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XPS and DRS of Au/TiO_2 catalysts: effect of pretreatment

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TiO_2 impregnated with $AuCl_3$ was subjected to different pretreatments and then characterized by XPS and DRS. After drying at 298 K under vacuum, the catalyst contains highly dispersed, nonmetallic Au species; whereas drying at 393 K in an oven caused the Au to be partially reduced and agglomerate. Further treatments of the oven-dried sample at higher temperatures resulted in the disappearance of Au signals in XPS except the one after a HTR/C/LTR (high-temperature reduction/calcination/low-temperature reduction) sequence. The high-temperature reduction at 773 K shifted the plasmon resonance peak in DRS to higher wavelength, and the following C and LTR treatment did not change the peak position. This peak shifting is interpreted as a change in the electronic status of the Au.

Keywords: XPS, DRS, Au/TiO_2, pretreatment effect

1. Introduction

Gold catalysts have been shown to actively catalyze either oxidation reactions or hydrogenation reactions [1–4]. The type of support and the Au particle size were considered to affect the reactivity significantly [3,4]. The pretreatment procedures were also found to significantly change the catalytic performance. Lin et al. [1] studied the CO oxidation reaction over Au/TiO_2 catalysts and found that a high-temperature reduction (HTR) was the necessary step to activate the impregnated $AuCl_3$/TiO_2 and a sequence of HTR–C (calcination)–LTR (low-temperature reduction) yielded an even more active catalyst. A similar pretreatment effect was found with the NO + CO reaction over the impregnated $AuCl_3$/TiO_2 [2]. This study analyzed differently treated $AuCl_3$/TiO_2 samples with X-ray photoelectron spectroscopy (XPS) and diffuse-reflectance ultraviolet-visible spectroscopy (DRS) techniques. The intention was to monitor the changes in the impregnated $AuCl_3$ and, if possible, to obtain spectroscopic evidence for the different activity with different pretreatment.

2. Experimental

All the $AuCl_3$/TiO_2 catalysts were prepared by incipient wetness impregnation. $AuCl_3$ (Johnson–Matthey, 65% Au) was dissolved in suitable amount of deionized water and added drop by drop onto TiO_2 (Degussa, P25, precalcined at 823 K for 1 h). The Au loading was nominally 1%. Typically the wet powders were dried in an oven at 393 K for 4 h and then stored in a desiccator for later use. Treatments at different temperatures and under different gas environments were conducted with this oven-dried sample. For the purpose of comparison, some incipiently wet powders were dried at room temperature under a low vacuum (10^{-2} Torr). Table 1 lists the description of different samples and the related treatment procedures.

X-ray photoelectron spectroscopy (XPS) experiments were conducted with a commercial ESCA unit (VG Microtech MT-500). The Mg Kα X-ray source was used and the anode was operated at 300 W power (15 kV, 20 mA). The hemispherical analyzer was operated in the mode of constant analyzer energy with a fixed pass energy of 100 and 20 eV, respectively, for the 0–1000 eV scan and a narrower scan around Au 4f. Approximately 0.5 g pretreated catalyst powder was air-exposed, pressed into a wafer, then preevacuated to 10^{-6} Torr before being transferred into the main chamber. Scans were made when the vacuum reached the low 10^{-8} Torr range. The binding energy was calibrated with C 1s at 285.0 and O 1s at 530.0 eV; this usually caused a 2–4 eV shift in the energy scale. The scans with higher resolution around Au 4f used the same binding energy calibration formula as that used in the wide scan spectrum. The surface composition in terms of atomic ratios was calculated from the peak heights and the photoemission cross-sectional area [5].

Diffuse reflectance UV/visible spectroscopy (DRS) conducted with a commercial unit (Hitachi, U-3410, with 150 ⌀ integrating sphere) was used to examine the changes in the electronic state of the impregnated $AuCl_3$ after different pretreatments. The pretreated powder samples were air-exposed and loaded into the sample holder; the reference chamber was loaded with $BaSO_4$. The scan was made at 60 nm/min from 800 to 185 nm with a bandpass of 2 nm.

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Table 1
Pretreatment conditions used for the impregnated AuCl$_3$/TiO$_2$ catalysts.

