**Au/TiO₂ catalysts encapsulated in the mesopores of siliceous
MCM-48 – Reproducible synthesis, structural characterization
and activity for CO oxidation**

Vijay S. Narkhede^{a,b,c}, Andrea De Toni^c, Vaishali V. Narkhede^a, M. Guraya^c, J.W. (Hans)
Niemantsverdriet^b, M.W.E. van den Berg^c, W. Grünert^{c,*}, and Hermann Gies^{a,*}

*^aChair of Crystallography, Institute of Geology, Mineralogy and Geophysics, Ruhr-
University Bochum, 44780 Bochum, Germany*

*^bSchuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600
MB Eindhoven, The Netherlands*

*^cLaboratory of Industrial Chemistry, Faculty of Chemistry and Biochemistry, Ruhr-
University Bochum, Germany*

Corresponding authors:

Prof. Wolfgang Grünert, Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum,
P. O. Box 102148, D-44780 Bochum, Germany, Tel. +49 234 322 2088, Fax +49 234 321 4115,
email w.gruenert@techem.ruhr-uni-bochum.de
Prof. Hermann Gies, Lehrstuhl für Kristallographie, Ruhr-Universität Bochum, P. O. Box 102148,
D-44780 Bochum, Germany, Tel. +49 234 322 3512, Fax +49 234 321 4433, email
Hermann.Gies@rub.de

Keywords: Gold, Titania, MCM-48, host-guest systems, CO oxidation,

Abstract

A synthesis route leading to Au/TiO₂ clusters encaged in the three-dimensional channel system of siliceous MCM-48 was thoroughly studied to ensure reproducibility. Intermediate and final products were characterized by XRD, nitrogen physisorption, TEM, XPS and EXAFS. Via impregnation of MCM-48 with titanylacetylacetonate and subsequent deposition-precipitation using HAuCl₄, ionic gold was introduced into the matrix, but a minority of the gold ended up in large metal particles on the external MCM-48 surface in the (freeze-dried) samples. The ionic gold underwent gradual autoreduction at room temperature in Ar even under dark conditions, but at 273 K, it may be kept ionic for months. The catalysts exhibited 50 % CO conversion between 262 and 282 K, with good reproducibility. In addition, they achieved significant CO conversion with very low activation energy already at temperatures around 220 K; this low-temperature activity was less reproducible. Porosity analysis showed that the pore system was significantly perturbed after the Au introduction step without, however, precluding accessibility of the pore system. Therefore, further modification of the synthesis aiming at the conservation of the pore system may still bear promise for improvement.

1. Introduction

The nature and properties of gold nanoparticles dispersed on oxide supports have received much attention recently [1-3], because of their high activity in many industrially and environment-friendly important reactions. Originally gold, due to its inert nature in the bulk state, was regarded a poor catalyst (cf. [4]), until it was shown that gold in nanocrystal size with high dispersion on metal oxide supports exhibits considerable activity [5-8]. Today Au/metal oxide catalysts are known to be active in many reactions such as CO oxidation [1, 8], selective CO oxidation in a H₂-rich stream [9], reduction of NO_x [10], water gas shift reaction [3, 11], selective hydrogenation of unsaturated hydrocarbons [12], selective oxidation of alcohols [13], epoxidation of propylene [14], combustion of methane [15], etc.

Although gold catalysts are among the most widely studied systems in the last few years, in particular for the oxidation of carbon monoxide, reproducibility of catalyst preparations is a problem and, therefore, many questions such as influence of the support and of the preparation methods and/or conditions such as pH, light protection, temperatures, and more have yet to be answered. So far chemical vapor deposition (CVD) [16], co-precipitation [6], incipient wetness impregnation [17] and deposition-precipitation (DP) [18] methods have been applied to the synthesis of gold catalysts. Among them the DP process is considered to be one of the best methods to synthesize highly active gold catalysts, due to its good control of the particle size by adjustment of pH during particle formation. Based on a number of investigations two different kinds of supports, reducible or active supports such as TiO₂, Fe₂O₃, CeO₂ and non-reducible or inert supports such as MgO, Al₂O₃, SiO₂, have been distinguished in the literature [1, 8]. In the present

investigation we use mesoporous silica of framework structure type MCM-48 loaded with nano-sized TiO_2 -particles as a support for size-confined gold nanoparticles.

