, is interesting from an economic and environmental points of view, and some examples exist in the literature reporting the catalytic activity of copper-containing hydrotalcites [5,6], zeolites [7,8], and $Cu(OH)_x$ supported on different transition metal oxides [9,10]. It has also been reported that alkyne homocoupling occurs under typical conditions for Sonogashira cross-coupling reactions, both in homogeneous phase using Pd organocatalysts [11,12] and over heterogeneous Au/CeO_2 [13] and Au/La_2O_3 [14] catalysts. We recently investigated the mechanism of the Sonogashira reaction between iodobenzene (IB) and phenylacetylene (PA) on Au/CeO_2 catalysts and found that PA can be activated at cationic gold sites at the metal-support interface, producing a non-negligible amount of diphenyldiacetylene (DPDA), i.e., the product of PA homocoupling [15]. In this work, we combine DFT calculations with kinetic experiments to firstly determine the mechanism of PA homocoupling on heterogeneous gold catalysts and, consequently, to identify the nature of the gold active sites required to prepare an optimized heterogeneous catalyst for the homocoupling of alkynes.

2. Experimental section

2.1. Models and methods

The mechanism of PA homocoupling was investigated by means of periodic density functional theory, using the Perdew–Wang (PW91) exchange–correlation functional within the generalized gradient approach (GGA) [16,17] as implemented in the VASP code [18,19]. The valence density was expanded in a plane wave basis set with a kinetic energy cutoff of 500 eV, and the effect of the core electrons in the valence density was taken into account by means of the projected augmented wave (PAW) formalism [20]. Integration in the reciprocal space was carried out at the Γ k-point of the Brillouin zone. Transition states were located using the DIMER [21,22] and NEB [23] algorithms, and stationary points

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were characterized by pertinent frequency analysis calculations. Charge distributions were estimated using the theory of atoms in molecules (AIM) of Bader using the algorithm developed by Henkelman [24,25]. In the case of modeling CeO_2, the Hubbard repulsion term (U) with a value of 5 eV was applied to the cerium atoms in all calculations [26].

Neutral gold clusters and nanoparticles were modeled by means of an Au_3 system formed by three gold atoms and by an Au_{38} system having a typical cuboctahedral shape and ~1 nm diameter, respectively. A partially oxidized gold nanoparticle was obtained by adding 16 O atoms to the surface of the Au_{38} system, generating a $Au_{38}O_{16}$ model previously described [27]. These models were placed in a $25 \times 25 \times 25$ Å^3 cubic box, large enough as to avoid interactions between periodically repeated nanoparticles or adsorbates, and during the geometry optimizations, only the positions of the adsorbates and of the O atoms directly involved in the mechanism were allowed to fully relax.

A stoichiometric CeO_2 (1 1 1) surface was modeled by means of a (4×3) supercell slab containing 64 O atoms and 32 Ce atoms, and then, four different models were generated to simulate Au nanoparticles supported on CeO_2: (a) *AuO_x/CeO_2* model: a two atomic layer thick Au nano-rod containing 20 Au atoms was placed on the stoichiometric CeO_2 (1 1 1) surface and six additional oxygen atoms were added between the Au nano-rod and the CeO_2 surface Ce^{4+} sites. This model contains both metallic Au^0 and cationic $Au^{\delta+}$ species at the metal–support interface. (b) *Au_2O_3/CeO_2* model: a gold oxide strip consisting of 6 Au atoms and 9 O atoms was placed on the stoichiometric CeO_2 (1 1 1) surface, generating a system containing cationic Au^+ and Au^{3+} atoms. (c) *Au_{10}/CeO_2* model: a small cluster consisting of ten Au atoms arranged in two layers having 7 and 3 Au atoms, respectively, was placed on the stoichiometric CeO_2 (1 1 1) surface, resulting in a supported Au nanoparticle containing metallic low coordinated Au^0 atoms, and (d) *Au_9O_7/CeO_2* model: a small cluster consisting of nine Au atoms was placed on the stoichiometric CeO_2 (1 1 1) surface, and 7 O atoms were added at the metal-support interface, generating a system containing three low-coordinated metallic Au^0 atoms on top of the particle and four cationic Au^+ sites at the metal-support interface. To obtain the optimized structures of these models, the Ce and O atoms in the bottom layer of each system were kept fixed in their bulk optimized positions, while the atomic positions of the rest of the atoms were fully relaxed. In the study of the mechanism of PA homocoupling, only the positions of the adsorbates and of the O atoms directly involved in the mechanism were allowed to fully relax during the geometry optimizations.

