Preparation of supported gold nanoparticles by a modified incipient wetness impregnation method

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Abstract

In this work, we show that if the mere procedure of impregnation of oxide supports with chloroauric acid, which is well-known to lead to large gold particles, is followed by a step of washing with ammonia, small gold particles (3-4 nm) can be obtained after a treatment of calcination at 300°C on any type of oxide supports (alumina, titania, silica). Moreover, gold leaching is very limited during the washing step, and a large range of gold loadings (0.7 to 3.5 wt %) can be achieved. Elemental analysis, Raman spectroscopy and temperature programmed desorption under argon show that this ammonia post-treatment results in the removal of chloride ligands from the coordination sphere of Au(III) precursor and their replacement by ammine, leading to an ammino-hydroxo or an ammino-hydroxo-aquo gold complex and not to gold hydroxide. The Au/TiO_2 catalysts prepared with this modified procedure of impregnation are almost as active as those prepared by deposition-precipitation with urea in the CO oxidation reaction performed at room temperature.

1. Introduction

Among the various methods used to prepare supported gold catalysts, impregnation with the most common gold precursor, $HAuCl_4$, is considered as an inappropriate path to achieve highly active catalysts. Indeed, this method results in the formation of large and therefore catalytically inactive gold particles after thermal treatment. Such large particles arise from to the high amount of chlorine residues present in the solids after impregnation, which induce sintering of gold during the activation procedure.[1-3] Since this was the first method used to prepare gold based catalysts, this metal has long been considered as fairly inactive. Since the late eighties, several other preparation methods have been developed. Among them, the deposition-precipitation (DP) procedure allowed to produce small gold particles, and highly active gold catalysts in various reactions, and in particular in the extensively studied CO oxidation reaction.

This paper deals with the use of a modified impregnation procedure to obtain highly dispersed gold catalysts. In this procedure, the incipient wetness impregnation of oxide supports (TiO_2, Al_2O_3, SiO_2) was followed by a post-treatment of the resulting solid with an aqueous ammonia solution. Washing with ammonia has already been used to remove most of the chlorines present in Au/Al_2O_3 samples prepared by anion adsorption and to favour the formation of small gold particles during thermal activation.[4-6] Another group has also recently used a treatment under gaseous ammonia at room temperature followed by washing with water to remove the chlorines after impregnation and get small gold particles on titania.[7] In the present paper, catalysts with various gold loadings were prepared by the modified impregnation procedure mentioned just above, and the nature of the supported gold phase was characterized. Their activity in the CO oxidation reaction was compared with those of reference samples prepared by deposition-precipitation with urea (DP Urea).[8,9] DRIFTS

analyses under reaction mixture were also conducted in order to interpret the differences in activity.

2. Experimental

2.1 Sample preparation

The catalysts were prepared with supports TiO_2 P25 (titanoxid Degussa, 50 m^2/g, 70% Anatase, 30% Rutile), γ-Al_2O_3 (aluminoxid, Degussa, 110 m^2/g) and SiO_2 (Aerosil 300, Degussa, 250 m^2/g). Two preparation procedures were used, and in both cases the desired gold loadings were 0.7, 1 and 4 wt %.

Au/TiO_2, Au/γ-Al_2O_3 and Au/SiO_2 reference catalysts were prepared by the method of deposition-precipitation with urea (DP Urea) described in detail elsewhere.[8,9] Typically, a solution of $HAuCl_4$ (concentration depending on the desired gold loading) was prepared by dissolving the appropriate amount of $HAuCl_4,3H_2O$ in 100 mL of deionized water. Urea was added to the gold solution to achieve a concentration 100 times higher than the $HAuCl_4$ concentration. The support (1g) was then added and the suspension was stirred and heated to 80°C during 16 h in a reactor closed and kept away from light. Then, the solid was separated by centrifugation, washed three times with deionized water (with centrifugation between each washing) and dried under vacuum at room temperature for 2 h.

The modified impregnation procedure (ImpN) consisted of preparing samples with various gold loadings by incipient wetness impregnation of the supports, titania, alumina and silica (1-3g), with aqueous solution of $HAuCl_4$ of appropriate concentrations (typically 0.8mL/g support). The solution pH's were lower than 1. The samples were aged at room temperature (RT) for 1 h and then were washed twice with an aqueous ammonia solution (30

mL, 1M, pH=11.5) and twice with deionized water (30 mL), the solids were centrifuged between each washing. For SiO_2, the washings were performed at lower pH (pH=8) with a solution of NH_4Cl (0.25M) to avoid the dissolution of silica at high pH. The samples were dried under vacuum at room temperature for 2h.

2.2 Techniques

Chemical analyses were performed by inductively coupled plasma atom emission spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France).

Before characterization, all the samples, whatever the preparation procedure, were calcined in air at 300°C for 4 h (100 mL/min, 2°C/min from RT to 300°C then 4h at 300 °C). XRD analysis was carried out with a Siemens D500 diffractometer with Cu Kα radiation. TEM analysis was performed using a JEOL 100 CX II microscope. The histograms of the metal particle sizes were established from the measurement of 300 to 1000 particles. The size limit for the detection of gold particles on these supports is about 1 nm.

Temperature programmed desorption of the dried samples were performed under argon (TPD) (100 mL/min, 5°C/min from RT to 300 °C). The compounds produced during the TPD were monitored by mass spectrometry (Hiden Quadrupole HPR20). The main molecules detected in the gas phase during this treatment were H_2O (m/e=18 and 17), NH_3 (m/e=17 and 15), N_2 (m/e=28) and N_2O (m/e=44). Traces of NO (m/e=30) and NO_2 (m/e=46) were also detected.

The Raman spectra were recorded on a commercial RAMAN RXN1 analyser from Kaiser Optical Systems, Inc., (KOSI). It incorporates a laser working at 785 nm, a CCD detector providing full spectral collection of Raman data from 200 to 3500 cm^{-1} with a resolution of at least 4 cm^{-1} and holographic notch filters.

