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The Preparation of a Residue-free, Alumina-supported Gold Catalyst by Decomposition of an Azido-Gold(III) Complex and an Evaluation of the Effectiveness of the Catalyst for the Hydrogenation of Propyne

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Abstract. A 1 % w/w alumina-supported gold catalyst is described that is prepared from the impregnation of alumina with a solution of ammonium tetraazidoaurate(III), $NH_4[Au(N_3)_4]$. Decomposition of the azide precursor leads to a residue-free catalyst comprised of well-dispersed gold particles. This novel material is tested for propyne hydrogenation using pulse-flow techniques and displays 100 % selectivity to the partial hydrogenation product, propene, albeit in the presence of a large retention of hydrocarbon by the catalyst. The latter characteristic is associated with a support-mediated deactivation pathway. Comparing catalytic performance with a 1.45 % w/w Au/TiO_2 reference catalyst indicates that chlorine-free precursor compounds are not required to enhance catalytic activity for this particular reaction.

Introduction

Azido complexes of d block metals are characterized by thermal instability and their decomposition, which is often explosive, has limited their use in synthesis. However, we have exploited this aspect of their chemistry to prepare an alumina-supported palladium catalyst by thermal decomposition of a Pd^{II} azido complex in the presence of alumina.[1] Salts such as $PdCl_2$ or $Pd(NO_3)_2$ are typically used as Pd precursor compounds but these can potentially leave chemical residues, which could affect catalytic performance. Decomposition of tetramminepalladium(II) tetraazidopalladate(II) leads to the formation of Pd atoms, ammonia, and dinitrogen.[2] Thus, a controlled decomposition in the presence of alumina can be used to produce a residue-free Pd/Al_2O_3 catalyst, with the gaseous co-products readily separable from the solid Pd/alumina matrix. The Pd is well dispersed and the catalyst exhibits a distinct infrared spectrum for chemisorbed carbon monoxide.[1] Moreover, the Pd(azide)/Al_2O_3 catalyst subsequently proved invaluable in discerning morphological trends in alumina supported Pd catalysts,[3] which then enabled a structure-activity relationship for the hydrogenation of an α,β-unsaturated aldehyde over supported Pd catalysts to be developed.[4]

Klapötke and co-workers have previously synthesized and characterized a number of highly sensitive ammonium tetraazidoaurates(III) compounds.[5] This article describes a procedure for combining ammonium tetraazidoaurate(III) with a high surface area alumina to produce a new Au/Al_2O_3 reference catalyst, subsequently referred to as Au(azide)/Al_2O_3.

The selective hydrogenation of propyne has been used as a test reaction, enabling comparisons to be made with a recent study using a World Gold Council (WGC) reference catalyst: 1.45 wt % Au/TiO_2.[6] The Au precursor compound for the reference catalyst is tetrachloroauric(III) acid; catalysts prepared from this precursor can contain residues of chloride ion, and even sodium when a sodium salt is used for precipitation in the commonly used deposition-precipitation and co-precipitation techniques. Either may act as a catalyst poison, which has been examined in some detail.[7–9] Two main effects have been described: (i) chloride residues facilitate the sintering of Au particles during heat treatment, and (ii) they inhibit the catalytic activity by poisoning the active site.[7] The performance of the Au(azide)/Al_2O_3 catalyst in the designated test reaction compared with the reference catalyst provides information on how chloride residues may affect the application of supported gold catalysts in hydrogenation reactions.

Results and Discussion

McEwan and co-workers[10] and *Cárdenas-Lizana* and *Keane*[11] have reviewed the application of supported gold catalysts for selective hydrogenation reactions. Propyne hydrogenation is selected as a test reaction in this work. *Pérez-*

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Ramírez and co-workers have shown that supported gold catalysts can exhibit favorable propene yields.[12,13] *Lopez-Sanchez* and *Lennon* used pulse-flow methods to investigate the hydrogenation of propyne over two WGC reference catalysts: Au/TiO_2 and Au/Fe_2O_3.[6] That work showed the Au/TiO_2 catalyst to display complete selectivity to propene and progressive deactivation, whereas Au/Fe_2O_3 exhibited selectivity and deactivation patterns dependent on ageing, catalyst pre-treatment and reaction temperature; with the variability in performance of Au/Fe_2O_3 attributed to support effects.[6] The same pulse-flow methodology is adopted here, permitting direct comparison between Au(azide)/Al_2O_3 and Au/TiO_2. The Au/Fe_2O_3 catalyst is a less suitable comparator in this instance, due to the complexity evident in the Au/Fe_2O_3-C_3H_4-H_2 reaction system.

