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Conte, M., Davies, C.J., Morgan, D.J. et al. (3 more authors) (2014) Characterization of Au3+ species in Au/C catalysts for the hydrochlorination reaction of acetylene. Catalysis Letters, 144 (1). pp. 1-8. ISSN 1011-372X

https://doi.org/10.1007/s10562-013-1138-8

Characterization of Au^{3+} species in Au/C catalysts for the hydrochlorination reaction of acetylene

Marco Conte,[a,b,*] Catherine J. Davies,[a] David J. Morgan,[a] Albert F. Carley,[a] Peter Johnston,[c] and Graham J. Hutchings [a,*]

[a] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK
[b] Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK
[c] Johnson Matthey Catalysts, Orchard Road, Royston, Herts, SG8 5HE, UK

*E-mail: m.conte@sheffield.ac.uk , Hutch@cardiff.ac.uk

Abstract

A set of Au/C catalysts for the gas phase hydrochlorination of acetylene to vinyl chloride monomer were prepared using a range of strong acids as impregnating solvents and varying the preparation drying temperature. The most active catalyst is the material prepared using aqua regia as solvent with an intermediate drying temperature of 140 °C. The effects of the catalyst preparation parameters on the catalytic activity are examined using XPS and TPR as analytical tools. In particular, the use of thermal reduction methods allows the determination of kinetic parameters for the reduction of Au^{3+} to Au^0 by means of H_2. These data support the existence of a redox cycle between Au^{3+}/Au^0 when carbon is used as support.

Keywords: gold, carbon, acetylene hydrochlorination, XPS, TPR

1. Introduction

Au/C catalysts are active materials for the synthesis of vinyl chloride monomer (VCM) by the direct hydrochlorination of acetylene with hydrochloric acid in the gas phase [1-3]. Current industrial manufacture routes of VCM use the oxychlorination reaction of ethylene in presence of copper salts [4,5], or direct hydrochlorination in presence of mercuric chloride catalysts [6,7]. However, the latter synthesis is not a green process due to the volatility of the active $HgCl_2$ component that can be dispersed into the environment. Despite this disadvantage, the route using acetylene is considered to be a strong competitor to the process based on ethene as feedstock due to a renewed interest in coal as feedstock which is economically advantageous in certain locations.

Nevertheless, despite the excellent activity of Au/C catalysts for this reaction, these materials can be affected by deactivation in long term use, due to reduction of Au^{3+} centres [8] or oligomer formation [9] over the catalyst surface. The former operating at reaction temperatures in the range of ca. 200 ^{o}C and the latter at reaction temperatures of ca. 100 ^{o}C. Studies carried out for these catalysts identified Au^{3+} as active site for this reaction. On the other hand, recent work implemented to address this important aspect also showed that an excess of Au^{3+} does not contribute to the catalyst activity and that is likely that the active Au^{3+} species are located at the Au/C interface [10,11]. It is in fact ascertained that among the solvents used to dissolve the $HAuCl_4$ precursor, HNO_3 has an oxidation effect on both the gold nanoparticles and the functional groups on the carbon surface, while HCl has a nucleation effect towards gold on the carbon support. However, despite the use of sophisticated analytical tools to determine the source of the catalytic activity in correlation with the preparation route, this still did not provide an unambiguous answer capable of certain correlation of the catalytic activity, and in turn the catalyst deactivation, with the fine tuning of the catalyst preparation procedure.

This prompted us to study Au/C catalysts by means of temperature programmed reduction. This methodology is widely used in heterogeneous catalysis, mainly to determine the bulk content of an oxidised metal species. However, it is also possible to use an elegant property of TPR plots developed by Kissinger [12] that is currently mainly used to study crystallization of glasses [13,14]. Thermograms collected using different temperature gradients can provide kinetic data concerning the reduction process of the metal. Using this approach we are able to identify a correlation between the catalytic activity and the ease of reduction of the Au^{3+} centres in the catalyst, as well as to display the effect of the counter-ion introduced in the preparation procedure in the stabilization and reduction of Au^{3+} species.

2. Experimental

2.1 Catalyst preparation

All the catalysts were prepared by a wet impregnation method. The gold precursor, $HAuCl_4 \cdot xH_2O$ (Alfa Aesar, 40 mg, assay 49%) was dissolved in aqua regia (3:1 HCl (Fisher, 32%) : HNO_3 (Fisher, 70%) by volume, 5.4 ml) and the solution added dropwise with stirring to the activated carbon support (Norit ROX 0.8) (1.98 g) in order to obtain a catalyst with a final metal loading of 1% wt. Stirring was continued at ambient temperature until NO_x production subsided, approximately 10 min. The product was dried for 16 h at 110 °C and used as a catalyst. Variations to this protocol were introduced by changing drying temperature, (110, 140 and 180 ^{o}C), and the use of pure acids e.g. HCl and HNO_3.