Sample	Pretreatment procedures
DR	Vacuum-dried at room temperature
DO	Oven-dried at 393 K for 4 h
LTR	DO sample followed by flowing H_2 reduction at 473 K for 2 h
C	DO sample followed by flowing O_2 calcination at 673 K for 1 h
HTR	DO sample followed by flowing H_2 reduction at 773 K for 1 h
HTR/C	HTR sample followed by flowing O_2 calcination at 673 K for 2 h
HTR/C/LTR	HTR/C sample followed by flowing H_2 reduction at 473 K for 2 h

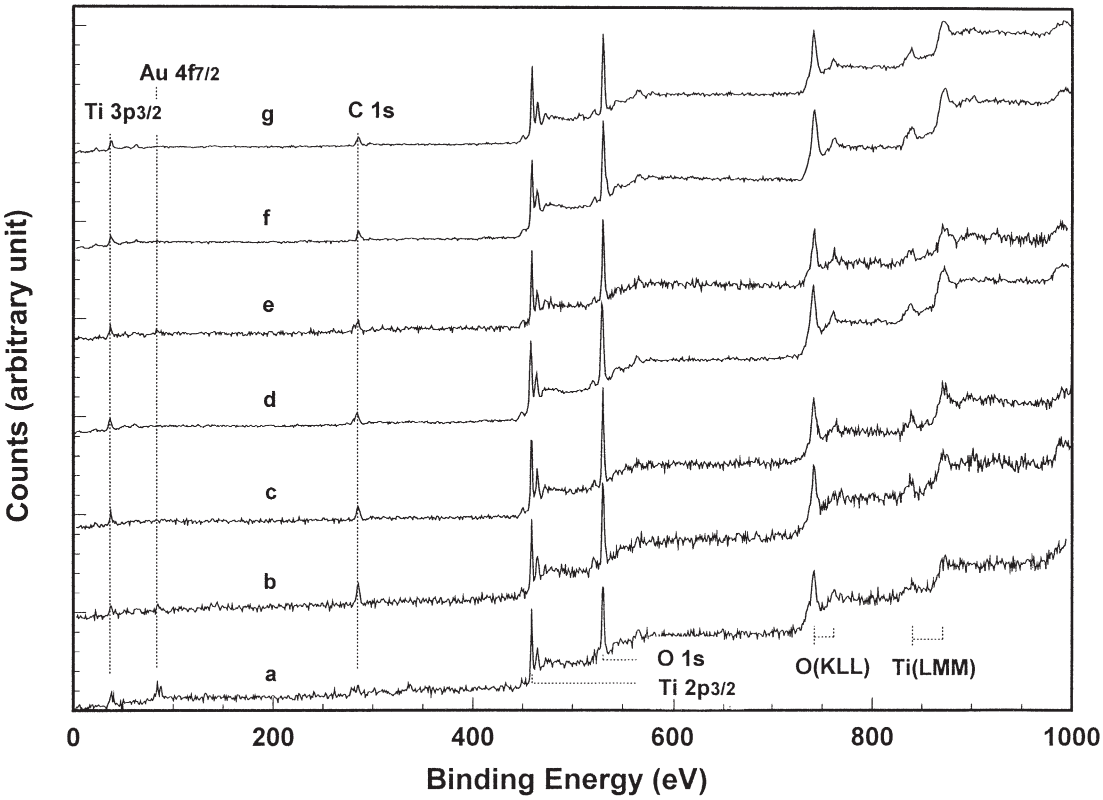

Figure 1. XPS spectra of impregnated AuCl$_3$/TiO$_2$ after different pretreatments: (a) DR, (b) DO, (c) HTR, (d) HTR/C, (e) HTR/C/LTR, (f) LTR, and (g) C.

3. Results

3.1. XPS

The full-range XPS spectra of the AuCl$_3$/TiO$_2$ after different pretreatments are shown in figure 1. It is clear that the Au 4f$_{7/2}$ signal is relatively weak except for the DR, DO, and HTR/C/LTR samples; the DR sample showed the most intense Au 4f$_{7/2}$ signal. The estimated atomic ratios of Au/Ti and O/Ti of these samples are listed in table 2. The reason for the higher O/Ti ratio of the HTR sample is not known but was also found in earlier reports on Rh/TiO$_2$ and Pt/TiO$_2$ [6]. If a 1% Au loading were at 100% dispersion over a 50 m^2/g support the surface Au density would be approximately 6×10^{17} atoms/m^2. When comparing to the Ti surface density of $5–7 \times 10^{18}$ atoms/m^2 on TiO$_2$ (rutile) this corresponds to a Au/Ti ratio of 0.1. This ratio is close to the observed Au/Ti ratio of the DR sample, indicating that its Au species is highly dispersed. A 393 K drying in an oven (the DO sample) caused a lowering in the Au/Ti ratio. Further pretreatment of the DO sample at higher temperatures resulted in the disappearance of the Au signal in the XPS spectra. The exceptionally higher Au/Ti ratio of the HTR/C/LTR sample indicates a redispersion of the Au, but the cause of redisperion is not known at this moment.