The infrared study was conducted with an IFS 66V (Bruker) using a DRIFTS cell. The sample compartment was filled with the dried solids. The samples (20 mg) were treated *in situ* in the DRIFTS cell under $20\%O_2$ in He (25 mL/min) from RT to 300 °C (2°C/min) then 300 °C for 4h in order to reproduce the *ex situ* calcination conditions. The cell was purged with He at room temperature before introduction of 1%CO/He (50 mL/min) or $1\%CO/2\%O_2$/He (50 mL/min). The spectrum recorded under He was used as reference and the intensity of the spectrum under CO and CO/O_2 atmosphere was expressed as $Log(I_{CO}/I_{ref})$. The spectra are presented after substraction of the CO gas-phase.

CO oxidation reaction was performed at room temperature and atmospheric pressure with a feed of 1% CO and 2% O_2 (balanced with He), with a total flow rate of 230 mL/min, in a flow-type packed-bed reactor. Before reaction, the dried gold catalysts (25 or 50 mg) were pretreated with a mixture of 20% O_2 in He (25 mL/min) from RT to 300 °C (2°C/min) then 300 °C for 4h in order to reproduce the *ex situ* calcination conditions. The CO consumption and CO_2 production were monitored with a Maihak Gas Analyser S710. The activity was expressed as the number of mole of CO converted by second and gram of gold ($mol._{CO}.s^{-1}.mol_{Au}^{-1}$). The turnover frequency (TOF) was calculated with the assumption that the gold particles are cubo-octahedral, and that all the surface gold atoms are equally active, which is obviously not correct since only low coordinated gold sites can adsorb CO. The dispersion was expressed as the N_s/N_t ratio, where N_s represents the number of surface atoms and N_t the total number of atoms in the particle. An average dispersion D was calculated using the particle size distribution estimated by TEM and the weighed dispersions calculated for each particle size range of the histogram.

3. Results and discussion

3.1 Characterization of the gold catalysts

Table 1 reports the gold loading in the DP Urea and ImpN samples, as well as the average gold particle size measured by TEM after calcination at 300 °C. As expected from our former studies,[8,9] most of the gold in solution is deposited on the supports with the method of deposition-precipitation with urea, and the average gold particle sizes are small except for silica, which presents a low gold loading and a very large particle size.

More unexpected is that in the case of the ImpN samples, the gold loading is also close to the nominal gold amount. This result indicates that the loss of gold during the ammonia post-treatment of the impregnated samples is limited, whatever the support and the gold loading. The chlorine content is also very low for all the samples (< 200 ppm, which is the detection limit of ICP-EOS), which suggests that the ammonia treatment is very efficient in the removal of the chlorine residues after impregnation. Probably as a consequence of that, as indicated in section Introduction, the average gold particle sizes are small and close to those obtained from DP Urea samples. Moreover, the particle size obtained on silica after the post-impregnation treatment with ammonium chloride are much smaller than that achieved by DP Urea and close to those observed for the other supports. This is quite interesting because it is still challenging to prepare small gold particles on SiO_2 using a simple method.

Figures 1 and 2A reveal that the particle size distribution of ImpN Au/TiO$_2$ (4 wt %) (Figure 1B) is slightly broader and shifted towards larger size (Figure 2A) than for the DP Urea sample (Figures 1A). The TEM micrographs also show that the repartition of the gold particles onto the support is less homogeneous for the ImpN than for the DP Urea sample. Indeed, for the ImpN sample although most of the gold particles are well separated from each

other, some metallic particles are gathered on the same particle of support while other areas seem to be free of gold particles (Figure 1B). For lower gold loading (0.7 wt %) (Figure 3), the gold particles of the two types of samples are more similar in average size and size distribution. The same trends are observed for the other supports. The non uniform repartition of the gold particles on support for the high loaded sample probably arises from the step of incipient wetness impregnation itself since there is no specific interaction between most of the gold precursor and the support in contrast with DP Urea.[8,9]

Figure 4 presents the TEM pictures of gold particles supported on TiO_2, Al_2O_3 and SiO_2 prepared by the ImpN method with a gold loading of 1 wt%. It shows that the repartition of the gold nanoparticles on the surface of the different supports is homogeneous. The particle size distributions and average particle sizes are similar for the TiO_2 and Al_2O_3 supports, but for silica, the size distribution is broader, and the average particle size slightly larger.

Figure 5 shows two sets of Raman spectra for the 4 wt % Au/TiO_2 and Au/Al_2O_3 impregnated samples, one after impregnation and drying at RT (spectra a) and the other after the ammonia treatment and drying at RT (spectra b). The Raman spectra of the unwashed samples (spectra a) exhibit two intense bands at 323 and 346 cm^{-1}, which both are characteristic of Au-Cl vibrations. Indeed, in the literature,[10] these peaks are respectively attributed to the out-of phase stretching mode (v_5) (323 cm^{-1}) and the symmetric stretching vibrations (v_1) (346 cm^{-1}) of the Au-Cl bonds in the $[AuCl_4]^-$ complex in solution. Thus, one can deduce that gold chloride species is present onto the support after impregnation and that drying at room temperature probably does not change the gold speciation. After the ammonia treatment, the Au-Cl stretching bands have totally disappeared in both spectra (spectra b). A very weak and broad band centered at 560 cm^{-1} can be observed for the Au/Al_2O_3 catalyst. In the other sample, it may be also present, but hidden by the vibration bands of titania. Such a

peak can be assigned to Au-O or Au-N vibrations, due to the replacement of chlorine by oxygen or nitrogen atoms in the coordination sphere of Au^{3+} during the washing step.[10]

Some authors claimed that the Au chloride present on the support is converted into a gold hydroxide $Au(OH)_3$ during the ammonia post-treatment in liquid,[4-6] or in gas phase.[7] In order to investigate this assumption, the 4 wt% Au/TiO_2 sample prepared by impregnation was washed with water on the one hand, and with NaOH (10^{-3} M, pH=11) at the same pH as for ammonia washing on the other hand, and in both cases according to the same procedure as for the ammonia treatment. The results are reported in Table 2. Only the ammonia post-treatment leads to the preservation of a high gold loading. In contrast, most of the gold is removed upon washing with NaOH and small amount of gold still remains on the support after washing with water, in agreement with former results.[8] Thus, the nature of the basic solution used during the post-impregnation treatment has a stronger influence on the gold loading in the final catalyst than the pH. Elemental analysis reveals that the sample washed with ammonia contains nitrogen with an N/Au atomic ratio around 2 (Table 2).

