

Influence of the support crystal structure of WO₃/Au catalysts in CO oxidation

Tamás Firkala^{1,2}, Balázs Fórizs¹, Eszter Drotár², András Tompos², Attila L. Tóth³,

Katalin Varga-Josepovits⁴, Krisztina László⁵, Markku Leskelä⁶, Imre Miklós

Szilágyi^{1,6,7*}

¹Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1111 Budapest, Szt. Gellért tér 4. Hungary;

²Institute of Materials and Environmental Chemistry, Research Centre of Natural Sciences, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri út 59–67. Hungary

³Institute for Technical Physics and Materials Science, Research Centre of Natural Sciences, Hungarian Academy of Sciences, H-1121 Konkoly–Thege út 29–33. Budapest, Hungary;

⁴Department of Atomic Physics, Budapest University of Technology and Economics, H-1111 Budapest, Budafoki út 8. Hungary;

⁵Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, P.O. Box 92, H-1521 Budapest, Hungary;

⁶Department of Chemistry, University of Helsinki, A.I. Virtasen aukio 1, Helsinki, FI-00550, Finland;

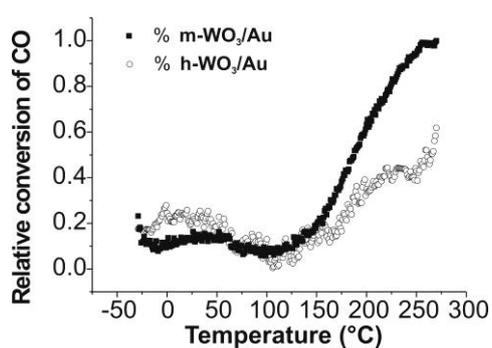
⁷Technical Analytical Chemistry Research Group of the Hungarian Academy of Sciences, Budapest University of Technology and Economics, H-1111 Budapest, Szt. Gellért tér 4., Hungary

*Corresponding author: imre.szilagyi@mail.bme.hu

Abstract

Gold nanoparticles (partially below 5 nm in diameter) were successfully deposited on hexagonal and monoclinic WO₃ supports by deposition–precipitation, which had been considered previously not feasible owing to the low isoelectronic point of WO₃. The catalysts were characterized by TEM, SEM, N₂-adsorption, XRD, and XPS. In CO oxidation m-WO₃/Au showed better catalytic activity over 100 °C than h-WO₃/Au. This was explained by that m-WO₃ had higher surface OH coverage, resulting in larger Au nanoparticle loading and thus better catalytic activity.

Graphical abstract



Keywords

WO₃, Au, CO oxidation, catalysis, structure, composition, support

Introduction

Heterogeneous gold catalysts are intensively investigated, as the outstanding catalytic activity of this metal in nanosize has been proven in a lot of reactions and under various

circumstances [1]. It is well known that the activity of gold catalysts highly depends on the gold nanoparticle size, the properties of the support material [2], the preparation process [3], the conditions of the pretreatment [4] etc. Oxidation reactions (e.g. oxidation of alcohols [5], alkenes [6], monosaccharides [7] and carbon monoxide [8]) are good examples for the very high activity of gold catalysts.

The oxidation circumstances of CO by Au nanoparticles have garnered a lot of attention recently [9-11]. CO is a toxic gas, which can irreversibly bond to hemoglobin in human blood, converting it to carboxyhemoglobin, if the concentration of CO approaches 100 ppm in the atmosphere [12].

Semiconductor oxides (TiO_2 , WO_3 , SnO_2 , ZnO , V_2O_5 , etc.), which are widely studied as heterogeneous catalysts [13], can be supports for catalytic Au nanoparticles as well [14-16]. Tungsten oxide (WO_3) is a well-known catalyst (e.g. for the selective oxidation of olefins or sulfides [17], reforming reactions [18], etc.), and the application of WO_3 supported noble metal (Pt, Pd) catalysts in CO oxidation is well known [19]. Nevertheless, to the best of our knowledge, the investigation of a WO_3/Au catalyst in CO oxidation has been reported only in one study [20].