Catalyst Characterization

The novel preparation of the Au(azide)/Al_2O_3 catalyst is described in the Experimental Section. Atomic absorption spectrophotometry (Perkin-Elmer 1100B Atomic Absorption Spectrophotometer) revealed the gold content of the Au(azide)/Al_2O_3 sample to be 0.83 ± 0.01 wt-%, with the error representing one standard deviation of three replicate measurements. No nitrogen was detectable via elemental analysis (Exeter Analytical Elemental Analyser CE440) and no chloride was detectable with a Sherwood chloride analyzer 926 (Mk II) at a detection limit of 10 $mg{\cdot}L^{-1}$ chlorine. The surface area of the catalyst determined by a Micrometrics Gemini III 2375 Surface Area Analyzer was ca. 120 $m^2{\cdot}g^{-1}$, indicating the preparative technique to have a negligible effect on total surface area. After reaction testing at 523 K a surface area of 106 $m^2{\cdot}g^{-1}$ was determined. Transmission electron microscopy (TEM) was performed with a JEOL-1200EX microscope, operating at a primary beam energy of 80 kV. The Au(azide)/Al_2O_3 sample indicated the presence of gold particles of mean particle size 3.0 ± 1.7 nm, with the error representing one standard deviation. Thus, the metal is well dispersed and exhibits a narrow particle size distribution. A Perkin-Elmer Lambda 9 UV/Vis/NIR spectrophotometer fitted with a PE Integrating Sphere coated with barium sulfate was used to obtain the diffuse reflectance UV spectrum of the Au(azide)/Al_2O_3 catalyst and revealed the presence of a broad band at ca. 520 nm. This feature corresponds to a gold plasmon transition and confirmed the presence of metallic gold nanoparticles deposited on the alumina.[14] As with other supported gold catalysts,[15] the presence of oxidized gold cannot be excluded.

Au(azide)/Al_2O_3

The Au(azide)/Al_2O_3 catalyst activity in the gas phase hydrogenation of propyne was studied at reaction temperatures of 323, 423, 523 and 663 K using a pulse-flow methodology. Fresh amounts of sample reduced at 523 K were used for each measurement. The C_3 pulse composition after reaction at the four selected reaction temperatures is displayed in Figure 1.

At 323 K no reaction products are detected. The lack of hydrogenation activity is attributed to a minimal supply of atomic hydrogen at this temperature. Dissociative adsorption of hydrogen over gold foil does not occur below 473 K,[16] although *Bond* and co-workers have shown that this temperature can be lowered to ca. 400 K to affect hydrogenation processes when small gold particles are used.[17] Indeed, consistent with that work, Figure 1b indicates a small degree of activity at 423 K, with propene detected as the only reaction product (propene: 0.86 $\mu mol{\cdot}g_{cat}^{-1}$ for pulse 1). Over the pulse sequence studied, no significant deactivation is apparent although some propyne retention is observed, which is approximately constant after pulse 4 (Figure 1b). This corresponds to