In an attempt to identify the nature of the gold species present in the ImpN samples, we monitored by mass spectrometry the species produced during TPD under argon with the 4 wt% Au/TiO_2 ImpN sample (Figure 6A). A blank experiment was also performed with the TiO_2 support impregnated by an HCl solution of the same chlorine concentration as that of the $HAuCl_4$ impregnation solution, and then washed with the ammonia solution (Figure 6B). For Au/TiO_2 and TiO_2, a broad peak of water (m/e = 18) is observed between 80 and 300 °C. Around 270 °C, the release of NH_3 (m/e = 17 and 15) is also observed in both samples, and could arise from the desorption of NH_3 from the support. For the Au/TiO_2 sample, additional peaks are observed around 140 °C with sharp peaks of production of H_2O, N_2 and N_2O. No NH_3 is released, as confirmed by the monitoring of m/e=15 (not shown). Since the experiments were carried out under inert atmosphere, the production of N_2 and N_2O can only

arise from the decomposition of the gold (III) species formed during the ammonia post-treatment. This may indicate that this species contained NH_3 ligands and that the auto-reduction of Au^{III} into Au^0 by the ammine ligands occurred around 140 °C, leading to the formation of N_2 and N_2O. The gold (III) species present on the titania surface after the ammonia washings could then contain ammine ligands, but is certainly not $Au(OH)_3$. According to papers reporting ammonia washing,[4-6] gold chloride is claimed to be transformed into gold hydroxide, but no characterization was performed to prove it, the only element of information provided being that chlorine was eliminated. It is known that in a solution of $HAuCl_4$ at high pH (around 11), there is hydrolysis of the Au-Cl bonds and replacement by Au-OH bonds to give $[Au(OH)_3Cl]^-$ and/or $[Au(OH)_4]^-$ complexes, but not $Au(OH)_3$.[10-12] The washing of the 4 wt% Au/TiO_2 sample with a NaOH solution at pH 11 results in the removal of a large part of the gold (Table 2). This is consistent with the fact that the $[Au(OH)_4]^-$ or $[Au(OH)_3Cl]^-$ complex cannot interact with the titania surface also negatively charged (pH> PZC(TiO_2) = 4-6). One can deduce that the gold species formed during washing with ammonia and sodium hydroxide are different since they remain on the support. We therefore propose that the gold species formed during the ammonia post-treatment could be an ammino-hydroxo or an ammino-hydroxo-aquo gold cation complex $[Au(NH_3)_2(H_2O)_{2-x}(OH)_x]^{(3-x)+}$. Reaction between chlorinated gold complexes and ammonia is described in the literature and several ammine gold complexes have been studied.[13-15] The cationic nature of this complex consistent with the fact that almost no gold is leached out during the washing step with ammonia. Indeed, at the pH of the washing (pH 11), the support surfaces of TiO_2 (PZC =4-6), Al_2O_3 (PZC =7-9), SiO_2 (PZC =1-2) are all negatively charged, so electrostatic interaction between the cation gold complex and the support surface is possible. If such interpretation is correct, one should expect that the samples reach an upper limit in gold loading due the limited capacity of cation adsorption of the supports. This may

be the reason for which a higher proportion of gold is leached out at high loading (4 wt %) than at low loading (Table 1). It must be added that it is also possible that the cationic gold complex formed during the ammonia post-treatment is grafted onto the support, and that some oxygen atoms of the gold complex belong to the oxide surface. However, it is not easy to go much further in the characterization of the gold complex. The XAFS technique, which *a priori* is the best method of characterization of the coordination sphere of metal complexes is helpless in the present case since it cannot allow to distinguish N from O atoms, and the peak of second neighbour, which would allow to determine whether the complex is grafted or in electrostatic interaction, is too weak to provide reliable information.

3.2 CO oxidation activity and DRIFTS analysis

The catalytic properties of gold catalysts supported on TiO_2, Al_2O_3 and SiO_2 prepared by ImpN and DP Urea were compared in the reaction of CO oxidation at 25 °C, after *in situ* calcination at 300 °C for 4 hours under 20% O_2 in He. First of all, the catalysts supported on Al_2O_3 and SiO_2 are inactive at room temperature, whatever the preparation methods. These results are consistent with previous studies, which showed that the catalytic activity in CO oxidation strongly depends on the nature of the support, and that reducible supports such as TiO_2 or Fe_2O_3, usually lead to catalysts much more active than unreducible ones such as SiO_2 or Al_2O_3, and even if the gold particle sizes are identical.[16-18]

In the following, we will only consider the results obtained for the Au/TiO_2 samples. Comparisons of the CO oxidation activities and Turnover Frequency (TOF) of the two types of catalysts at the pseudo-steady state (after 90 min) for equivalent gold content are reported in Table 3. All the catalysts on TiO_2 are active, but a general trend is that the catalysts prepared by DP Urea are more active than those prepared by ImpN, whatever the gold content. The TOF, calculated from the average gold dispersion of each sample, which takes

into account the number of surface atoms exposed, are similar for a given procedure of preparation, DP Urea or ImpN, whatever the gold loading. The performances of the ImpN catalysts approach those of DP Urea catalysts, with a TOF ratio close to 2. It is known that not only the activity, but also the TOF of the gold catalysts in CO oxidation strongly increase when the gold particles reach size smaller than 2-3 nm.[19-21, 22-24] Here, the lower activity of the ImpN catalysts can be related to the fact that their average particle size is slightly larger and their particle size is broader than those of the DP Urea samples (Table 1 and Figure 2).