Immobilizing gold nanoparticles on WO_3 surfaces was done mainly by physical methods (e.g. by sputtering [20]). The otherwise widely used deposition-precipitation of Au was considered to be impossible on WO_3 previously, due to the low isoelectronic point of WO_3 [21].

Recently a new way has been developed to deposit Au nanoparticles through deposition-precipitation, but it has been used only on Al_2O_3 and SiO_2 supports [22-23]. It was unclear whether this method can be used also on an oxide with low isoelectronic point (i.e. WO_3).

WO₃ has different crystalline modifications (e.g. monoclinic, hexagonal [24]). Recently, it was revealed that the hexagonal (h-) and monoclinic (m-) forms of WO₃ behaved quite differently in gas sensing [25-30] and photocatalysis [31]. However, it was unclear how they would influence in general the catalytic activity of WO₃, and in particular how they would affect catalysis when they are used as supports for Au nanoparticles.

Therefore, we aimed to prepare WO₃/Au catalysts and demonstrate that Au nanoparticles can be deposited on WO₃ from solution by the deposition-precipitation method. In addition, we explored the activity of WO₃/Au catalysts in CO oxidation, and also investigated the influence of the crystal structure (monoclinic or hexagonal) of the WO₃ support on catalysis. Recently a new way was developed to prepare h-WO₃ and m-WO₃ by annealing (NH₄)_xWO_{3-y} [27], which enabled preparing them with very similar morphologies. This ensured that mostly the different WO₃ crystal structures could have effect on catalysis, while the morphologies influenced it to a smaller extent.

Therefore, in this paper we report on the different catalytic activity of m-WO₃/Au and h-WO₃/Au composites. Gold nanoparticles were synthesized on m-WO₃ and h-WO₃ with deposition-precipitation (reducing HAuCl₄ solution) and consecutive pretreatment (annealing in air at 350 °C). Transmission electron microscopy (TEM), scanning electron microscopy (SEM), low temperature nitrogen adsorption measurement, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the catalysts. The catalytic activity of the composites was tested in CO oxidation.

Experimental

Preparation of Au/WO₃ catalysts

Preparing m-WO₃ and h-WO₃ supports. Hexagonal WO₃ and monoclinic WO₃ samples were prepared by annealing hexagonal ammonium tungsten bronze, (NH₄)_{0.33-x}WO_{3-y} in air at 470 °C and 600 °C, respectively [25]. The precursor (NH₄)_{0.33-x}WO_{3-y} was obtained by the partial reduction of ammonium paratungstate tetrahydrate (APT), (NH₄)₁₀[H₂W₁₂O₄₂]·4H₂O, in H₂ at 400 °C [32]).

Deposition–precipitation (DP) of Au nanoparticles. 0.5 g of hexagonal or monoclinic WO₃ was suspended in 150 ml of 3.1*10⁻⁴ M chloroauric acid (HAuCl₄) solution. The reaction mixture was stirred for 1 h; then 4 M NH₄OH was added to maintain pH 7 in the whole process. After 75 min the reaction was completed, and the liquid phase became colorless. The as-prepared catalysts were washed with de-ionized water and centrifuged three times at room temperature. Consecutively, the catalysts were dried overnight at 60 °C. Prior to the CO oxidation test reactions, the catalysts were pretreated at 350 °C for 1 h in air atmosphere (50 ml min⁻¹ flow rate), so that the gold-amine complexes could be completely decomposed and gold nanoparticles could be formed.

Catalyst characterization

Transmission electron microscope (TEM) images about the WO₃/Au samples were recorded on a FEI Morgagni 268b instrument operated at 100 keV. At least 200 nanoparticles were measured on the TEM images to define the particle size distribution.