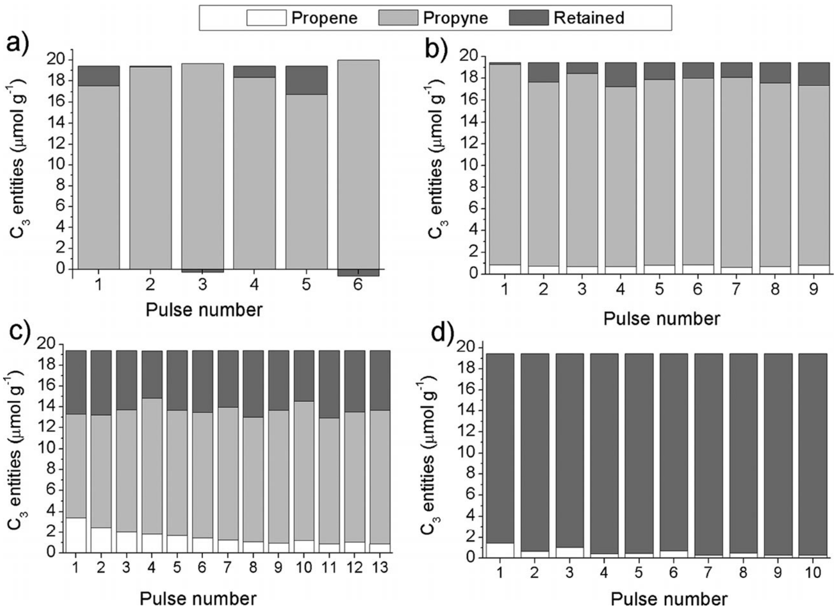

Figure 1. Carbon mass balance profiles corresponding to propyne hydrogenation over the Au(azide)/Al_2O_3 catalyst at the following reaction temperatures: (a) 323 K, (b) 423 K, (c) 523 K, and (d) 623 K. The catalyst was reduced at 523 K prior to reaction testing in all cases.

cumulative propyne retention of 13.4 µmol·g^{-1} over the 9 pulses studied.

Pulse-flow propyne hydrogenation studies on a reference Au/TiO_2 catalyst at 423 K are characterized by selective propene production similarly accompanied by propyne retention.[6] At approximately steady-state conditions, propene production for the Au/TiO_2 catalyst corresponds to approximately 2 µmol propene per g_{cat},[6] compared with 0.9 µmol propene per g_{cat} seen in Figure 1b. Specific activity, as defined in the Experimental Section, is a means of assessing the reactivity of supported gold catalysts.[18] Table 1 compares the specific activity of the Au(azide)/Al_2O_3 and Au/TiO_2 catalysts at pseudo-steady state for a reaction temperature of 423 K. This normalization of alkene production with respect to mass of gold shows the Au(azide)/Al_2O_3 catalyst to exhibit 79 % of the activity achievable with the reference catalyst. Although the propene yields are lower for the Au(azide)/Al_2O_3 catalyst, the general characteristics, as evidenced by low propene yields accompanied by propyne retention, are broadly comparable to the trends reported for the reference material.

Table 1. Specific activity values for the formation of propene over Au(azide)/Al_2O_3 and Au/TiO_2 catalysts at 423 K. The propene production values represent a pseudo-steady state regime and correspond to the 9th and 8th pulse values observed for the Au(azide)/Al_2O_3 and Au/TiO_2 catalysts, respectively. The Au/TiO_2 data is obtained from the literature.[6]

Catalyst	Au /wt-%	Propene production /propene µmol·g_{cat}^{-1}	Specific activity /propene µmol·g_{Au}^{-1}
Au(azide)/Al_2O_3	0.83	0.90	108
Au/TiO_2	1.45	2.00	138

Figure 1c shows the results for experiments performed at 523 K. Compared with the 423 K data (Figure 1b), the quantity of propene increased significantly in the first pulses (pulse 1 produced 3.42 µmol propene per g_{cat}) but this progressively decreased on increasing pulse number. The amount of propene stabilized at ca. 0.9 µmol·g_{cat}^{-1} by pulse 9 with a propyne conversion of 34.3 %. Figure 1c also shows propyne retention to become more substantial at this temperature and corresponds to 4–6 µmol·g_{cat}^{-1} per pulse, signifying 20–30 % propyne retention for each pulse. Previous elevated temperature propyne hydrogenation pulse-flow studies on two WGC reference catalysts – Au/TiO_2 and Au/Fe_2O_3 – similarly showed decreasing propene yields on successive pulsing accompanied by large degrees of propyne retention.[6]

Increasing reaction temperature is expected to favor the dissociative adsorption of molecular hydrogen and enhance hydrogen supply at the catalyst surface. However, Figure 1c indicates the increasing temperature also permits access to a deactivation channel, as evidenced by decreasing propene yields on continued pulsing. Deactivation has previously been reported for pent-1-ene hydrogenation over gold catalysts, and was associated with the formation of carbonaceous residues.[17] Further, *Azizi* et al. reported significant deactivation above 573 K for the hydrogenation of ethyne over a ceria-supported gold catalyst due to polymerization processes.[19]

Figure 1d shows that increasing the temperature further to 623 K accentuates this deactivation pathway, as evidenced by lower activity and almost complete retention of the incident propyne molecules by the catalyst.