Also shown in table 2 are the peak positions of Au 4f$_{7/2}$ and Ti 2p$_{3/2}$. All these samples have the Ti 2p$_{3/2}$ peak located at 458.7–458.9 eV, consistent with that observed in TiO$_2$ and TiO$_2$-supported metal catalysts [6,7]. This indicates that the binding energy calibration procedure used was reasonable. Figure 2 shows the scans from 78 to 96 eV of the DR, DO, HTR, and HTR/C/LTR samples. The Au 4f$_{7/2}$ peak position of the DR, DO and HTR/C/LTR samples was 84.2, 83.9, and 83.9 eV, respectively, which is not very different from the 83.9 eV of metallic Au [5]. The higher

Table 2
XPS analysis of impregnated AuCl$_3$/TiO$_2$ after different pretreatments.

Sample	Atomic ratio		Binding energy (eV)	
	Au/Ti	O/Ti	Au 4f$_{7/2}$	Ti 2p$_{3/2}$
DR	0.1	1.8	84.2	458.9
DO	0.04	2.0	83.9	458.8
LTR	N.D.[a]	2.0	N.D.	458.9
C	N.D.	2.0	N.D.	458.9
HTR	N.D.	2.4	N.D.	458.7
HTR/C	N.D.	2.0	N.D.	458.8
HTR/C/LTR	0.03	2.0	83.9	458.9

[a] Not detectable.

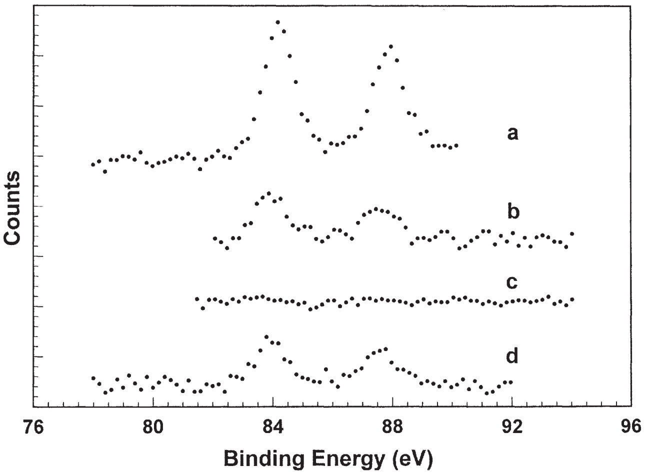

Figure 2. Au 4f$_{7/2}$ XPS spectra of impregnated AuCl$_3$/TiO$_2$ after different pretreatments: (a) DR, (b) DO, (c) HTR, and (d) HTR/C/LTR.

Au 4f$_{7/2}$ peak position of the DR sample suggests that it contained more unreduced Au species.

3.2. DRS

The DRS spectra of these samples are shown in figure 3. The most prominent features of these samples are the absorbance bands at 220, 270–330, and at around 550 nm. The Degussa P-25 TiO$_2$ was reported to show a strong absorbance at around 330 and below 250 nm [8]. Since all the samples studied showed almost the same spectral features below 400 nm, it is considered that TiO$_2$ contributed to most of the features in this region. That a vacuum-dried sample and a HTR sample had the same Au absorbance features below 400 nm is less likely.

The absorbance at around 550 nm was typically assigned as the plasmon resonance peak of Au particles [9,10]. Duff and Baiker [9] reported that small Au colloidal particles (1–2 nm) showed a peak near 500 nm. Torigoe and Esumi [10] reported a broad absorbance band from 535 to 568 nm due to the plasmon resonance of ultra-fine gold particles (10 nm), and that for bulk Au at >600 nm. From figure 3 it can be found that this absorbance peak was observed in all samples except the DR sample. This indicates that the DR sample contained no metallic Au, whereas the presence of a plasmon resonance signal in the DO sample indicated that the reduction of loaded Au occurred during the 393 K drying step. Further treatment of the DO sample increased the size of this plasmon resonance peak. Besides, the HTR treatment caused a peak shifting from 550 to 570 nm and the following C and LTR treatment did not change the peak position. Although the plasmon resonance peak position shifting to higher wave length could occur with increasing particle size, the similar Au/Ti ratio but different plasmon peak position of the DO and the HTR/C/LTR samples indicate that the attribution only to particle size is inadequate. Therefore, the peak shifting to 570 nm for the HTR, HTR/C, and HTR/C/LTR samples was considered to be due to the changes in the electronic state of the Au surface species.