2.2 Catalytic tests and characterization of the products

Catalysts were tested for acetylene hydrochlorination in a fixed-bed glass microreactor. Acetylene (5 mL min^{-1}, 0.5 bar) and hydrogen chloride (6 mL min^{-1}, 1 bar) were fed though a mixing vessel and preheater (70 ^{o}C), and further mixed in a N_2 flow (10 mL min^{-1}, 1 bar) via calibrated mass flow controllers to a heated glass reactor containing catalyst (200 mg), with a total GHSV of 740 h^{-1}. A reaction temperature of 180 ^{o}C was chosen, and blank tests using an empty reactor filled with quartz wool did not reveal any catalytic activity, even at 250 ^{o}C with the reactants under these flow conditions, SiC (2 x 2.5g) was used to extend the bed length, above and below the catalyst itself, separated by quartz wool. The pressure of the reactants, HCl, C_2H_2 and N_2, was chosen both for safety reasons and to test the catalyst under mild conditions. The gas phase products were analyzed on-line by GC using a Varian 450GC equipped with a flame ionisation detector (FID). Chromatographic separation and identification of the products was carried out using a Porapak N packed column (6 ft x 1/8” stainless steel).

2.3 Characterization of the catalysts

2.3.1 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra DLD spectrometer using a monochromatised AlKα X-ray source (120 W) with an analyzer pass energy of 160 eV for survey scans and 40 eV for detailed elemental scans. Binding energies are referenced to the C(1s) binding energy of carbon, taken to be 284.7 eV.

2.3.2 Temperature programmed reduction

Temperature programmed reduction (TPR) analysis was carried out on a Thermo TPD/R/O 1100 Series instrument equipped with a thermal conductivity detector (TCD). The sample (100 mg) was heated up to 800 °C at a ramp rate of 5 ^{o}C min^{-1}, under a flow of hydrogen (10% in Ar, 20 mL min^{-1}). For activation energy determination, heating ramp rates of 5, 10 and 15 °C min^{-1} were also used.

Calibration of the TPR plots for the Au^{3+} amount was carried out for the Au/C sample prepared at 140 ^{o}C using HCl as a solvent used as standard.

3. Results and discussion

3.1 Catalytic activity for the catalysts under different preparation conditions

Three sets of Au/C catalysts were prepared under three different experimental conditions. In particular, the role of the drying temperature and the nature of the acid used to impregnate Au^{3+} in the carbon matrixes was investigated.

As impregnated Au^{3+} on carbon undergoes reduction to Au^{0} by effect of C present in the carbon matrix, and this can result in a different initial Au^{3+}/Au^{0} ratio and in turn the catalyst activity, drying temperatures of 110, 140 and 180 ^{o}C were chosen for investigation. Additionally, three different acid mixtures were also used to prepare the catalysts, namely: aqua regia, and its pure constituents HCl and HNO$_3$. The reason is twofold: (i) to evaluate the effect of the single acid components to the reaction and (ii) to address the effect that the counter-ion can have to the reduction temperature of the metal. In fact, very limited literature is present on this subject, and as the reducibility properties can affect the catalytic activity, it was considered of interest to evaluate this effect singularly. Therefore, in order to restrict the number of variables that can affect the catalytic performance, the reducibility of Au^{3+} species was investigated by studying the effect of C as well as of H_2 (see section 3.3), without the simultaneous presence of reagents.

In view of these experimental and methodological considerations, to assess the effect of C present in the carbon matrix the catalysts were tested for VCM formation using the set of catalysts dried at 110 °C (Fig. 1), 140 °C (Fig. 2) and 180 °C (Fig.3). The selectivity to VCM was > 99.9 % and therefore the conversions practically represents the yield of VCM as only trace amounts of 1of 1,2- dichlorethane and chlorinated oligomers are observed. From these data, a correlation, that is not immediately apparent, between the catalyst preparation factors and the conversion is present. In fact, it appears that catalysts obtained using HCl only as a solvent always give a poorer performance than those prepared using HNO_3 or aqua regia. HCl is a known sintering agent for gold, and this can affect the catalytic activity if the particles are too large (> 20 nm) [11, 15]. On the other hand HNO_3 displays an activity comparable to that of aqua regia and its use leads to the most active catalyst when temperatures of 110 and 180 °C are used. On the other hand the most active catalyst within the whole set is the one prepared using aqua regia at 140 °C, thus suggesting a synergistic effect of these two acids to the final activity.