Scanning electron microscopy (SEM) characterization was performed by a LEO-1550 FEG SEM instrument.

Surface area values were deduced from low temperature nitrogen adsorption data (Quantachrome NOVA 2000E) according to the multi point BET model [33].

Powder X-ray diffraction (XRD) patterns were measured by a PANalytical X'pert Pro MPD X-ray diffractometer using Cu K α radiation.

X-ray Photoelectron (XPS) spectra from the surface of the samples were recorded by a VG Microtech instrument using Mg K α radiation. The spectrometer was calibrated with the binding energy of the C1s line (285 eV).

Temperature programmed oxidation of CO

Temperature programmed oxidation (TPO) of CO was measured in the temperature range from -30 to 270 °C with a heating rate of 5 °C min $^{-1}$ in a U-tube quartz reactor. 25mg of each catalyst was mixed with 125 mg Al $_2$ O $_3$ in order to make a catalyst bed to facilitate formation of plug like flow, and to inhibit the catalysts to occlude the filter. Prior to the CO oxidation reaction, the catalyst samples were pretreated at 350 °C for 1 h in air atmosphere (50 ml min $^{-1}$ flow rate) to generate catalytically active gold nanoparticles on the catalyst supports. Upon completion of the pretreatment, the samples were cooled in helium gas flow. When temperature reached -30 °C, helium flow was replaced with the flow of the gaseous reaction mixture (70 ml min $^{-1}$), in which the volume ratios were 1.5/1.5/67 for CO/O $_2$ /He, respectively. The outlet gas flow was monitored by a quadruple mass spectrometer (Prisma QMS 200, Pfeiffer Vacuum Technology) recording the $m/z = 28^+$, 32^+ , and 44^+ signals of consumed CO and O $_2$ and as-formed CO $_2$, respectively.

Results and discussion

Structure, morphology and composition

According to our previous studies, deposition–precipitation method with HAuCl_4 and NH_3 solution results gold-amine complexes directly bonded to a metal oxide catalyst support such as SiO_2 or Al_2O_3 . In the present work, conditions of catalyst preparations on WO_3 support were similar to that used previously at the Au/SiO_2 and $\text{Au/Al}_2\text{O}_3$ catalysts [22-23]. In the case of WO_3 supports, it was noticed that small portion of the complexes started to degrade during the deposition–precipitation process, resulting in sub 5 nm nanoparticles (observed on TEM images not shown here). However, the dominant part of the Au nanoparticles was obtained, only when the amine complexes degraded in air flow during the pretreatment process at 350 °C.

Based on SEM (Fig. 1) and TEM (Fig. 2) images, the estimated size of the h- and m- WO_3 support particles were 50-70 nm and 60-90 nm, respectively. The surface area values (S_{BET}) were 11 and 6.5 m^2/g for pure h- and m- WO_3 particles, respectively.

After the pretreatment process, SEM (Fig. 1) and TEM (Fig. 2) showed that large portion of Au nanoparticles was under the critical 5 nm (Fig. 3), which is required to generate catalytic activity [34]. The supports influenced the Au particle size, as in the case of h- WO_3 43 % of Au particles was under 5 nm, while in the case of m- WO_3 this value was 37 %.

According to XRD patterns (Fig. 4), the supports were pure h- WO_3 (ICDD 85-2460) and m- WO_3 (ICDD 43-1035). Gold (ICDD 04-0784) was identified at about 38° in the case of both catalyst supports (see insets in Fig. 4). No impurities were detected by XRD on the WO_3/Au samples.

The oxidation states of tungsten, oxygen and gold atoms were investigated by XPS (Fig. 5). Though XPS is a surface analytical method with an average information depth of 10 nm, it gave a good estimate also about the bulk composition of the particles. The particle size of our samples was between 50-90 nm. If 70 nm is taken as an average particle size and spherical particles with 35 nm average particle radius are assumed, then XPS can give

information about the outer 10 nm shell of the particles. The volume of the outer 10 nm shell is ca. the half (49 %) of the volume of the whole particle. Thus the XPS signal came from half of the complete volume of the particles, which provided a good estimate of the bulk composition of the nanoparticles.