Figure 7 shows the DRIFTS spectra in the carbonyl region of the 4 wt % Au/TiO_2 catalysts prepared by ImpN and DP Urea, *in situ* calcined and exposed to a flow of 1%CO in He at RT. After exposure of the DP Urea sample to CO for one minute, two CO bands can be observed at 2107 (intense) and 2164 cm^{-1} as well as a double band at 2340 and 2360 cm^{-1} characteristic of CO_2 in the gas phase. The band at 2107 cm^{-1} is assigned to CO adsorbed on the low coordination sites of metallic gold particles.[25-28] This band is broad and may contain several contributions. The peak at 2164 cm^{-1} can be attributed to CO adsorbed on cations, either Au^+ gold species,[27,29-32] or cations of the support.[33] For the ImpN sample after one minute of exposure, these two bands are shifted to 2119 and 2169 cm^{-1} respectively, and two other bands at 2183 and 2349 cm^{-1} are also visible. They can be assigned respectively to the adsorption of CO and CO_2 on support Ti^{4+} cations.[25,34] It is worth noting that the band at 2164 (DP Urea) or 2169 cm^{-1} (ImpN) is the only one still present after flushing the cell by He for 10 min (not shown), which indicates a strong interaction of CO with the associated adsorption sites. The high stability of this CO band allows us to assign it to CO adsorbed on Au^+ and not on the support, since CO adsorbed on support cations is known to be easily eliminated during evacuation at room temperature.[33,35] Regarding the metallic gold sites, which are considered as the active sites or at least as one of the active sites in the CO oxidation reaction, the difference of CO frequency between both samples (2107 for DP Urea and 2119 cm^{-1} for

ImpN) may result from a difference of CO coverage on the metal particle surface. Indeed, a shift towards higher wavenumber is usually observed when the CO coverage on gold particle decreases.[25,36,37] Since the number of low coordination sites decreases when the gold particle size increases, and CO adsorbs on low coordination sites, this result can be interpreted by a lower density of adsorbed CO molecules on the gold particles of the ImpN sample. This is consistent with the fact that this sample contains a lower proportion of small particles (Figures 1 and 2A), and that it is less active than the 4 wt % DP Urea sample.

Figure 7 also shows the evolution of these spectra after exposure to 1%CO/He at RT for longer time, 10 and 60 min. An additional band can be observed at 2075 cm^{-1} in the spectrum of the ImpN sample after 10 min of exposure. This contribution is not clearly visible in that of the DP Urea sample after 10 min, but may be present as a shoulder; after 60 min of exposure, the band is clearly visible. Moreover, the band at 2164 cm^{-1} has almost disappeared after 10 min under CO for the DP Urea sample, while the bands at 2169 and 2183 cm^{-1} are still present for the ImpN sample.

The presence of CO bands at lower frequency than that of CO adsorbed on Au^0 around 2100 cm^{-1} has been reported in several papers. [25,28,38-40] Bands of bridge-bonded CO on gold are located at still lower frequency, 1950-2000 cm^{-1}, [25,28,38] therefore this assignement can be discarded. Bands in the same range as ours (2050-2080 cm^{-1}) have been observed on Au/TiO$_2$ and assigned by Boccuzzi et al., first to CO adsorbed on metallic gold sites at the perimeter of the particle in contact with the support [39,40] and then to CO adsorbed on Au$^{\delta-}$ sites of small gold clusters, the negative arising from electron transfer from the partially reduced support towards metallic gold particles. [28]

Figure 8 shows the DRIFTS spectra of the same samples after 60 min of exposure at RT to a flow of 1%CO/2%O$_2$/He to reproduce the conditions of CO oxidation reaction. The two spectra are almost similar except a small band at 2168 cm^{-1} that is only visible in the

spectrum of the ImpN sample. The band of CO adsorbed on metallic gold have almost the same position (2115 cm^{-1}). CO_2 in the gas phase, produced by the reaction of CO oxidation, is clearly visible with the bands at 2361 and 2340 cm^{-1}, indicating that both catalysts are active. Interestingly, the band at 2075 cm^{-1} has disappeared, which would suggest that the corresponding gold adsorption site is highly unstable under oxidizing atmosphere. Boccuzzi et al. also observed that CO band (2055 cm^{-1}) present on Au/TiO_2 samples reduced under H_2,[28] disappeared upon O_2 adsorption due to annealing of the negative charge on gold. We can tentatively propose that the band at 2075 cm^{-1}, which appears with time under CO atmosphere (Figure 7), could be related to the progressive formation of oxygen vacancies on the TiO_2 surface under CO, resulting in an electron transfer from these oxygen vacancies towards the metallic gold particles located in their vicinity. To confirm this hypothesis, additional experiments of EPR spectroscopy for instance are needed to investigate the formation of Ti^{3+} sites after CO adsorption, but this is beyond the scope of the present paper.

5. Conclusion

In this work, we have been successful in the preparation of small gold particles on various supports (alumina, titania, silica) by incipient wetness impregnation followed by an ammonia post-treatment. This procedure is easy to handle and the ammonia washing removes the chloride ligands responsible for the formation of large gold particles after classical impregnation followed by thermal treatment, but keeps a large part of gold on the support. We got evidence that the new gold compound formed upon washing is not an hydroxide as proposed in the literature, but an ammino-hydroxo-aquo cationic gold complex

$[Au(NH_3)_2(H_2O)_{2-x}(OH)_x]^{(3-x)+}$, which can interact with the support surface either electrostatically, or through grafting, and then prevent the gold leaching. The resulting gold particles are slightly larger and moderately less active in CO oxidation than those prepared by deposition-precipitation with urea. This difference in activity is related to the lower CO coverage observed for the ImpN sample by DRIFTS analysis under CO/He mixture.