These effects are better summarized displaying the conversion as a function of both the drying temperature and the kind of acid as a two dimensional surface (Fig. 4). The most active catalyst is found in a region of intermediate temperature and HNO_3 amount. However, as the literature available for this reaction, reports Au^{3+} as active species for this process [8-11], in order to correlate the contour plot in figure 4 with the Au^{3+} amount, XPS was carried out for all the catalysts (Table 1 and Fig. 5).

The most important observation from these data is that it is not true that the higher the amount of Au^{3+} the higher is the activity. For example, the catalyst prepared in HCl at a drying temperature of 110 °C shows a very high amount of Au^{3+} ca. 67% atomic fraction, yet it is one of the least active of the whole set with a conversion value of ca.

20%. In contrast, as expected, catalysts with low amount of Au^{3+}, ca. 10%, are not active and these give conversions in the range of 10-15%. The maximum activity of ca. 70% is observed at around 20 % Au^{3+} atomic surface composition. Attempts to explain this experimental observation have been published recently [10,11] and they possibly correlate with the presence of Au^{3+} species at the Au/C interface. However, as all the literature available for this reaction identify the reduction of Au^{3+} to Au^0 as one of the reasons for catalyst deactivation in long term use, we speculated that another factor must be operating, and a parameter so far neglected it is how easily these gold species could be reduced. In fact, if a catalyst presents a large Au^{3+} amount, but this is easy to reduce, it will be less effective than a catalyst with a lesser Au^{3+} amount but more difficult to reduce.

3.2 TPR analysis of the Au/C catalysts

Against this background we decided to investigate the catalysts by means of temperature programmed reduction (TPR) using H_2 as reducing agent. This technique is often used to quantify the amount of oxidized metal species in a heterogeneous catalyst, while in our case we wanted to obtain information on the energetics for the reduction of Au^{3+} to Au^0.

It should be stressed that any quantitative kinetic parameter obtained by means of reduction with H_2, cannot find a direct correlation with the reduction of Au^{3+} by means of C or C_2H_2 under reaction conditions because the two reactions are different.
However, as the reduction of Au^{3+} in carbon matrices follow a first order kinetics [16], that the hydrochlorination reaction is first order in C_2H_2 and that our data support a first order dependency for the reduction of Au^{3+} by H_2 (see section 3.3), we consider the results reported in this and the following sections to retain value. In fact, the actual study of the reduction of Au^{3+} under reaction conditions is complicated by the enhancing effect of HCl [17] as well as possible changes in the catalyst structure under reaction conditions These effects can also sum up to the kind of carbon used as support, which can lead to particles that are larger after reaction thus also affecting the reactivity [11]. And finally, the reduction under reaction conditions would still be affected by gas reactants flow and ratio [17] as well as and obviously temperature. For

all this reasons we wanted to restrict the effect of Au^{3+} reduction, by forcing the catalyst to reduce gold species only, without any other effect, in order to consider the reduction process singularly.

A first method to obtain this information is to determine the temperature at which the reduction of Au^{3+} to Au^0 occurs. Representative thermograms in the range from 50 to 800 ^oC for the catalysts prepared at a drying temperature of 140 ^oC are reported in figure 6. The band between 200 and 300 ^oC is the one associated with the Au^{3+} reduction [18], while those between 450 and 800 ^oC are associated with the reduction of carbon functional groups like carboxylic, ester, ether and lactone groups that are always present in commercial activated carbons for catalysis applications [19, 20]. In principle this TPR method could be used also to evaluate changes in the carbon matrix, however this is beyond the purposes of the current manuscript and we will therefore focus in the analysis of the Au^{3+} features only.