Recently it was shown that while m-WO₃ is completely oxidized, the structure of h-WO₃ is partially reduced. This was explained by that stabilizing cations (Na⁺, K⁺, NH₄⁺, etc) (or water molecules) were always present in the hexagonal channels of h-WO₃, and they stabilized the metastable hexagonal framework [27]. Due to the presence of W⁵⁺ and W⁴⁺ atoms, there were less surface OH groups and water molecules on the surface of h-WO₃, compared to m-WO₃ [31].

The different oxidation states of tungsten were confirmed by XPS in the case of the h- and m-WO₃ supports of Au nanoparticles as well. In the m-WO₃/Au catalyst, the m-WO₃ support was basically completely oxidized with 96.7 % W⁶⁺ atoms detected (W4f_{7/2} peak: 37.3 eV; W4f_{5/2} peak: 35.1 eV). The small amount of W⁵⁺ atoms (3.3 %; W4f_{7/2} peak: 36.2 eV; W4f_{5/2} peak: 33.6 eV) is due to that m-WO₃ usually obtains a greenish color in the high vacuum of the XPS chamber and its surface gets slightly reduced. However, in as-prepared form, m-WO₃ is completely oxidized. In the h-WO₃/Au catalyst, the h-WO₃ support contained also W⁴⁺ atoms besides W⁶⁺ and W⁵⁺ species (93.6 %, 5%, 1.5%; W4f_{7/2} peaks: 37.2, 36.2, 35.2 eV; W4f_{5/2} peaks: 35.1, 33.6, 32.9 eV for W⁶⁺, W⁵⁺, W⁴⁺, respectively).

The amount of surface O²⁻, OH⁻ and H₂O species (530.9, 531.6, 533.5 eV, respectively) was also examined by XPS. Their normalized ratios showed that the amount of surface OH⁻ was ca. 25 % larger on m-WO₃/Au (1.00/0.69/0.11 for O²⁻/OH⁻/H₂O respectively), compared to h-WO₃/Au (1.00/0.55/0.10 for O²⁻/OH⁻/H₂O respectively). It can be noted that H₂O was present on the surface of h-WO₃ both in physically adsorbed and chemically bonded forms [35], and XPS measures their overall amount.

According to XPS, gold was present only in metallic form (Au4f_{7/2} peak: 83.5 eV; Au4f_{5/2} peak: 87.2 eV) [36-38]. The gold loading of the WO₃ supports was different, i.e. 5.3 mass% Au was present on m-WO₃, while only 3.7 mass% on h-WO₃. The support h-WO₃ had larger specific surface, which might result in larger gold loading; however, the opposite was observed. Thus, the larger amount of Au on the m-WO₃ support can be explained only by that the amount of surface OH groups was larger on m-WO₃, compared to h-WO₃. The larger OH density over m-WO₃ probably meant more reaction and then nucleation sites for Au reduction and Au nanoparticle formation.

Temperature programmed oxidation of CO

The TPO test results of h-WO₃/Au and m-WO₃/Au catalysts are presented in Fig 6. Below 100 °C both catalysts exhibited minor activity. In this temperature region (between -30 and 100 °C) the hexagonal support seemed to be better for catalytic activity. There was a minimum in the catalytic activity of both catalysts around 100 °C. From 100 °C the conversion of CO started to increase again in the case of both catalysts, and from this point the activity of m-WO₃/Au superseded increasingly that of Au/h-WO₃. The activity of both catalysts rose especially dramatically after 150 °C.