Because of their transparency, high thermal and chemical stability, and their mechanical robustness the silica-based mesoporous materials such as SBA-15, MCM-41, MCM-48, etc. are thought to be useful carriers or matrices for the functional molecules or nanoparticles [19-21]. Their mesoporous structures can thus be explored as host or matrix to immobilize catalytically active species on and, simultaneously, for providing nano-size confinement inside the channel system. Literature is available on highly dispersed metal or metal oxide nanoparticles inside the pore system of SBA-15 and MCM-41 materials [22-24], however such studies on MCM-48 materials are scarce, probably due to the difficulty in the preparation of MCM-48 in suitable quality. Recently we reported on the deposition of Cu, Zn acetates within the pore system of mesoporous MCM-48 and their subsequent decomposition to metal oxide nano-clusters (e.g., [22, 25, 26]). After reduction in hydrogen, these catalysts exhibited methanol synthesis activity, although they proved inferior to companion preparations in which a metalorganic zinc precursor and a wider pore system was employed [27]. Furthermore we also explored the deposition of TiO_2 particles into MCM-48 as a support for size-confined Au particles [28]. Subsequent deposition of gold nanoparticles into this TiO_2 -containing MCM-48 resulted in a catalyst highly active in CO oxidation [29]. Such catalysts can be useful for studies on the role of the support in the catalytic process because the quantities of support (TiO_2) and gold are in the same order of magnitude.

The preparation used in [29] suffered from a poor reproducibility as has been frequently reported in the literature for syntheses of supported gold particles. This prompted

us to study the preparation route and the influence of various parameters on it more systematically. Attention was focused on a version of the preparation in which the TiO_2 was loaded into MCM-48 via an aqueous route (using titanium acetyl acetate) instead of the more cumbersome tetrabutyl orthotitanate route. The composites underwent thorough characterization by means of X-ray powder diffraction (XRD), Transmission Electron Microscopy (TEM), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), porosity analysis by nitrogen physisorption, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAFS). Moreover the Au/ TiO_2 -MCM-48 catalysts were tested in CO oxidation and showed high activity.

2. Experimental

2.1 Synthesis

Pure silica MCM-48 was obtained following the method described by Gies et al. [29]. In a typical synthesis, 1.0 M NaOH was taken in a polypropylene bottle or (preferably) in a teflon-lined autoclave, and cetyltrimethylammonium-chloride (CTACl, Aldrich, 25% solution in water) was added drop-wise under continuous stirring. After that, tetraethoxysilane, (TEOS Merck), was added dropwise until the gel was homogeneous. The final molar gel composition of the synthesis mixture was 1 (TEOS) : 0.70 (CTACl) : 0.5 (NaOH) : 64 (H_2O). The sealed bottle (autoclave) was transferred to an oven heated at 363 K where the gel was kept for 4 days. Thereafter, the sample was thoroughly washed with water and dried overnight at room temperature. The dried product was calcined finally at 813 K for 5 h with a heating rate of 1 K/min.

The synthesis of TiO_2 -MCM-48 and Au/ TiO_2 -MCM-48 is summarized in Figure 1. TiO_2 -MCM-48 was synthesized by a post-synthetic wet impregnation method as fol-

lows. 0.52 g of titanylacetylacetonate ($\text{TiO}(\text{acac})_2$, Merck) was taken in 100 ml of pure ethanol, subsequently 100 ml of redistilled water was slowly added while continuous vigorous stirring. This procedure gives a very clear solution of $\text{TiO}(\text{acac})_2$ in the ethanol-water mixture. The impregnation of the calcined and carefully dried MCM-48 (0.6 g) was carried out by stirring the sample for 2 h with the alcoholic solution of Ti salt. The mixture was then centrifuged or filtered, and the solid product was washed thoroughly with redistilled water. Thereafter the cake was allowed to dry overnight at room temperature. Thermal decomposition of the deposited Ti salts was performed in a muffle oven in air by heating the sample at 573 K or at 603 K for 5 h (temperature ramp – 1 K/min). The difference in the decomposition temperature had no influence on the final catalytic activities.