From the thermograms two important aspects are immediately evident: among the various catalysts the area of the Au^{3+} band is different, but also and more importantly their positions. The area of the bands relates with the amount of Au^{3+} present in the samples. In general, this is one of the primary uses of TPR in catalysis, i.e. the determination of the bulk content amount of oxidized species. By using TPR determinations, the optimal Au^{3+} amount would be in the range of ca. 30%, with excess amounts not affecting the reactivity of the catalyst [10] However, for our purposes the most important feature of these thermograms is the change in reduction temperature of gold per different catalysts (table 1). The reduction of the Au^{3+} centres, and so their reduction temperature, are related to the redox potential of the metal [18]. The higher is the temperature, the more energy consuming is the reduction process, and in turn the lower the reduction redox potential has to be. And this will qualitatively be true, regardless if the reduction takes place by C, C_2H_2 or H_2. This is an important aspect because it goes beyond the nature of the specific metal in use, and it clearly shows that the energetic of the reduction process, and in turn the redox potential of the metal, is a function of the local environment in which the metal cation, in this case Au^{3+}, is located and the nature of counter-ion species.

From the data in Table 1, it is possible to observe that the catalysts prepared at a drying temperature of 110 ^oC present the similar reduction temperature of Au^{3+} at ca.

270 °C. However, when the drying temperature is increased, differences in the reduction temperature appear, with interesting results. The first observation is that when pure HCl and pure HNO_3 are used, if the catalyst drying temperature is increased the reduction temperature of Au^{3+} also increases (of ca. 10 °C). Moreover, when HCl is used, the Au^{3+} reduction temperature is invariably higher when compared with HNO_3. Chloride ions are stronger ligands than nitrate [18, 21], and therefore are more capable of stabilising Au in the higher oxidation state. This is reflected in a higher reduction temperature, and in turn a lower reduction redox potential. It is interesting to note that catalysts prepared using HCl were invariably poorer than those prepared by using HNO_3 or aqua regia, and this could not be due solely to a change in particle size, after reaction, but also to a change in reduction potential and so the metal reducibility. Previous studies [11, 15] on the possible sintering of Au nanoparticles on Au/C catalysts for this reaction showed an increase of ca. 5% when HCl was used as a solvent, and negligible when HNO_3 only was used.

A correlation of the activity of chlorinated metal salts with the hydrochlorination reaction of acetylene was first postulated in 1985 [22], and a trend of increased activity versus increase of standard reduction electrode potential was observed [22, 23]. It was on this basis that Au was postulated to be an active metal for this reaction [24, 25]. The data reported here, would suggest that this correlation is applicable not only among different metals, but also within the same metal (in this case Au), when the local reduction potential is changed by the effect of the ligand.

In contrast, when aqua regia is used, if the drying temperature of the catalyst is increased, the Au^{3+} reduction temperature is decreasing, thus suggesting a final synergistic effect of the two acids in the catalyst preparation process. Aqua regia as a solvent shows a lower reduction temperature for Au^{3+} in presence of hydrogen, when compared to HCl and HNO_3, and the catalysts show a higher catalytic activity accordingly.

There is, however, a distinctive feature of aqua regia-prepared materials that differs from the use of the pure acids. The most active catalyst is not the one prepared at 180 °C with a reduction temperature of 252 °C, but the one prepared at 140 °C with a reduction temperature of 268 ^{o}C (Fig. 7). This probably indicates that there is another factor that further contributes to the catalytic activity which has yet to be identified.

3.3 Reduction of Au^{3+} by H_2 and Kissinger equation

In order address this aspect, and to further assess the reducibility of Au^{3+}, additional information can be extracted from TPR analysis, by varying the ramp rate of the heating [26]. In this case, assuming an Arrhenius dependence of the rate constant of the reduction reaction, and knowing the reaction order model, it is possible to determine the activation energy of a reduction reaction using the Kissinger equation [27, 28], (eq.1).

$$\ln (\beta/T^2_{max}) = \ln (AR/E_a) + \ln [n (1 - \alpha_{max})^{n-1}] – E_a /RT_{max} \quad \text{(eq. 1)}$$

Where E_a is the activation energy, A the pre-exponential factor, β the heating rate, n is the order of the reaction, α is the conversion degree, T is the temperature and R is the gas constant; the index max indicates the maximum of the reaction rate, with T_{max} the temperature at which the maximum of the Au^{3+} reduction step occurs. The equation originally made use of differential thermal gravimetry, thermal analysis, or differential scanning calorimetry data and it has found application in the analysis of crystallization processes [29] or glass transition temperatures [30], because it has the advantage to rely on non-isothermal data. Reduction of Au^{3+} in lignite carbon matrixes, showed that the Au^{3+} to Au^0 reduction occur via a first order kinetic [16]. Assuming in our case, the same kinetics, the equation 1 can be rewritten as (eq.2):

$$\ln (\beta/T^2_{max}) = \ln (AR/E_a) – E_a/RT_{max} \quad \text{(eq. 2)}$$

It is then possible to determine the activation energy of the reduction process and the pre-exponential factor, by plotting $\ln(\beta/T^2_{max})$ versus 1/T from the slope and the intercept of the resulting straight line respectively.