On the one hand, due to larger specific surface and larger portion of loaded Au nanoparticles below 5 nm h-WO₃ was expected to be a better catalyst support. On the other hand, the larger amount of Au nanoparticles might be an advantage for using the m-WO₃ support. According to the catalysis tests, Au/m-WO₃ had significantly larger activity above 100 °C, which means that the 43 % larger Au load of the m-WO₃ support was the decisive on the catalytic activity, and its influence surpassed the effect of the larger specific surface of h-WO₃ and larger portion of Au nanoparticles below 5 nm.

Recently, it was revealed that the higher surface OH density of m-WO₃ was responsible for that it was a better photocatalyst than h-WO₃ [31]. In the present study, the larger amount of surface OH groups on m-WO₃ resulted in larger Au nanoparticle loading on m-WO₃ and better activity of the m-WO₃/Au catalyst, compared to the h-WO₃/Au composite. Thus, though not directly as in photocatalysis, but in an indirect way the higher surface OH density of m-WO₃ was responsible for that m-WO₃ was a better support for the catalytic Au nanoparticles, compared to h-WO₃.

The conversion reached with the Au/m-WO₃ catalyst in CO oxidation is not outstanding compared to previous supported Au catalysts [9-11,20], mostly due to the relatively low specific surface of the m-WO₃ support. However, the aim of the present study was not to prepare the best catalyst for CO oxidation, but to study how the crystal structure of the WO₃ support influences the activity of Au/WO₃ catalysts.

Conclusion

In this work Au/WO₃ catalysts with different WO₃ support crystal forms (hexagonal or monoclinic) were investigated. Au nanoparticles with diameters partially smaller than 5 nm were prepared on WO₃ substrates for the first time with the deposition and precipitation method using HAuCl₄ and NH₄OH solutions, followed by a pretreatment in air at 350 °C. Previously it was considered not possible to deposit Au nanoparticles with this method on an oxide with low isoelectronic point (i.e. WO₃). The as-prepared Au/h-WO₃ and Au/m-WO₃ catalysts were characterized with TEM, SEM, N₂-BET specific surface measurement, XRD and XPS.

To reveal the effect of support crystal structure, the catalysts were tested in the oxidation reaction of CO. The catalyst m-WO₃/Au showed considerably larger catalytic

activity over 100 °C compared to h-WO₃/Au. The reason for this is that m-WO₃ is completely oxidized and its surface is rich in OH groups, which are beneficial for Au nanoparticle nucleation. In contrast, h-WO₃ is partially reduced due to stabilizing cation impurities in its structure, resulting in lower surface OH coverage, and thus lower Au nanoparticle loading and lower catalytic activity. This means that m-WO₃ is a better support for catalytic Au nanoparticles.

Acknowledgements

I. M. S. thanks for a János Bolyai Research Fellowship of the Hungarian Academy of Sciences and a Marie Curie Intra-European Fellowship (PIEF-GA-2009-235655). TÉT_10-1-2011-0045 and OTKA-PD-109129 grants are gratefully acknowledged. Consultation with Dr. Ferenc Somodi (Institute for Collaborative Biotechnologies, University of California, Santa Barbara, CA, USA) about the catalysis test results is acknowledged.

References

- [1] Thompson D (1998) *Gold Bull* 31:111.
- [2] Haruta M (1997) *Catal Today* 36:153.
- [3] Pilasombat R, Daly H, Goguet A, Breen JP, Burch R, C. Hardacre, Thompsett D, (2012) *Catal Today* 180:131.
- [4] Wang L, He L, Liu Y, Cao Y, He H, Fan K, Zhuang J (2009) *J Catal* 264:145.
- [5] Choudhary V, Dumbre D (2011) *Catal Commun* 13:82.
- [6] Ahn HG, Choi BM, Lee DJ (2006) *J Nanosci Nanotechnol* 11:3599.
- [7] Baatz C, Prüße U (2007) *Catal Today* 122:325.