The conventional deposition-precipitation technique was employed for gold encapsulation in the mesoporous TiO_2 -MCM-48 matrix. In a typical synthesis, 43.4 ml of an aqueous solution (5.078×10^{-3} M, 8 wt% gold with respect to support) of $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ (Aldrich) were heated at 343 K in a water bath wrapped in an aluminum foil to exclude light. The initial pH was around 2.5, which was slowly adjusted to neutral value 7 by drop-wise addition of a 0.1 molar NaOH solution to initiate hydrolysis of the Au-Cl bonds. After the pH had been constant for 30 min, 0.5 g of dried TiO_2 -MCM-48 were dispersed into the solution. pH excursions into the acidic region ($\text{pH} \rightarrow 5 \dots 6$) were reversed by adding 0.1 N. After the pH had been constant for 15 min, the suspension was stirred for another hour at the same temperature. Finally the suspension was cooled, filtered and washed with redistilled water. The resulting cake was freeze-dried under vacuum. After the preparation, samples were stored protected from light either in a glove

box at room temperature or in a refrigerator (inside an evacuated desiccator) at ca. 275 K.

2.2 Characterization

X-ray powder diffraction experiments were carried out using a Huber Guinier imaging plate camera G670 with Cu K α

☐ radiation ($\lambda = 1.5406$ Å)

glass capillary. A Siemens diffractometer D5000 with Cu K α

☐ radiation in mode

Debye-Scherrer geometry was employed for low angle XRD measurements. For the structure analysis of the deposited nano-gold particles the program suite FullProf was used [30]. The chemical composition of the samples was determined by ICP-OES (UNICAM PU 7000). For digestion each sample was dissolved in a mixture of 5 ml nitric acid, 1 ml hydrochloric acid and 1 ml hydrofluoric acid. Subsequently the acid mixture was evaporated in a fume hood, and the residue re-dissolved in 1 ml nitric acid. This solution was washed into a volumetric flask containing demineralised water.

N₂ adsorption measurements of MCM-48 were performed with a Quantachrome Autosorb automated gas sorption system using the Autosorb software for the analysis. Samples were outgassed at 523 K prior to measurement, with the exception of the full Au/TiO₂-MCM-48 catalyst which was outgassed only at 373 K.

Transmission electron microscopy (TEM) was performed using a Hitachi H-8100 instrument operating at accelerating voltages up to 200 kV with a single crystal LaB₆ filament. X-ray photoelectron spectra were collected with two different instruments, a Kratos Axis Ultra DLD spectrometer equipped with a standard AlK α excitation source ($h\nu = 1486.6$ eV), hemispherical analyzer operated at a constant pass energy of 40 eV (aged sample) and with a Leybold LH10 instrument equipped with a Specs EA 10/100 MCD

electron analyser, run with AlK α excitation, the analyzer operated with a pass energy of 82.9 eV (fresh sample). The appropriate corrections for the charging effect were made with help of the Si 2p signal, which was set to 103.4 eV. After a Shirley background subtraction, a combination of Gaussian-Lorentzian sum form and exponential asymmetric blend function based upon Voigt-type approximations has been used for the analysis of XP spectra. XAFS spectra at the Au LIII edge (11919 eV) were measured at Hasylab X1 station (Hamburg, Germany) using a Si(311) monochromator that was detuned to 50 % of the maximum intensity to avoid the higher harmonics. Spectra were measured in transmission using a gold foil for energy reference. Data treatment was carried out using the software package VIPER [31] as described earlier [32].