TPR profiles were collected using temperature ramps of 5, 10 and 15 ^{o}C for the catalysts prepared in HCl, aqua regia and HNO_3 , dried at 110, 140 and 180 °C. A representative set of thermograms is reported for the series in aqua regia at 140 ^{o}C (Fig. 8). The values obtained for the activation energies of all the catalysts, applying the procedure described above, are shown in table 1. The activation energies, were in a range from 40 kJ mol^{-1} for the catalyst prepared using aqua regia to 70 kJ mol^{-1} for the catalyst obtained using HCl (both dried at 180 ^{o}C). Interestingly, the most active catalyst for the hydrochlorination reaction of acetylene was the material obtained using aqua regia impregnated at 140 ^{o}C with an intermediate activation energy for the Au^{3+} reduction of ca. 50 kJ mol^{-1} (Fig. 9). It should also be noted that the E_a values reported in table 1 do not exactly follow the same trend of the single reduction temperatures reported on the same table described in section 3.2. This discrepancy can be explained considering that the E_a are obtained from a set of three different experiments per catalysts at different gradients, so an average value and that the final E_a value correlates with the frequency factor of the reaction for the specific catalyst. This also intrinsically shows the limitations in the use of H_2 as sole reducing agent far from reaction conditions in presence of C_2H_2 and HCl. On the other hand, it allows us to build a qualitative model that can explain why catalysts prepared using aqua regia are the most active.

Considering the observed effect of the reducibility of Au^{3+} and the activity for the hydrochlorination reaction, i.e. the more reducible a catalyst (high redox reduction potential) the more active it is, the expected trend would have been that: the higher was the E_a for the reduction of Au^{3+} and the lower to be the conversion for the hydrochlorination reaction. However, this trend is not always respected. This can be tentatively explained by assuming the existence of a threshold energy value below which Au^{3+} is too reducible to be active, thus preventing Au to be part of an effective redox cycle Au^{3+}/Au^{0}. In fact, in front of an average reduction energy barrier of 50 kJ mol^{-1} for our catalysts, by comparison, literature values for the reduction (i.e. nucleation and growth) of Au^{3+} over supports like: SiO_2, MgO and TiO_2 span from 12 to 6 kJ mol^{-1} respectively [31, 32]. To date, none of the Au catalysts prepared using supports other than carbon has been found to be active for the hydrochlorination reaction of acetylene [1, 11], and this confirms that carbon can stabilize Au^{3+} species. On the other hand, we are attempting to extract information from a reduction process by means of using H_2 as a probe when the hydrochlorination reaction is likely to occur via formation of a C_2H_2/Au/HCl complex where a simultaneous approach of the two substrates take place over Au^{3+} centres [17] and hence this can induce limitations in our model. However, as we have shown that the overall conversion does not correlate with the total amount of Au^{3+} (section 3.1) it is likely that this correlates instead with the amount of Au^{3+} centres at the Au/C interface, and this is also a factor that we consider operating to explain the deviations that we observed in our model.

4. Conclusions

It has been shown that TPR can be a useful characterisation technique for the investigation of metal cations in a heterogeneous catalyst; in particular, it was possible to determine the amount of Au^{3+} in the bulk material and the effect that counter-ions like chloride or nitrates could have on the redox electrode potential of the metal. In detail, chlorides had a strong stabilization effect which led to a diminished catalytic activity. On the other hand Au^{3+} centres that are too easy to reduce have a detrimental effect on the catalyst performance. Active catalysts result from an intermediate situation. This would support the existence of a redox cycle Au^{3+}/Au^0 [33] where reducibility and stability of the cation would be a compromise between substrate activation and Au centres reoxidation in order to ensure a constant catalytic activity. Though, despite the limitations in the data treatment by thermal reduction using H_2, this can still be an alternative way to evaluate these catalysts in a qualitative manner. In fact, the role of the reducibility of the metal centre is a factor so far neglected in many reactions involving gold.

Acknowledgements The authors thank Johnson Matthey Plc and World Gold Council for financial support.

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Tables, figures and captions

Table 1. Drying temperature, Au^{3+} amount, reduction temperature and activation energies for the Au^{3+} to Au^0 reduction by H_2, for Au/C catalysts prepared using HCl, HNO_3 and aqua regia as impregnating solvent, and drying temperatures of 110, 140 and 180 °C.