Acknowledgement

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Table 1: Characteristics of the DP Urea and ImpN samples

Support	Preparation	Gold loading (wt %) (theoretical)	Average Particle size (nm)	Standard deviation (nm)
TiO_2	DP Urea	3.2 (4)	3.2	0.70
TiO_2	ImpN	3.3 (4)	3.6	0.83
TiO_2	DP Urea	1 (1)	2.9	0.35
TiO_2	ImpN	0.97 (1)	3.2	0.6
TiO_2	DP Urea	0.62 (0.7)	3.1	0.42
TiO_2	ImpN	0.7 (0.7)	3.3	0.61
Al_2O_3	DP Urea	3.3 (4)	2.3	0.54
Al_2O_3	ImpN	3.4 (4)	3.8	0.82
Al_2O_3	ImpN	0.97 (1)	3.1	0.63
SiO_2	DP Urea	1.1 (4)	23[*]	-
SiO_2	ImpN	0.94 (1)	4.0	1.67

The chlorine content is below 200 ppm (detection limit) for all the samples.

[*] estimated by XRD.

Table 2: Characteristics of the 4 wt% Au/TiO_2 sample prepared by impregnation, unwashed washed with water, NaOH (10^{-3} M, pH=11), and ammonia (1 M, pH=11.5)

Post-impregnation treatment	Gold loading (wt %)	Chlorine content (wt %)	Nitrogen content (wt%)	Average particle size (nm)	Standard deviation (nm)
none	4	-	-	> 10	
H_2O	1.3	0.3	-	6	1.82
NH_3, H_2O (1 M)	3.4	< 200 ppm	0.4	3.4	0.71
NaOH (10^{-3} M)	0.1	< 200 ppm	-	-	-

Table 3: Comparison of the CO conversion rates and TOF at room temperature (25°C) of DP Urea and ImpN Au/TiO$_2$ catalysts after 90 min of reaction at the pseudo-steady state

Catalyst	CO conversion rate ($mol_{CO}.s^{-1}.mol_{Au}^{-1}$)	Average Dispersion	TOF (s^{-1})	Samples DPU / ImpN TOF Ratio
4 wt% DP Urea	0.29	0.39	0.74	2.2
4 wt% ImpN	0.12	0.35	0.34	
1 wt% DP Urea	0.35	0.45	0.77	2.7
1 wt% ImpN	0.11	0.39	0.28	
0.7 wt% DP Urea	0.35	0.47	0.74	2
0.7 wt% ImpN	0.15	0.40	0.37	

Figure Captions

Figure 1. TEM image and particle size distribution of the 4 wt% Au/TiO_2 catalysts prepared by DP Urea (A) and ImpN (B) after calcination at 300°C.

Figure 2. Shapes of the particle size distributions for A) the 4 wt% Au/TiO_2 and B) the 0.7 wt% Au/TiO_2 prepared by DP Urea (solid line) and ImpN(dashed line).

Figure 3. TEM image and particle size distribution of the 0.7 wt% Au/TiO_2 catalysts prepared by DP Urea (A) and ImpN (B) after calcination at 300°C.

Figure 4. TEM images and particle size distribution of samples prepared by ImpN (1 wt% Au) on TiO_2 (A), Al_2O_3 (B) and SiO_2 (C).

Figure 5. Raman spectra of the 4 wt% Au/TiO_2 (A) and Au/Al_2O_3 (B) samples prepared by ImpN before (a) and after (b) the ammonia post-treatment.

Figure 6. TPD under Argon followed by mass spectrometry of a) 4 wt%Au/TiO_2 and b) TiO_2 after post-impregnation treatment with ammonia. The monitored species are H_2O (m/e=18 and 17), NH_3 (m/e=17), N_2 (m/e)=28 and N_2O (m/e)=44.

Figure 7. DRIFTS spectra of the 4 wt% Au/TiO_2 catalysts prepared by DP Urea and ImpN after exposure to 1%CO/He for 1, 10 or 60 minutes.