2.3 Catalytic activity

CO oxidation was performed at atmospheric pressure and at temperatures typically in the range of 210-310 K, using a plug flow reactor with an inner diameter of 4 mm. The measurements were conducted under dynamic conditions while ramping the temperature with 2 K/min. The reaction temperature was measured directly in the fixed bed using a K type thermocouple. A mixture of 1 % CO in synthetic air was passed over 50 mg of Au-TiO₂-MCM-48 catalyst (grain size 250-500 μ m) with a flow rate of 67 ml/min, which corresponds to a space velocity of 80,000 ml/h g_{cat}. CO and CO₂ concentrations were measured using an Uras 14 infrared analyzer module (ABB Corp.). The regime was slightly varied in the duration of the project. In the standard regime (A), the catalyst was cooled to 230 K and then heated up in the feed. After the first temperature ramp, the sample was cooled to 210 K or below, then the next (second or a third) ramp was started. In an earlier regime (B), the feed was dosed on the catalyst at room temperature and only

then the catalyst was cooled to 210 K to start the first ramp.

3. Results and discussion

3.1. Characterization of intermediates and final catalysts

The following data summarize the experience of six independent preparations along this route. XRD and N₂ physisorption were performed on four of the samples after each step (except for porosimetry analysis of the full catalyst, which was made only in three cases). The results obtained were very similar. As an example, results of one batch, which will be further referred to as the “reference batch” are shown in Fig. 2 and 4.

X-ray diffractograms of the pristine MCM-48, the TiO₂-loaded support and the full catalyst are shown in Figure 2. The low-angle scan shows that the MCM-48 used possessed excellent periodicity. The introduction of the heavy elements Ti and Au lead to a drastic decrease of peak intensity in the MCM-48 pattern, which can be explained by the loss of scattering contrast between pore and wall, because the porosity of the material was preserved (see below). No Bragg peaks for TiO₂ were found. From an earlier EXAFS study [28], the TiO₂ phase can indeed be expected to be highly disordered. From ICP-OES, the Ti content of this material was 6.8 wt%, for the remaining materials, the Ti content was in the range 7.1 – 8.3 wt%.

After gold introduction, the XRD pattern shows that the parent structure of the mesoporous host was maintained as well, but the signal was rather weak, in agreement with our previous work [29]. It will be shown below (physisorption data) that this attenuation is at least partly due to structural damage although the porosity of the material

remained high and the pores remained accessible. In the high-angle region shown in Figure 2, there is a very small peak at $\sim 38^\circ$, which we attribute to metallic gold with FCC phase, indicating that there are small gold particles in the sample although no reduction step has taken place. The intensity of this gold signal varied significantly among the catalyst batches prepared. The total gold content of the samples prepared was 3.1 wt-%, the Au contents of the remaining samples ranged between 2.8 and 4.0 %.

In order to obtain more detailed information about the crystal structure of the nano-gold particles, Rietveld analysis of the deposited metal phase has been performed with a sample exhibiting a more intense gold signal. A summary of the refinement is given in Table 1 and Figure 3. Since gold crystallizes in a FCC lattice there are no fractional co-ordinates of atoms to refine. Only lattice parameter and profile parameters are refined in the fitting procedure. Compared to bulk gold with $a = 4.0783 \text{ \AA}$ lattice parameter, a slightly larger value was determined for the nanoparticulate gold, $a = 4.0971(3) \text{ \AA}$. The width of the Au signals was also used to estimate the average particle size via the Scherrer equation. From the diffractogram shown in Fig. 3, a size of 11.3 nm was obtained, which clearly exceeds the pore dimensions.

Pore-size distributions of pristine and TiO_2 -loaded MCM-48 (reference batch) and a complete Au/TiO_2 -MCM-48 catalyst are presented in Figure 4, and the porosity data are summarized in Table 2. The results confirm the good quality of the siliceous matrix. The decrease of BET surface area and pore volume upon TiO_2 introduction is only slightly above the expectations due to introduction of a non-porous component. The decrease of the average pore size is beyond the detection limit, however, the pore-size distribution curve tails towards smaller values now. After introduction of gold, the pore system was

much more perturbed. The pore-size distribution became significantly broader, tailing now strongly into the micropore range, and the most abundant pore size decreased below 2 nm. These changes relatively to the TiO_2 -loaded sample are more than can be justified by the amount of AuOx species deposited in the pores, and the rather narrow second pore size maximum at 3.5 nm confirms that the pore system has suffered during the gold deposition.