- [8] Laguna OH, Centeno MA, Romero-Sarria F, Odriozola JA (2011) *Catal Today* 172:118.
- [9] Ma Z, Dai S (2011) *Nano Res* 4:3.
- [10] Wenqiang M, Fuyi C (2013) *Catal Lett* 143:84.
- [11] Haruta M (2014) *Angew Chem Int Ed* 3:52.
- [12] Bourgeois D (2009) *Structure* 17:1427.
- [13] Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) *Chem Rev* 95:69.
- [14] Roos M, Böcking D, Gyimah KO, Kucerova G, Bansmann J, Biskupek J, Kaiser U, Hüsing N, Behm RJ (2011) *Beilstein J Nanotechnol* 2:593.
- [15] Li W, Wang A, Yang X, Huang Y, Zhang T (2012) *Chem Commun* 48:9183
- [16] Fu Q, Weber A, Flytzani-Stephanopoulos M (2001) *Catal Lett* 77:87.
- [17] Koo DH, Kim M, Chang S (2005) *Org Lett* 7:5015.
- [18] Oka K, Nishiguchi T, Kanai H, Utani K, Imamura S (2006) *Appl Catal A* 309:187.
- [19] Lesnyak VV, Ishchenko EV, Gut IN, Yatsimirskii AV, Boldyreva OY (2007) *Russ J Phys Chem A* 81:874.
- [20] Veith GM, Lupini AR, Pennycook SJ, Villa A, Prati L, Dudney NJ (2007) *Catal Today* 122:248.
- [21] Haruta M (2004) *J New Mater Electrochem System* 7:163.
- [22] Somodi F, Borbáth I, Hegedűs M, Tompos A, Sajó IE, Szegedi Á, Rojas S, Fierro JLG, Margitfalvi JL, (2008) *Appl Catal A* 347:216.
- [23] Somodi F, Borbáth I, Hegedűs M, Lázár K, Sajó IE, Geszti O, Rojas S, Fierro JLG, Margitfalvi JL, (2009) *Appl Surf Sci* 256:726.
- [24] E. Lassner, W.D. Schubert, Tungsten. Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compounds (Kluwer Academic/Plenum Publishers, New York, 1999).

- [25] Szilágyi IM, Saukko S, Mizsei J, Tóth AL, Madarász J, Pokol G (2010) *Solid State Sci* 12:1857.
- [26] Szilágyi IM, Wang L, Gouma PI, Balázsi C, Madarász J, Pokol G (2009) *Mater Res Bull* 44:505.
- [27] Szilágyi IM, Madarász J, Pokol G, Király P, Tárkányi G, Saukko S, Mizsei J, Tóth AL, Szabó A, Varga-Josepovits K (2008) *Chem Mater* 20:4116.
- [28] Balázsi C, Wang L, Zayim EO, Szilágyi IM, Sedlackova K, Pfeifer J, Tóth AL, Gouma PI (2008) *J Eur Ceram Soc* 28:913.
- [29] Szilágyi IM, Saukko S, Mizsei J, Király P, Tárkányi G, Tóth AL, Szabó A, Varga-Josepovits K, Madarász J, Pokol G (2008) *Mater Sci Forum* 589:161.
- [30] Wang L, Pfeifer J, Balázsi C, Szilágyi IM, Gouma PI (2007) *Proc SPIE* 6769:67690E.
- [31] Szilágyi IM, Fórizs B, Rosseler O, Szegedi Á, Németh P, Király P, Tárkányi G, Vajna B, Varga-Josepovits K, László K, Tóth AL, Baranyai P, Leskelä M (2012) *J Catal* 294:119.
- [32] Szilágyi IM, Hange F, J. Madarász J, Pokol G (2006) *Eur J Inorg Chem* 17:3413.
- [33] Brunauer S, Emmett P, Teller E (1938) *J Am Chem Soc* 60:309.
- [34] G. C. Bond, C. Louis, D.T. Thompson, *Catalysis by gold* (Imperial College Press, London, 2006).
- [35] Szilágyi IM, Pfeifer J, Balázsi C, Tóth AL, Varga-Josepovits K, Madarász J, Pokol G (2008) *J Therm Anal Calorim* 94:499.
- [36] Bogdanchikova N, Pestryakov A, Tuzovskaya I, Zepeda TA, Farias MH, Tiznado H, Martynyuk O (2013) *Fuel* 110:40.
- [37] Ning L, Zhang W, Yan H, Pang H, Ma H, Yu Y (2013) *J Coll Interfac Sci* 403:91.
- [38] Xu J, Huang J, Liu YM, Cao Y, Li YX, Fan KN (2011) *Catal Lett* 141:198.