Figure 8. DRIFTS spectra of the 4 wt% Au/TiO_2 catalysts prepared by DP Urea (grey line) and ImpN (black line) after exposure to 1%CO / 2%O_2 / He for 60 min.
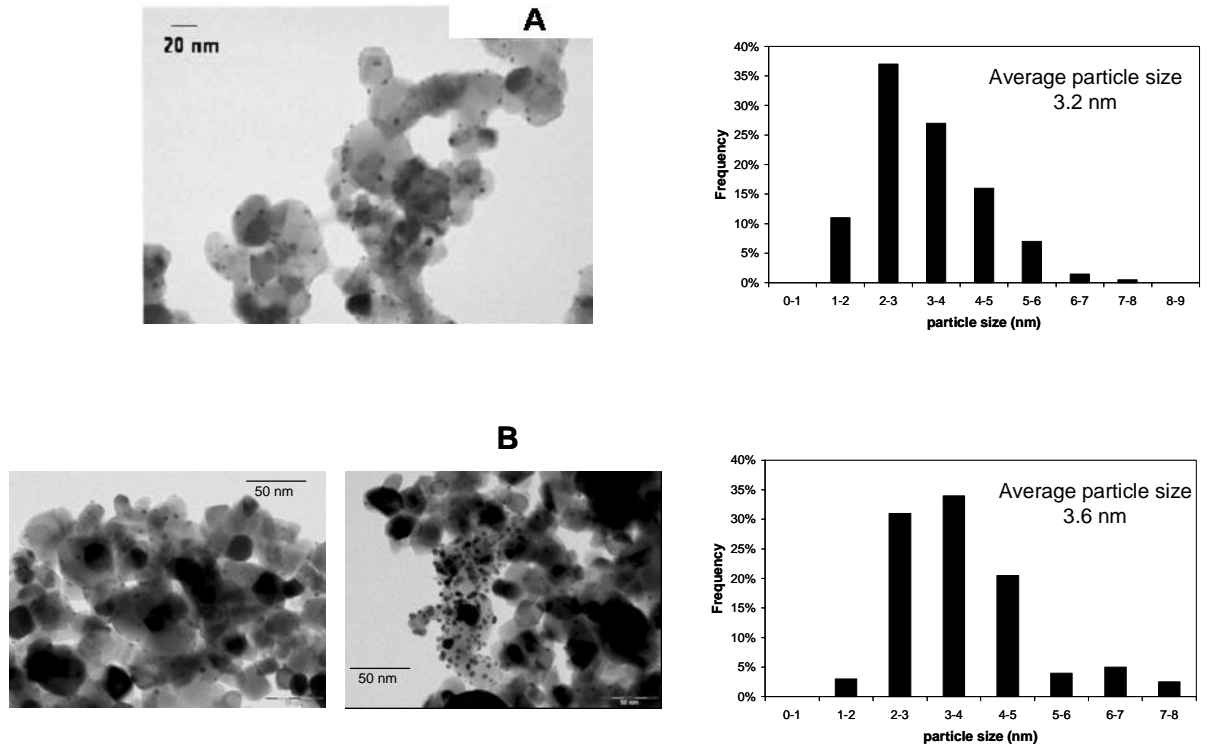