Acid or mixture	Drying temperature (°C)	Au^{3+} (%)[a]	Reduction temperature (°C)	E_a (kJ mol^{-1})[b]
HCl	110	67.3	272	43.3 ± 5.3
HCl	140	18.5	281	53.6 ± 5.9
HCl	180	12.4	280	71.8 ± 5.0
HNO_3	110	43.6	278	53.6 ± 5.9
HNO_3	140	16.7	275	54.2 ± 2.6
HNO_3	180	18.9	271	45.0 ± 3.4
aqua regia	110	53.5	270	71.8 ± 5.0
aqua regia	140	22.3	268	50.4 ± 4.1
aqua regia	180	11.4	252	39.6 ± 2.6

([a]) determined from XPS

([b]) The experimental error for the activation energy, E_a, was calculated from the least square regression line of $\ln(\beta/T^2_{max})$ versus 1/T.

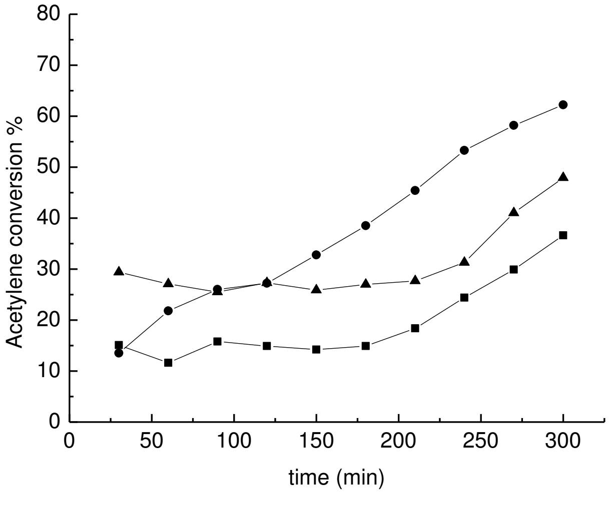

Fig. 1 Acetylene conversion by catalysts impregnated at drying temperature of 110 ^{o}C using: HCl drying the catalysts at different temperatures of: (■) aqua regia, (●) HNO_3 and (▲) HCl as solvents.

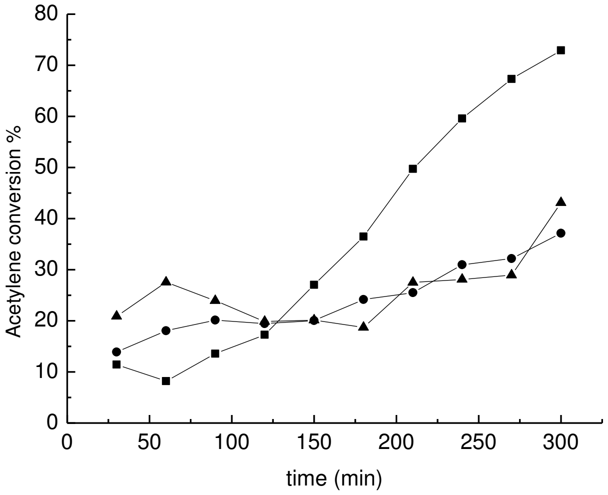

Fig. 2 Acetylene conversion by catalysts impregnated at drying temperature of 140 ^{o}C using: HCl drying the catalysts at different temperatures of: (■) aqua regia, (●) HNO_3 and (▲) HCl as solvents.

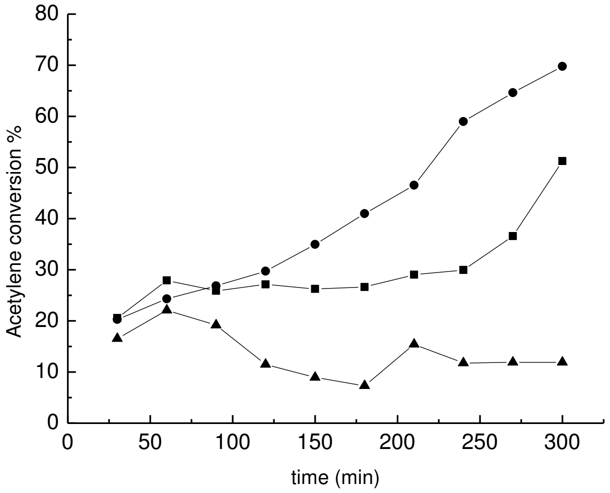

Fig. 3 Acetylene conversion by catalysts impregnated at drying temperature of 180 ^{o}C using: HCl drying the catalysts at different temperatures of: (■) aqua regia, (●) HNO_3 and (▲) HCl as solvents.

