

Hydrogen-promoted oxidation over hydrophobic Au/FLG catalysts

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Introduction

One of the specificities of gold catalysts is their activity in oxidation reactions, at much lower temperatures than those required by e.g. Pt catalysts, which makes them particularly suited to environmental applications, such as the preferential oxidation of CO in hydrogen-rich streams (PROX) [1]. In order to exhibit this unique property, gold nanoparticles (Au NP) are generally supported over oxides of transition metals. In these catalysts, oxygen activation is ensured by the gold/support interaction. However, over the years, it has appeared that, when the oxidation was performed in the presence of a so-called “sacrificial reductant” such as hydrogen, the presence of the reducible oxide was not required.

Hence, alternative supports can be associated with gold. Passivated silicas, for example, have proven useful in (1) enhancing the rate of the e.g. gold-catalyzed aerobic co-oxidations of higher alkanes and alkenes by maximizing dispersion of the catalyst powder within the apolar liquid media [2] and (2) evidencing the intrinsic activity of Au NP towards hydrogen-mediated gas phase oxidations [3]. Furthermore, when dispersed over these alkyl-terminated oxide surfaces, Au NP exhibit superior selectivity and durability in e.g. the PROX reaction. Thus, with the perspective of further investigating the potential of hydrophobic gold catalysts and studying hydrogen-mediated oxygen activation over them, we considered unfunctionalized, pristine few-layer graphene (FLG) as a 2D, carbon-rich surface, virtually free of oxygen-containing functions, to support Au NP.

In this communication, we will show that FLG-supported Au NP can activate oxygen at low temperature (< 300°C) in the presence of hydrogen and that the kinetics of oxygen activation are quite similar to those observed over oxide-supported gold catalysts.

Materials and Methods

6.48 wt.% Au/FLG was obtained under sonication, according to a recently developed optimized protocol [4], by NaBH₄ (10 eq / Au) reduction of AuPPh₃Cl in DMF (10⁻³ M) in the presence of home-made, pristine FLG flakes annealed at 900°C under Ar (Au/FLG = 10 wt.%), followed by drying (air, 130°C, 24 h). The catalyst exhibits gold crystallite of 5.8 nm on average (XRD analysis).

The reaction between oxygen and hydrogen was performed in a fully automated (CETRIB SARL, France) fixed-bed flow reactor (i.d. 10 mm) loaded with 26 mg of the catalyst powder (1.68 mg / 8.6 μmol Au with ca. 24% dispersion). The 0.5-2% O₂ / 12-80% H₂ (+ 0.4% CO for PROX or 0.1% CH₄) gas mixture (balanced in He), was then introduced at a total flow rate of 100 mL min⁻¹ (1 atm, GHSV ~ 15,000 h⁻¹). The catalyst was heated at 1° min⁻¹ from 20 to 300°C and then cooled down at the same rate. Several temperature cycles were performed in order to probe the stability of the catalyst under the reactive gas mixture, which was further evidenced by post-evaluation characterization (TGA, XRD, etc...). O₂ conversions

were determined on the basis of on-line Compact Gas Chromatograph (Interscience, Belgium) analysis, using external calibration. Turnover frequencies (TOF) are defined as the number of mole of oxygen converted per number of mole of surface gold per hour.

Results and Discussion

Just like support-promoted oxygen activation [5], hydrogen-only mediated oxygen activation is only slightly influenced by the partial pressure of molecular oxygen in the feed. A partial order of reaction in oxygen of 0.16 is indeed found over Au/FLG by varying the oxygen content from 0.5 to 2% in the 48% H₂/He feed. However, the rate of oxygen activation can be markedly enhanced by increasing the hydrogen content of the feed (Figure 1a).

On the other hand, introducing even low amount of methane or carbon monoxide in the feed slightly inhibits oxygen activation (Figure 1b).

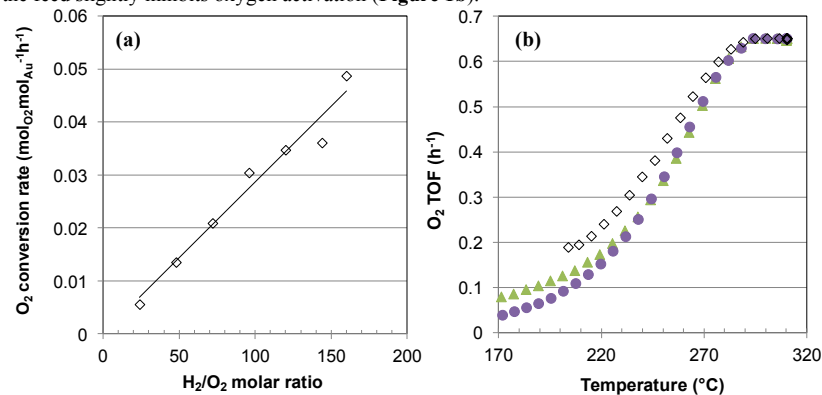


Figure 1. (a) Influence of the H₂/O₂ ratio on Au/FLG-catalyzed oxygen activation in a 0.5% O₂/12-80% H₂/He mixture at 206°C.

(b) Impact of the presence of CO (●) and CH₄ (▲) traces co-fed with hydrogen on the rate of oxygen activation in the O₂ + H₂ reaction with H₂/O₂ = 160 (◇).

Significance

The low reactivity towards water of the FLG support facilitates the study of the kinetics of gold-catalyzed hydrogen-mediated oxygen activation with potential benefit in the development of more selective low temperature hydrocarbon oxidation processes.

References

1. Ivanova, S.; Petit, C.; Pitchon, V.; Caps, V. *ChemCatChem* **2010**, 2, 556.
2. Guillois, K.; Burel, L.; Tuel, A.; Caps, V. *Applied Catalysis A* **2012**, 415-416, 1.
3. Gajan, D.; Guillois, K.; Delichère, P.; Basset, J.-M.; Candy, J.-P.; Caps, V.; Copéret, C.; Lesage, A.; Emsley, L. *Journal of the American Chemical Society* **2009**, 131, 14667.
4. Vigneron, F.; Piquet, A.; Baaziz, W.; Ronot, P.; Boos, A.; Janowska, I.; Pham-Huu, C.; Petit, C.; Caps, V. *Catalysis Today* **2014**, accepted.
5. Quinet, E.; Piccolo, L.; Morfin, F.; Avenier, P.; Diehl, F.; Caps, V.; Rousset, J.-L. *Journal of Catalysis* **2009**, 268, 384.