Figures

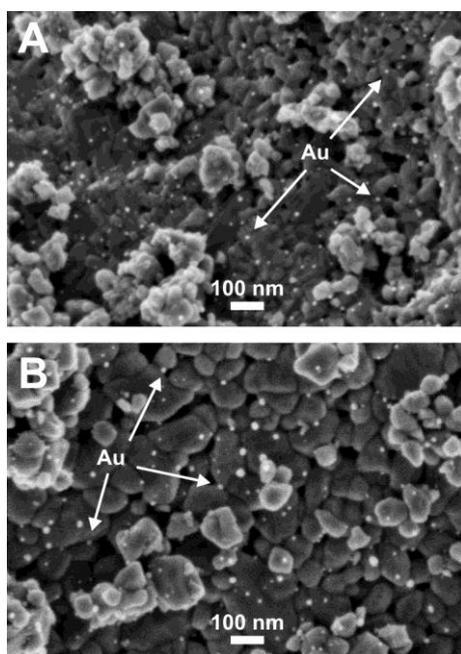


Fig. 1. SEM images of (a) h-WO₃/Au and (b) m-WO₃/Au

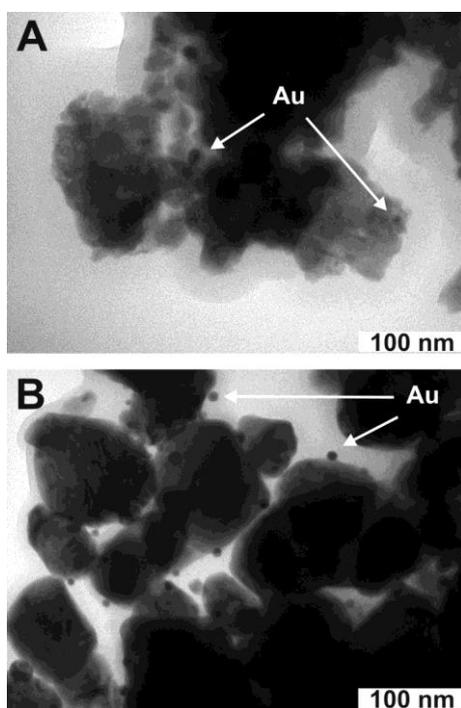


Fig. 2. TEM images of (a) h-WO₃/Au and (b) m-WO₃/Au

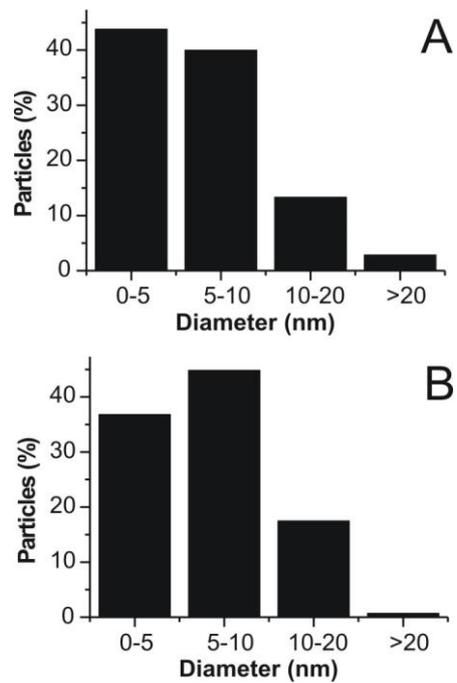


Fig. 3. Size distribution of gold nanoparticles on (a) h-WO₃ and (b) m-WO₃ supports