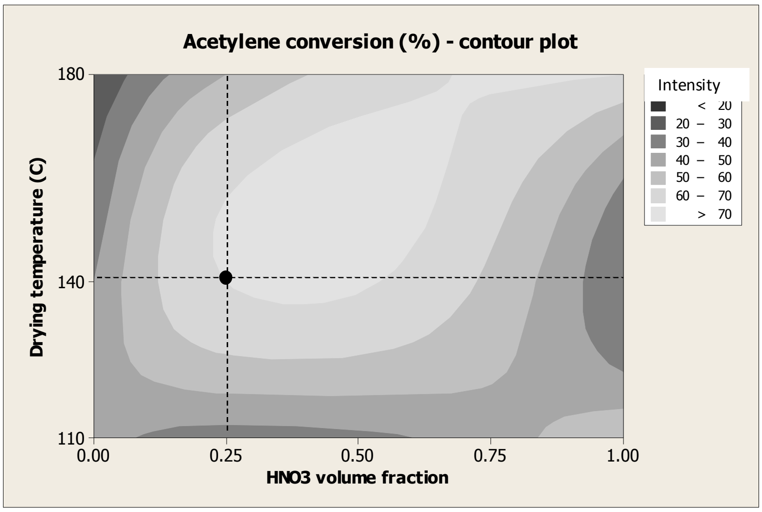

Fig. 4 Contour plot of the acetylene conversion (%), versus drying temperature (^{o}C) and HNO_3 volume fraction (where HNO_3 volume fraction of 0 equals to a HCl volume fraction of 1; HNO_3 volume fraction of 0.25 represents aqua regia composition, and a volume fraction of 1 equals to pure HNO_3 and no HCl). The black filled circle represents the most active catalyst and the dotted lines its coordinates. This same graphical notations for HNO_3 and the most active catalyst, is used also for figures 5, 7 and 9.

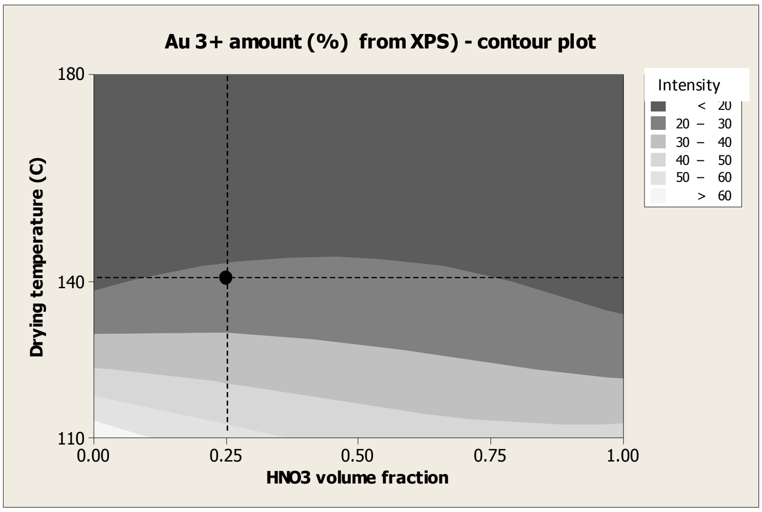

Fig. 5 Contour plot of the amount of Au^{3+} (as atomic fraction %) obtained from XPS, versus drying temperature (^{o}C) and HNO_3 volume fraction.

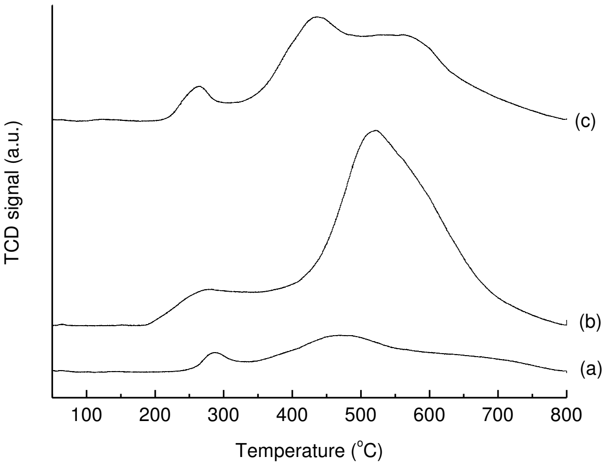

Fig. 6 Representative TPR thermograms for Au/C catalysts prepared at a drying temperature of 140 ^{o}C using: (a) HCl, (b) HNO_3 and (c) aqua regia.