The inset of Fig. 4 gives the pore size distributions of the three samples analyzed, which shows that the damage seen is not accidental, on the contrary, in one case it was even more pronounced. In fact, in preliminary experiments it was observed that MCM-48 matrices with less structural perfection were partly or even totally dissolved during the gold deposition step. The BET surface area measured after gold deposition was still large (Fig. 4, Table 2), but the BET data have to be taken with caution because they may have been influenced by the considerable microporosity formed in the samples. However, the high pore volume of 0.6 - 0.8 ml/g confirms that the porosity of the matrix was largely maintained during gold deposition and the pore system remained accessible.

Figure 5 shows TEM micrographs of Au/TiO_2 -MCM-48 catalysts from two different batches. They exhibit the typical lattice fringes of a well ordered and well maintained silica MCM-48 host structure, i.e. the perturbations of the pore system indicated by the physisorption measurements seem to affect only part of the material. In addition the TEM micrographs also show a modulation of scattering intensity with tiny dark patches in the pores, which apparently arise from gold deposited in the pore system. The presence of gold and titanium in these grains was confirmed by EDX. The fact that the distribution of these patches is not periodic inside the pore system is also supported

by the diffraction experiment and is in accord with common experience. In the micrograph of the reference batch (Fig. 5b), there is also a rather large particle, actually an agglomerate of smaller ones (3-5 nm size), which is clearly deposited on the external support surface. Such features were observed in most micrographs taken from this material. In addition, tiny black particles are concentrated on some parts of the external surface, probably at pore entrances. It will be shown below that the majority of gold species is unreduced in the initial sample whereas a minority is already in the metallic state giving rise, for instance, to the XRD signals discussed above. The external particles seen in Fig. 5b certainly belong to the phase detected by XRD. In the micrograph shown in Fig. 5a, particles cannot be observed either on the external surface or near the pore mouths, and these features were absent in all images taken from this batch. This agrees with the observation that the extent of Au metal detectable by XRD varied among the batches.

XPS and XAFS spectra were measured to establish the electronic state of gold in the catalysts prepared. An XPS spectrum of the reference catalyst is presented in Figure 6. During the measurement, the sample was cooled to 143 K to avoid reduction of the gold species under the X-ray beam, which occurred extensively at room temperature. This reduction could not be completely avoided even by cooling, therefore data acquisition time had to be limited, which resulted in noisy spectra as shown in the figure. Even though the sample had been stored for 5 months ($T = 277$ K, dark, in Ar), the spectrum clearly shows ionic gold: The Au $4f_{7/2}$ binding energy is 86.8 eV, which may be compared with values reported for Au_2O_3 (85.9 eV [33]) and $\text{Au(I)(PPh}_3\text{)NO}_3$ (84.9 eV [34, 35]). Apparently, Au is predominantly in the +3 oxidation state. However, the gold 4f

doublet is not well resolved, which indicates the presence of a second state. It has been tried to fit this signal shape with a second signal, and the result is shown in the figure. It should be noted, however, that an unambiguous fit could not be obtained without introducing a constraint for the BE of the minor state, because there is no feature (peak or shoulder) which would fix its position. This minor species is obviously Au(0). In the fit shown in the figure, its BE was constrained to 84.2 eV, which resulted in a Au(0) percentage of 18 %.

Reduction of the ionic Au species is apparently very facile not only under the X-ray beam: it occurs also at room temperature in the dark. Freshly prepared samples took a violet color typical of Au(0) nanoparticles upon (dark) storage in a glove box at room temperature for 2-3 weeks. Figure 6 also reports an XPS spectrum of a Au/TiO₂-MCM-48 catalyst kept under similar conditions for ca. 8 months. It is obvious that no ionic gold is left in the near-surface region of this sample, and the dramatic influence of the small temperature difference between 295 and 277 K on the gold autoreduction rate is remarkable.