Benchmarked against the performance of the Au/TiO_2 reference catalyst, Figure 1 shows the Au(azide)/Al_2O_3 catalyst not to exhibit remarkable performance in selectively hydrogenating propyne to propene. However, with respect to the selection of Au precursor compounds for selective hydrogenation reactions, this outcome does indicate that chlorine-free precursor compounds do not convey any specific benefits regarding enhanced catalytic activity for this particular reaction. Indirectly, this work then endorses the continued use of tetrachloroauric acid as the precursor of choice for supported gold catalysts.

The Alumina Support

Blank experiments performed on the alumina support material (Figure 2) showed no propene or propane formation for a range of temperatures up to 623 K, establishing the propene formation observed in Figure 1 to be gold-mediated. Figure 2 also indicates that the support material is primarily responsible for the substantial degree of propyne retention. This is particularly evident at elevated temperatures (≥ 523 K). The consumption of incident hydrocarbon is attributed to a propyne oligomerization process that is accelerated at higher temperatures. This process will additionally block active sites on the metal and is thought to contribute to the deactivation trends observed in Figure 1. The origin of this phenomenon is thought to be Lewis acid sites on the alumina that form via dehydration and de-hydroxylation stages at elevated temperatures.[20] Further work using support materials exhibiting different degrees of Lewis acidity (e.g. β-AlF_3 and α-AlF_3)[21] would assist in establishing the validity of this assertion. Given the extent of retention evident in Figure 1d and Figure 2, the majority of the oligomeric material is thought to be associated with the alumina surface. *Ossipoff* and *Cant* have shown that oligomerization processes play a significant role in the hydrogenation of propyne over supported copper catalysts.[22]

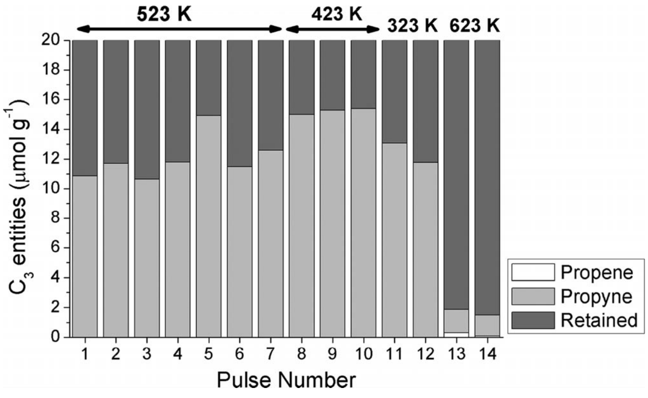

Figure 2. Carbon mass balance profile for propyne hydrogenation over alumina at a range of temperatures: pulses 1–7, 523 K; pulses 8–10, 423 K; pulses 11–12, 323 K and pulses 13–14, 623 K. The alumina was exposed to a reduction treatment at 523 K prior to reaction testing.

Catalyst Reduction Temperature

Earlier studies on a Au/Fe_2O_3 catalyst showed that propene yields could be improved and maintained by adoption of a high temperature reduction process, where the reduction in hydrogen was performed at 663 K.[6] This approach was applied to the Au(azide)/Al_2O_3 catalyst, where the catalyst was reduced at 663 K then propyne hydrogenation examined at 523 K; the results are presented in Figure 3. Compared with the catalyst reduced at 523 K and reaction tested at the same temperature (Figure 1c), the quantities of propene are low, and decrease with increasing pulse number: 2.04 to 0.30 μmol propene per g_{cat} in pulse 1 and pulse 8, respectively. Additionally, the propyne retention is increased.