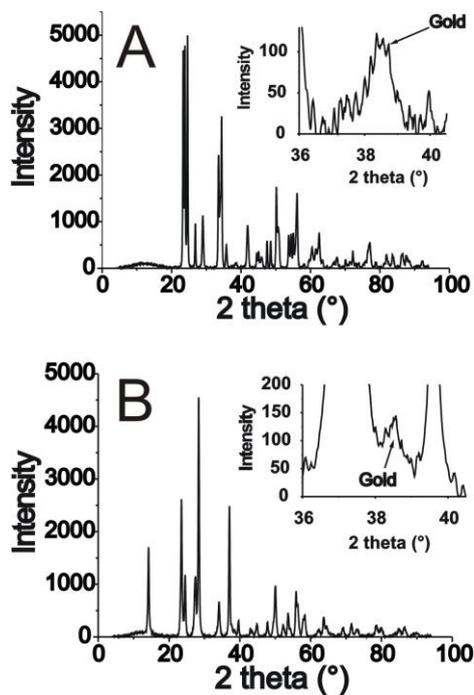


Fig. 4. XRD patterns of (a) h-WO₃/Au and (b) m-WO₃/Au. The insets show the presence of gold on the surface of the WO₃ supports.

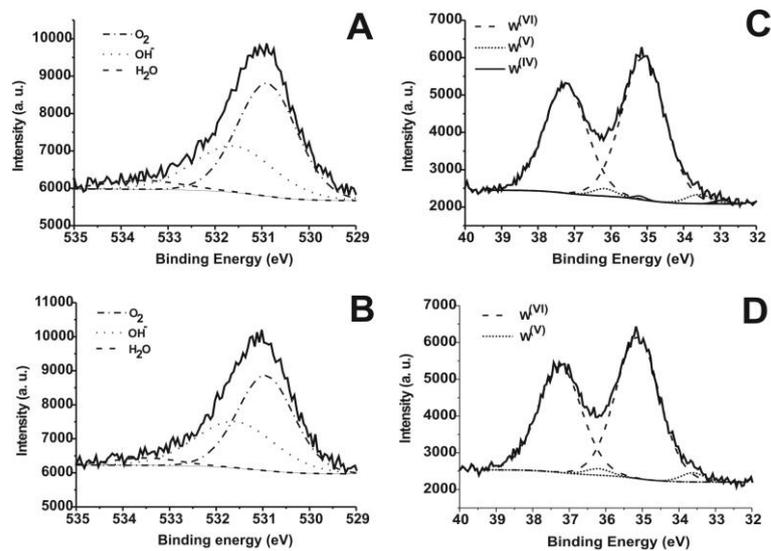


Fig. 5. XPS spectra of (a) O1s region of h-WO₃/Au; (b) O1s region of m-WO₃/Au; (c) W4f region of h-WO₃/Au; (d) W4f region of m-WO₃/Au

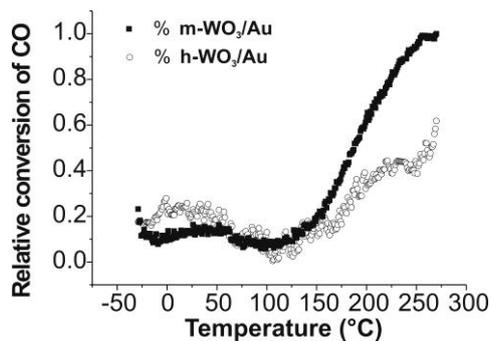


Fig. 6. Activity of h-WO₃/Au and m-WO₃/Au catalysts in CO oxidation