Notably, the observed binding energy of Au 4f_{7/2} at 83.4 eV is lower than the usual binding energy of pure metallic gold (84.0 eV) as has been often reported in the literature (e.g. [36-38]), a more recent example being [39], where gold nanoparticles (average diameter – ca. 3 nm) on γ -Al₂O₃-, ZrO₂-, and TiO₂-supports synthesized by laser vaporization show the Au 4f_{7/2} binding energy at 83.1, 83.9 and 83.4 eV, respectively. These shifts have been frequently interpreted as indicating an electron transfer from the support to the metal although other possible reasons (differential charging, initial or final-state effects due to the small number of atoms in the particles [40-42]) cannot usually be

ruled out as an origin of the effect. No binding-energy shift was found on Au/TiO₂ (110) and Au/SiO₂ model catalysts [43] where a small particle size and good contact between support and metal were clearly demonstrated. A recent analysis of the Auger parameter in supported gold catalysts showed that the negative XPS binding energy shift is not likely to be due to electron transfer [38]. In fact, for our fresh sample (Fig. 6), any attempt to fit the line shape keeping the Au(0) contribution below 84 eV was unsuccessful. Hence, we will not draw any conclusions from the XPS binding energies.

In Figure 7, XANES (a) and EXAFS (b) spectra of three freshly synthesized Au/TiO₂-MCM-48 catalysts are compared with spectra of reference compounds. The XANES region shows immediately that the predominant oxidation state in the samples is Au(III). The Fourier-transformed, k^2 -weighted EXAFS spectra consist of two signals, the intensity of which varies to some extent. The first signal is apparently an Au-O coordination, because it appears at a quite different distance than the Au-Cl coordination in auric acid. The spectra show that gold is predominantly coordinated to oxygen. The second peak is due to an Au-Au coordination which could arise from metal or from oxide particles. This question can be decided by analyzing the spectrum in k^3 -weighting, which emphasizes the presence of heavier neighbours, i.e. the Au-Au contribution. An example is shown in Figure 8, where the distances at which Au-Au scattering signals from bulk metal are expected, are marked by arrows. It is obvious from this figure that the major higher shells of Au(0) at 4.8 and 5.6 Å (uncorrected) occur also in the initial Au/TiO₂-MCM-48 catalyst. It was attempted to simulate this spectrum by superposition of the spectra of Au(OH)₃ [44] and with bulk Au, and reasonable agreement was obtained when the proportion of Au metal in the sample was set to 8 %. Hence, some gold metal

particles are present already in the initial catalyst, and the presence of higher shells in their EXAFS spectrum shows that their size should be in the order of several nanometers.

3.2. Catalytic activity in CO oxidation

Figure 9 shows CO conversion data of two catalysts, among them the reference batch. The measurements prove the high activity of the catalysts although they slightly differ in detail. With the reference batch measured in regime A (first contact of catalyst with feed at low temperatures), CO conversion set in between 240 and 250 K, 50 % conversion were achieved at 271 K and complete conversion below 300 K. When the sample was cooled down again, ca. 13 % conversion were seen even at 220 K. Below 250 K, the CO conversion decreased very slowly with decreasing temperature, i.e., the activation energy is very low. Such behavior has been reported earlier [45] and attributed to the catalytic activity of the gold surfaces exposed whereas the Au-TiO_x interface sites responsible for the upsurge of CO conversion at somewhat higher temperatures are still blocked by carbonate species. In the second temperature ramp, the light-off temperature was slightly deteriorated (277 K), and a further upshift to 284 K was seen in the third temperature ramp. Remarkably, the low-temperature activity was not deteriorated although the CO conversions at higher temperatures clearly decayed. If the former reflects a (constant) size of the Au surface area, the latter would, according to Haruta's notion, be related to the Au/TiO_x perimeter. Constant low-temperature conversion at increasing light-off temperature would then indicate a decrease of the perimeter at constant surface area, i.e., a change in particle shape from a flat to a more bulky form.

Figure 9 shows also an experiment according to regime B (first contact of catalyst with feed at room temperature). Here, low-temperature conversion occurred already in

the first ramp. The example shows a more stable sample: its light-off temperature was 269 K, its activity did not suffer any loss in activity in the 2nd ramp, and just a 3 K shift in the third ramp. The stability obtained in this regime was somewhat better although not always as good as shown in Fig.9.