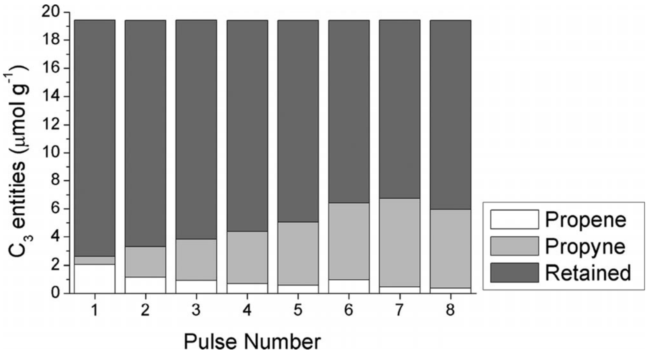

Figure 3. Carbon mass balance profile for the Au(azide)/Al_2O_3 catalyst after reduction/pre-treatment at 663 K then propyne hydrogenation reaction testing at 523 K.

Clearly, a high temperature reduction stage is non-beneficial for alumina-supported gold catalysts. Moreover, the negative response of the Au(azide)/Al_2O_3 catalyst compared with the Au/Fe_2O_3 catalyst is a further indication of the importance of the support material in affecting favorable transformations in a relatively straight-forward hydrogenation reaction.

Propene Hydrogenation

In order to elucidate the origin of the 100 % propene selectivity observed (e.g. Figure 1c), several experiments were performed using a hydrogen:propene (3:1) mixture over the Au(azide)/Al_2O_3 catalyst to evaluate if this catalyst could hydrogenate propene. After a reduction stage at 573 K, a first series of experiments studied the passing of three pulses of the reactant mixture at increasing temperatures of 423, 523, 623, 723 and 773 K. A second series of experiments studied a Au(azide)/Al_2O_3 sample reduced similarly but the testing was performed isothermally at 523 K for a sequence of 10 pulses. In neither of the experiments were any quantities of propane observed. Furthermore, none of the hydrocarbon retention processes, clearly apparent in the propyne experiments (Figure 1), were observed. These results indicate that the gold catalyst cannot hydrogenate propene for temperatures up to 773 K and, furthermore, indicate the catalyst to be inherently 100 % selective to propene when exposed to mixtures of hydrogen and propyne. This outcome is consistent with recent reports on supported gold catalysts applied in alkyne hydrogenation reactions exhibiting high selectivity to the alkene.[12,23]

Conclusions

A 1 % alumina-supported gold catalyst was synthesized by the photo-decomposition of a gold-azide precursor complex and assessed using propyne hydrogenation as a test reaction. The main results can be summarized as follows:

(i) The catalyst, exhibiting metal particles of ca. 3 nm diameter is 100 % selective in the partial hydrogenation of propyne. The complete selectivity to propene is an inherent property of the catalyst, as hydrogenation to propane is not accessible within the temperature range studied.

(ii) Reaction temperatures $\geq$ 423 K are required to induce propene production but simultaneously this induces large retention of hydrocarbon feedstock by the catalyst. Blank experiments show the hydrocarbon retention pathway to be support-mediated.

(iii) Under comparable reaction conditions, the Au(azide)/Al_2O_3 catalyst exhibits a reduced propene yield compared to a reference Au/TiO_2 catalyst. This implies that chlorine-free precursor compounds are not required to enhance catalytic activity for this particular reaction.

Experimental Section

Catalyst Preparation: Ammonium tetraazidoaurate(III) was synthesized according to Equation (1) from ammonium tetrachloroaurate(III) with an excess of silver azide in methanol.

$$NH_4[AuCl_4] \xrightarrow[-4AgCl]{4AgN_3/CH_3OH} NH_4[Au(N_3)_4] \qquad (1)$$

Caution! The red-orange salt is an extremely shock-sensitive material, which exploded spontaneously during several attempts of solvent evaporation, similar as reported for Group 1 cation salts.[24–26] However, this ammonium salt can be handled with absolute caution in methanol solutions,[5] whereas tetraazidoaurates(III) containing large cations are relatively safe to handle.[24–28]