2.2. Experimental

2.2.1. Catalyst screening and scope

The solid catalyst (Au/Carbon and Au/CeO_2: 41 mg; Au/TiO_2, Au/ZnO, Au/Al_2O_3 and Au/Fe_2O_3: 65 mg, 2 mol% Au) was placed in a thick double-walled 2.5-ml glass reactor equipped with a magnetic stirrer. Then 1,3-dichlorobenzene (0.5 ml) and the corresponding alkyne (0.25 mmol) were added and the vial capped with the pressure system. Molecular oxygen gas was loaded through a needle until the manometer indicated c.a. 5 bars (0.75 mmol). Then, the reactor was placed stirred in a pre-heated oil bath at 170 °C and magnetically stirred for 18 h. After this time, the reactor was cooled with water and the gas released. Diethyl ether (1 ml) was added and the mixture was filtered and submitted to GC and GC–MS analysis after dodecane (22 µl, 0.1 mmol) was added as external standard.

2.2.2. Initial rate measurements

Initial rates were calculated from the slope of the first-order kinetic curves of the homocoupling of *ortho*-tolylacetylene under different pressures of oxygen or at different concentrations of alkyne. The points of the kinetic curves were obtained from independent batch experiments by stopping the reaction at different reaction times. For that, the solid catalyst (Au/C or Au/CeO_2: 41 mg, Au/ZnO: 65 mg; 2 mol% Au) was placed in a thick double-walled 2.5-ml glass reactor equipped with a magnetic stirrer. Then, 1,3-dichlorobenzene (0.5 ml) and the corresponding amount of *ortho*-tolylacetylene were added and the vial capped with the pressure system. Neat molecular oxygen gas was loaded through a needle until the manometer indicated the corresponding pressure. Then, the reactor was magnetically stirred in a pre-heated oil bath at 170 °C for the desired time. After this time, the reactor was cooled with water and the gas released. Diethyl ether (1 ml) was added and the whole mixture was filtered and submitted to GC and GC–MS analysis after dodecane (22 µl, 0.1 mmol) was added as an external standard. The yield of homocoupling of *ortho*-tolylacetylene was plotted versus time and the slope at low yields gives the initial rate in h^{-1}.

2.2.3. Leaching studies

Experiments were carried out following the procedure above detailed but at different reaction times. After representing these data in a plot-time yield graphics, a second set of experiments was carried out as follows: at c.a. 25% conversion, the gas was released and the solid catalyst was filtered at the reaction temperature collecting the filtrates in a second reactor equipped with a magnetic bar. This reactor was closed and placed under the same magnetically stirred bath oil at 170 °C after oxygen atmosphere was re-loaded (0.75 mmol). This protocol was followed for each data point. After the desired time, diethyl ether (1 ml) was added and the mixture was filtered and submitted to GC and GC–MS analysis after dodecane (5.6 µl, 0.025 mmol) was added as external standard. Comparison among the curves gives estimation about the presence of catalytically active species in solution. The results obtained for the batch reactions are similar to those corresponding to single reactions in which aliquots were periodically taken after release of the oxygen atmosphere and re-load.

2.2.4. Reusability studies

Experiments were carried out following the procedure above detailed but recovering the solid catalyst by decantation instead of filtration after diethyl ether (1 ml) addition. The solid was then washed three times with diethyl ether (1 ml), dried, and used in a second run.

3. Results and discussion

3.1. Theoretical study of reaction mechanism on gold catalyst models

In a first step, we investigated the mechanism of PA homocoupling on a small Au_3 cluster and on two different models of isolated gold nanoparticles, that is, a Au_{38} system containing only metallic low coordinated Au^0 sites (see Table 1), and a

Table 1
Calculated Bader charges on selected Au atoms in different gold catalyst models.

Model	Au^0	$Au^{\delta+}$	Au^+	Au^{3+}
Au_3	~0	–	–	–
Au_{38}	~0	–	–	–
Au_2O, Au_2O_3	–	–	0.47	1.19
$Au_{38}O_{16}$	~0	0.21	0.47	–
AuO_x/CeO_2	~0	0.33	0.65	
Au_2O_3/CeO_2			~0.76	~1.14
Au_{10}/CeO_2	~0			
Au_9O_7/CeO_2	~0		~0.64	