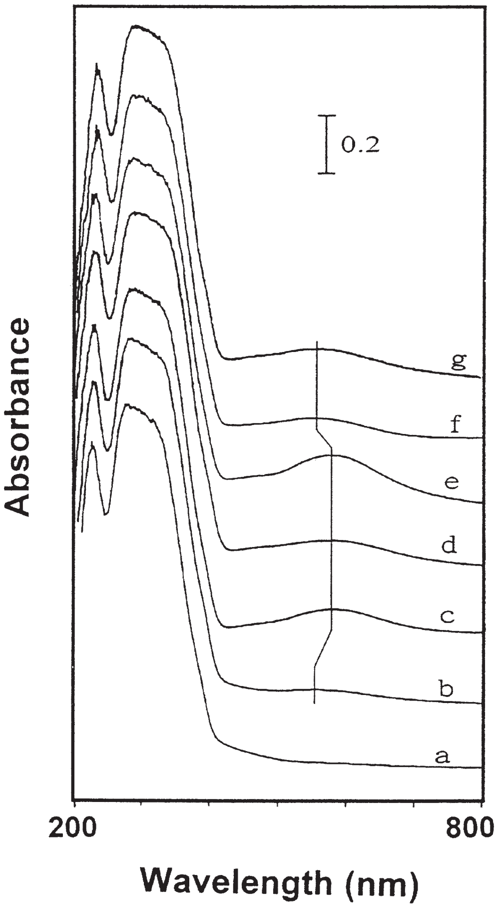

Figure 3. DRS spectra of impregnated AuCl$_3$/TiO$_2$ after different pretreatments: (a) DR, (b) DO, (c) HTR, (d) HTR/C, (e) HTR/C/LTR, (f) LTR, and (g) C.

4. Discussion

The loaded Au species appeared to be very mobile, because the DO had a lower Au/Ti ratio than the DR and a mild LTR completely diminished the Au signal in XPS. Since the DR sample had no Au metal plasmon resonance peak in DRS, it indicated the impregnated Au species were not reduced. However, no Cl signal could be observed in this and other samples from XPS. If all the Cl in the AuCl$_3$

Table 3
Pretreatment effect on the activity of impregnated AuCl$_3$/TiO$_2$.

Pretreatment	CO oxidation at 313 K[a]		CO + NO at 323 K[b]	
	μmol CO/(g-cat s)	μmol CO/(g-Au s)	μmol NO/(g-cat s)	μmol NO/(g-Au s)
LTR	<0.02	<2	0.02	2
C	<0.02	<2	0.03	3
HTR	(0.28)[c]	(12.2)[c]	0.19	18
HTR/C	20	200	0.36	33
HTR/C/LTR	23	230	0.73	66
(TiO$_2$)	0	–	0.02	–

[a] Data from 1% Au/TiO$_2$ reported in [24] unless otherwise specified.

[b] Data from 1% Au/TiO$_2$ reported in [2].

[c] Data from 2.3% Au/TiO$_2$ reported in [1].

precursor is retained and well dispersed on the surface, the estimated peak height ratio of Cl/Au would be approximately 0.6, but from the noise level in the XPS spectrum of the DR sample, the estimated Cl/Au peak ratio was no more than 0.2. This implies that the well-dispersed Au species in the DR sample have an average Cl/Au atomic ratio no more than 1, if the XPS is assumed to be sensitive enough for detecting such low levels of Cl. This suggests that the impregnated AuCl$_3$ changed its chemical identity after drying at 298 K. The various AuCl$_{4-n}$(OH)$_n^-$ species formed in the AuCl$_{3(aq)}$ solution [11] may help to explain these changes, but more experiments are needed before the structure of the loaded Au species can be concluded.

The presence of a Au metal plasmon peak in the DO sample showed that the reduction of Au species occurred during oven-drying at 393 K. Sermon and Bond [12] also found that an 48 h heating at 393 K in either air or vacuum could turn HAuCl$_4$-impregnated SiO$_2$ or Al$_2$O$_3$ mauve if the Au loading was lower than 1%; this color change indicated the formation of gold in colloidal dispersion. This indicates that at least part of the impregnated Au species over these supports could be easily reduced.