A 1 % w/w Au/Al_2O_3 catalyst was prepared according to the following procedure. A clear red (filtered) solution of $NH_4Au(N_3)_4$ (100 mg) in methanol (approx. 20 mL), generated according to the above equation under light exclusion, was poured onto a slurry of alumina (5.0 g, Degussa Oxid C, BET surface area = 109 $m^2 \cdot g^{-1}$) in methanol (75 ml). The resulting slurry was carefully shaken frequently and the container kept open for drying over a period of several days at ambient temperature in the presence of sunlight. The light-initiated decomposition process is described by Equation (2).

$$NH_4[Au(N_3)_4]/Al_2O_3\ (s) \rightarrow Au/Al_2O_3(s) + 6N_2(g) + NH_3(g) + 1/2H_2(g) \qquad (2)$$

With this procedure, the precursor compound readily partitioned into gaseous and solid phase components. The gaseous components comprised distinct molecules of high vapor pressure, which were vented readily from the remaining solid to leave an intimate mixing of metallic gold and the alumina support material, with no residue from the original precursor compound remaining. The solid, of light purple coloration, was air stable and was ground to produce a powder.

Reaction Testing: A pulse-flow micro-reactor system was used, that has been described elsewhere.[6,29] The catalyst sample was ground and sieved to give a grain fraction of 250–500 μm. Approximately

0.220 g of the catalyst sample was reduced in a 25 % H_2 in helium flow (67 mL·min^{-1}) while the temperature was raised from ambient temperature to the desired reduction temperature (typically 523 K) at 5 K·min^{-1}, then held for 2 h. The sample was set to the reaction temperature in a flow of helium. Pulses of reactant gas (78 µmol·g_{cat}^{-1}) of a 3:1 hydrogen/propyne mixture were injected into the helium carrier gas (50 mL·min^{-1}) by passing the carrier flow through a sample loop. Each pulse corresponds to an incident propyne pulse of 19.5 µmol propyne per g_{cat}. On elution from the catalyst bed, the full pulse was analyzed by on-line gas chromatography, using a Philips PU 4500 gas chromatograph equipped with a glass column packed with Porapak Type QS 80-100 and a thermal conductivity detector. The facility was also equipped with a quadrupole mass spectrometer (Leda Mass LM22). Helium (BOC, 99.995 % purity) and hydrogen (BOC, 99.99 % purity) were purified using in-line deoxygenating and drying traps. The propyne (BDH, 96 % purity) was purified through vacuum distillation prior to use. Blank experiments performed on the empty reactor at elevated temperatures displayed no activity. Blank experiments on alumina Degussa Oxid C were performed following the same catalyst pre-treatment and procedures described above. All experiments were performed at least twice, with the figure presented here being representative of those observed for the catalyst under the specified reaction conditions. Propene hydrogenation tests were performed following the same procedures described above. Propene (Messer Griesheim, 99.95 % purity) was used as received.

The following definitions are used:

$$X_{\mathrm{propyne}}\ (\%) = \frac{\mathrm{propyne}_0 - \mathrm{propyne}_t}{\mathrm{propyne}_0} \times 100,$$

$$S_{\mathrm{propene}}\ (\%) = \frac{\mathrm{propene}_t}{(\mathrm{propene}_t + \mathrm{propane}_t)} \times 100,$$

$$\mathrm{SA}\ (\mathrm{mol\ propene\ pulse}^{-1} g_{\mathrm{Au}}^{-1}) = \frac{\mathrm{moles\ propene\ pulse}^{-1}}{\mathrm{mass\ of\ Au}},$$

where $X_{propyne}$ and $S_{propene}$ represent the propyne conversion and propene selectivity, respectively. SA represents the specific activity [18].

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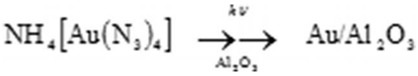
The Preparation of a Residue-free, Alumina-supported Gold Catalyst by Decomposition of an Azido-Gold(III) Complex and an Evaluation of the Effectiveness of the Catalyst for the Hydrogenation of Propyne



$$NH_4[Au(N_3)_4] \xrightarrow[Al_2O_3]{h\nu} Au/Al_2O_3$$