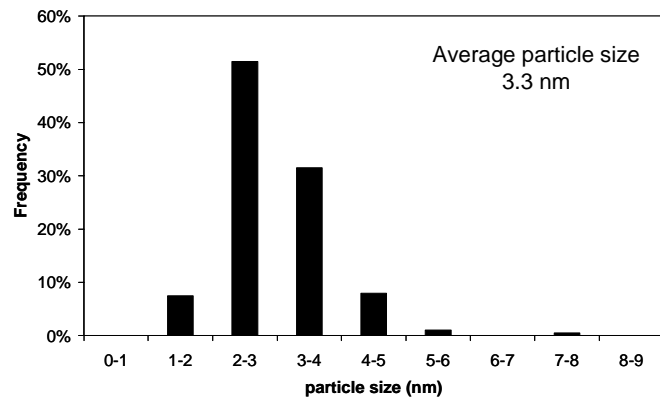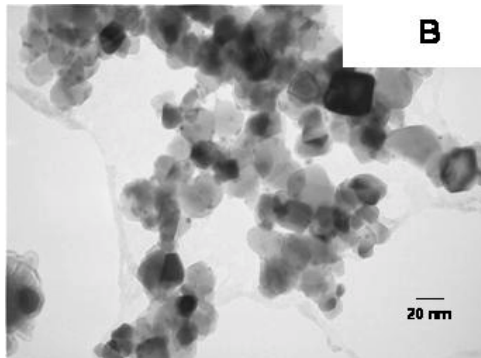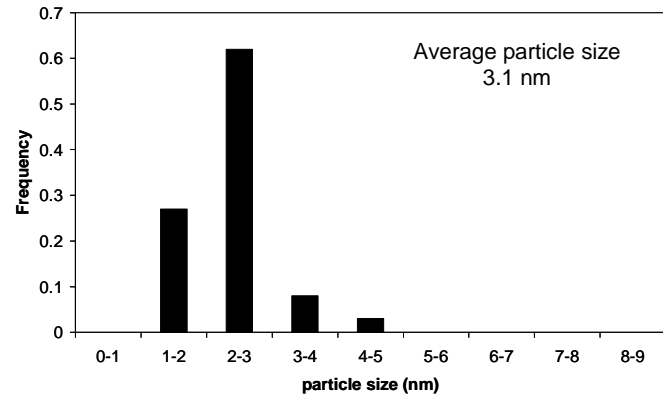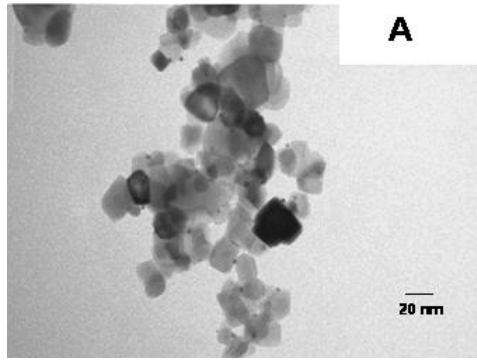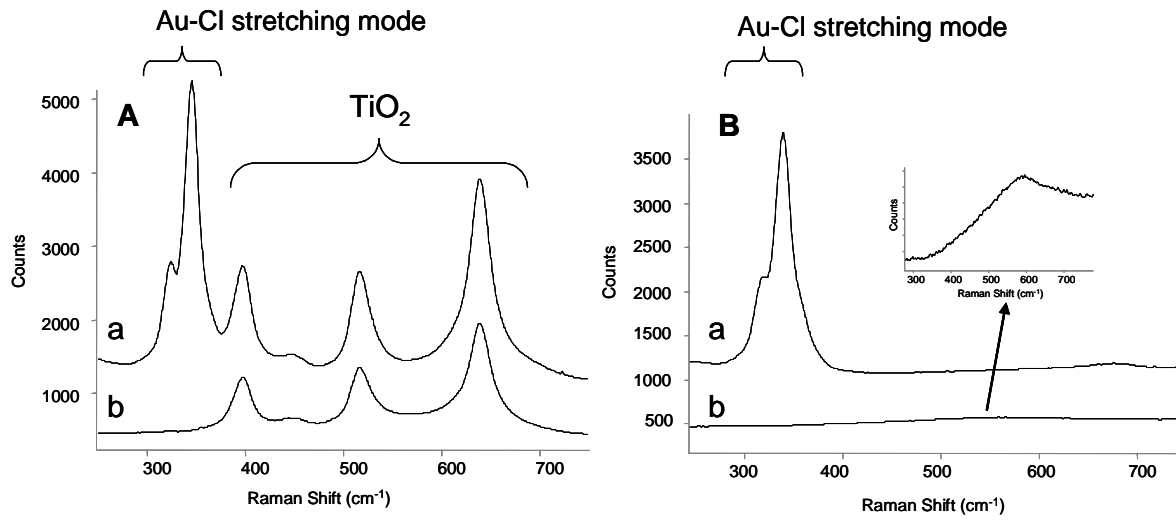