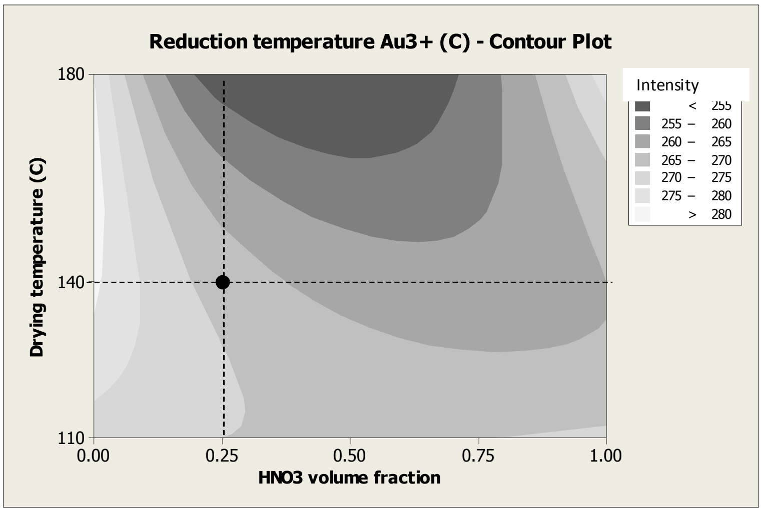

Fig. 7 Contour plot of the reduction temperature of Au^{3+} in presence of H_2, versus drying temperature (^oC) and HNO_3 volume fraction.

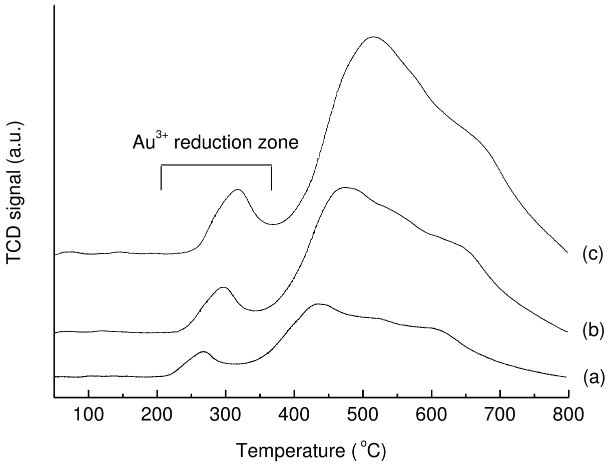

Fig. 8 Representative TPR thermograms for Au/C catalysts prepared at a drying temperature of 140 ^oC using aqua regia collected at different temperature gradient ramps: (a) 5 ^oC min^{-1}, (b) 10 ^oC min^{-1} and (c) 15 ^oC min^{-1}.

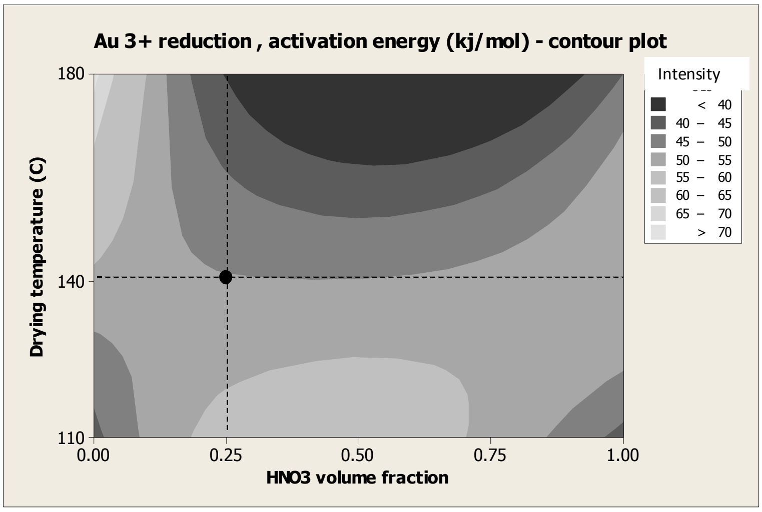

Fig. 9 Contour plot of the activation energy for the reduction of Au^{3+} to Au^0 in presence of H_2, versus drying temperature (^oC) and HNO_3 volume fraction.