The Au/Ti ratio in XPS is tentatively used to represent the Au dispersion; however, the near zero Au/Ti ratio of certain samples could be complicated by phenomena other than Au agglomeration. The transport of Au species deeper into the pore to result in a Au-depleted skin in the wafer is possible, but this alone is insufficient to explain the higher Au/Ti ratio of the HTR/C/LTR sample compared to either the HTR or the HTR/C sample. The TiO$_x$ decorating layer typically found with the TiO$_2$-supported metal catalysts after HTR may also exist, but the near zero Au/Ti ratio of the HTR/C sample makes this attribution somewhat ambiguous.

The Au 4f$_{7/2}$ peak position in XPS seemed insufficient to distinguish the chemical status of Au in these samples. Salama et al. [13] reported that the Au 4f$_{7/2}$ for Au^0 was at 83.8, AuCl at 85.75, and AuCl$_3$ at 87.5 eV, but Fernandez et al. [14] reported Au^0, Au$^+$, and Au^{3+} at ca. 83, 84.2, and 87 eV, respectively, for a HAuCl$_4$-deposited TiO$_2$ colloid. Although the Au$^+$ position in the latter report is similar to that of the DR sample, the unusually low Au^0 position in the same report made the interpretation questionable. Ocal and Ferrer [15] reported that the Au 4f$_{7/2}$ peak position was particularly sensitive to changes in the chemical surroundings. Besides, controversial interpretation on the binding energy shift can also be found in the literature [16,17]. Therefore, the use of the Au 4f$_{7/2}$ binding energy position for identifying the Au chemical state is considered invalid.

Due to the interference of TiO$_2$ absorbance, the bonding environment of the unreduced Au species could not be unambiguously revealed in the DRS spectra. An absorbance around 220 nm was observed in Au$_2$Cl$_{6(g)}$ [18], AuCl$_{4(l)}^-$ [19,20], AuCl$_{3(s)}$ [21] and zeolite-supported Au catalysts [22,23], and it was assigned to the ligand-to-metal charge transfer transition (LMCT) of AuCl$_3$ or AuCl$_4^-$ species. Similarly, the absorbance at 286 nm assigned to the ligand field (LF) contribution from AuCl$_{4(l)}^-$ [19,20], the absorbance at 320 nm assigned to the LF contribution from surface AuCl$_{3(s)}$ [21], the absorbance at 322–329 nm assigned to the LF contribution from AuCl$_{4(l)}^-$ [19,20], and the absorbance at 305 nm assigned to the LMCT in AuCl$_3$/Na-Y [23] may all contribute to but could not be resolved in the DRS spectra.

Table 3 compares the pretreatment effect on the impregnated AuCl$_3$/TiO$_2$ for the CO oxidation [1,24] and for the CO + NO reaction [2]. Very similar trends can be observed for both reactions, and the HTR, HTR/C, and HTR/C/LTR samples are significantly more active than the others. That the HTR step is sufficient to activate the catalyst seems to correlate with the shift in the Au plasmon peak observed in figure 3; the three more active catalysts showed the same Au plasmon resonance peak position. The HTR step seems to cause certain changes in the Au chemical environment that could not be attained via calcination at 673 K alone, and the calcination and LTR following HTR could not alter the changes. This seems to suggest that the chemical environment of the Au metal affects the catalytic activity although the Cl residue [1,3] and the TiO$_x$ decorating layer in SMSI [24] could complicate the so-called chemical environment. It has been proposed that Au–oxide support perimeter sites contribute to the high reactivity [1,3,4,24]. The higher activity of the HTR/C/LTR sample compared to the HTR sample could be due to the higher Au/Ti ratio of the former which suggests smaller Au particles, thus more perimeter sites.

5. Summary

In this study $AuCl_3$-impregnated TiO_2 was subjected to different pretreatments and then examined with XPS and DRS. The Au/Ti ratio from XPS indicates the dispersion followed a sequence as DR $>$ DO $>$ HTR/C/LTR $>$ HTR/C $\approx$ HTR $\approx$ LTR $\approx$ C. That no plasmon peak was observed with the DR sample indicated only nonmetallic Au species were present. Part of the impregnated Au species was found to be reduced and to agglomerate during the drying at 393 K in an oven. The plasmon resonance peak shift in DRS implied a change in the electronic state of Au metal after a HTR procedure. The HTR, HTR/C, and HTR/C/LTR samples showed a similar Au electronic state; the highest activity of the HTR/C/LTR among these three could be attributed to its highest Au/Ti ratio.

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