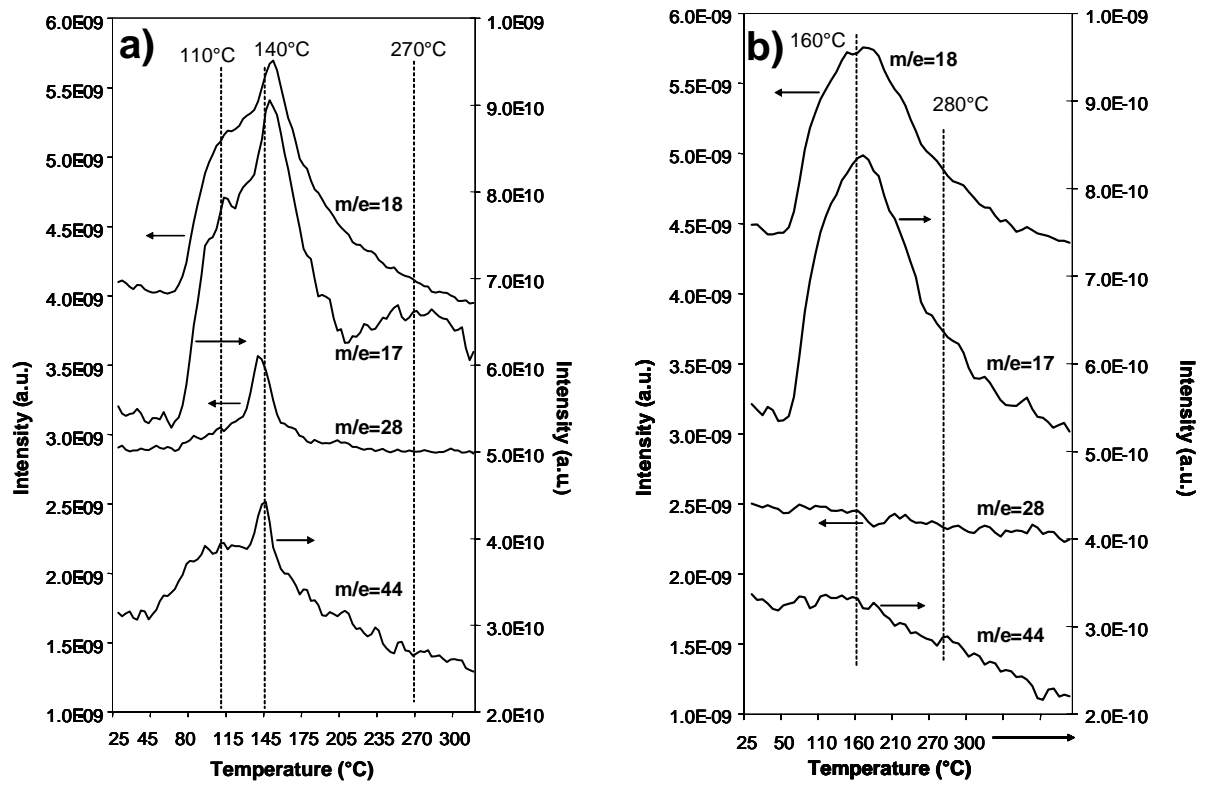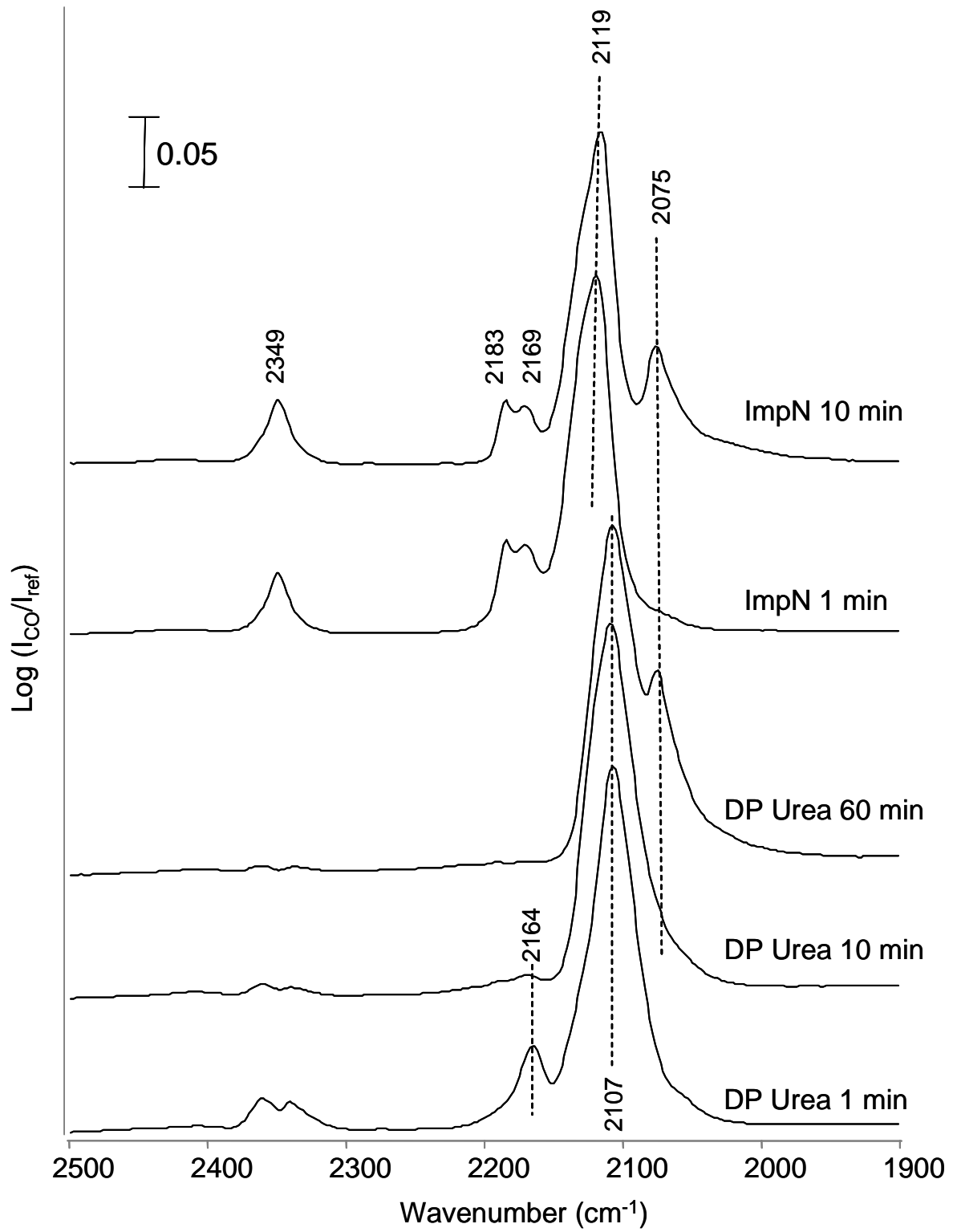
Fig. 1
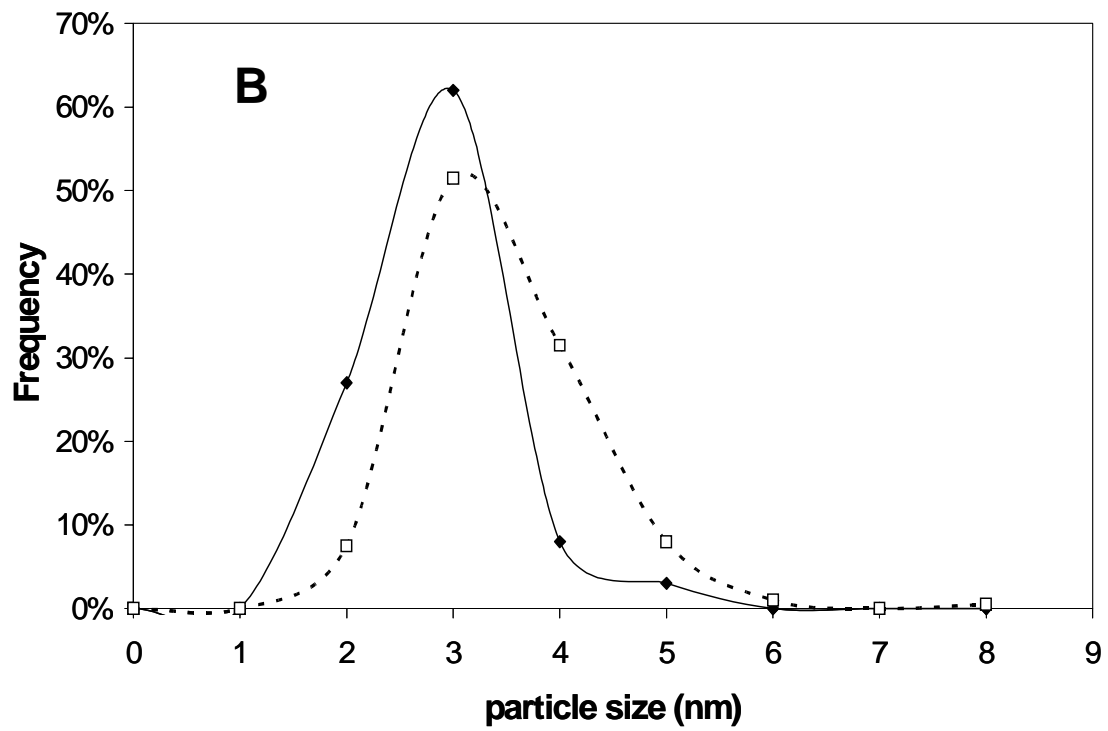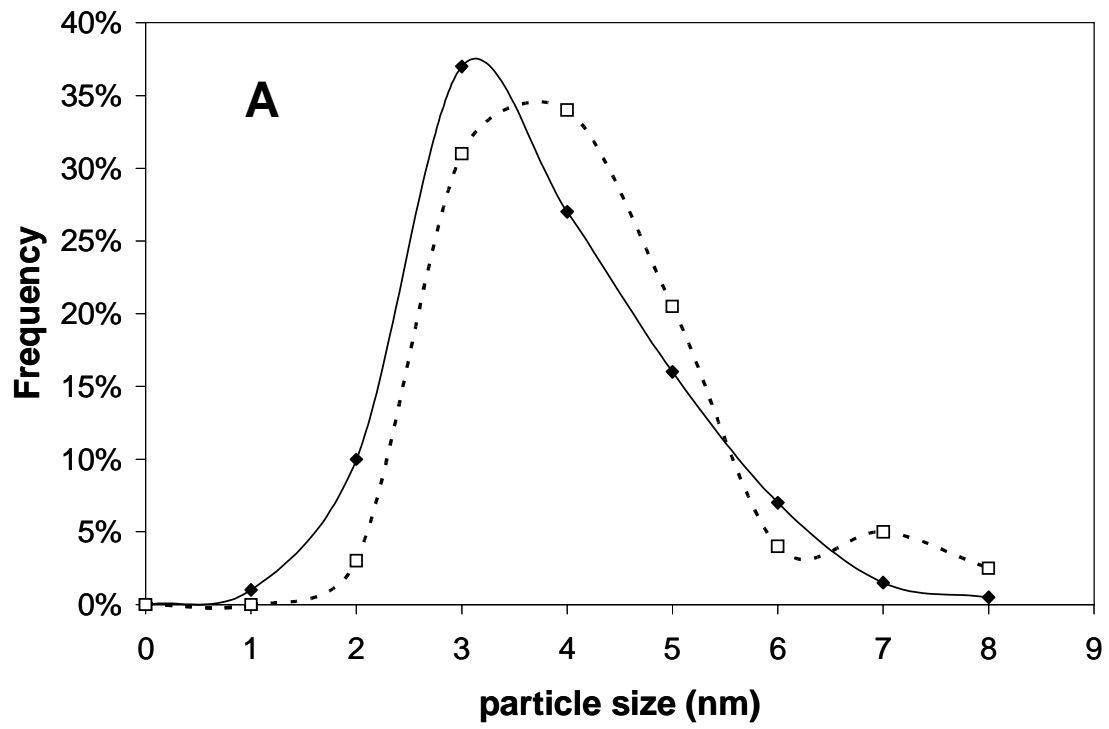
Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8