The reproducibility of the preparations was good. Among the six batches made with this procedure, 5 had light-off temperatures within a 20 K range (262-282 K, one at 294 K). The majority of the samples showed some deterioration between the successive ramps as indicated in Fig. 9. The T_{50} differences between 1st and 2nd ramp were between 0 and 10 K for 5 batches, with an outlier at 17 K, between 2nd and 3rd ramp, 4 of 5 batches were between 3 and 10 K. After the 3 ramps, 3 of the 5 batches subjected to the full procedure still achieved 50 % conversion below 290 K, the remaining ones below 310 K. As mentioned above, this deactivation hardly affected the low-temperature CO conversions, which were, however, less reproducible among the different batches: at 220 K, CO conversion was found between 4 and 13 %. This is clearly inferior to the reproducibility of the conversions in the normal temperature range. An explanation might be sought in the matrix damage leading to microporosity: a gold aggregate forming in a small pore may well be capped by the upper wall while most of the Au/TiO_x perimeter remains accessible.

3.3. Critical parameters in the preparation

It is well known that photoreduction of ionic Au precursors has an unfavorable impact on supported gold catalysts. This effect appears to be very dramatic with the catalyst type discussed here: after exposure of fresh catalysts to visible light, the light-off temperature increased to >423 K.

In [29], the TiO₂-MCM-48 stage of the synthesis had been performed by threefold impregnation of MCM-48 with tetrabutyl orthotitanate. The synthesis has been repeated in preliminary work for comparison, and no significant differences in catalytic activity were noted that could be ascribed to the use of different Ti sources. This is in line with earlier findings that the TiO₂-MCM-48 prepared by the two routes are indistinguishable by XAFS, the TiO₂ phase being highly disordered and with a short-range order closer to rutile than to anatase [28]. In fact, some earlier preparations yielded light-off temperatures of 253 K [28,46] with somewhat higher Ti content, which was not reproduced in the present study. The difference is, however, obviously not due to the stage of Ti introduction. This finding is consistent with the recent investigation by Schüth et al. [47] who studied the immobilization process of colloidal gold particles on TiO₂ supports with different phases and particle sizes. CO oxidation activities were not strongly influenced by the phase composition while the particle size of the support turned out to be relevant.

Concentrations of both HAuCl₄ and NaOH solutions have been found to play an important role for the success of the preparation. With the standard HAuCl₄ concentration ($5 \cdot 10^{-3}$ M), the concentration of NaOH used for pH adjustment was varied in the range of 0.01 - 1 M. The light-off temperatures achieved were >300 K using 1 M NaOH, 262-282 K (*vide supra*) with 0.1 M NaOH, and >320 K with 0,01 M NaOH. The unfavorable effect of the high concentrations is, certainly, due to pH fluctuations during dosing. The low concentrations lead to an extension of the experiment since a definite time was given for homogenization after each dose. Longer contact with the hot impregnation solution might well have caused more extensive structural damage than shown in the pore-size

distributions of Fig. 4, which may explain the activity losses observed.

The stability of the MCM-48 matrix is certainly a critical aspect of the synthesis. It was, however, found that good catalytic activity may be obtained even despite significant perturbations of the pore system, and the suggestion of activity losses due to matrix damage rests on plausibility arguments rather than on the limited scope of physisorption data. To prevent damage, the impregnation temperature was reduced to 323 K in some experiments, however, with adverse effects on the catalytic activity. Research is under way to further modify the synthesis for better conservation of the MCM-48 pore system.

Variation of the HAuCl_4 concentration did not lead to improvements either. The best catalysts were obtained in the concentration range mentioned above, double impregnation leading to deterioration rather than to improvements.

4. Conclusions

Gold may be reproducibly introduced into a MCM-48 matrix by a route that comprises impregnation of the siliceous matrix with titanylacetylacetonate and subsequent deposition-precipitation using HAuCl_4 . Characterization of intermediate and final products by XRD, nitrogen physisorption, TEM, XPS and EXAFS shows that the matrix remains intact after Ti introduction but suffers during the gold deposition step, and that the gold is largely deposited in ionic form, except for a minority which ends up in large metal particles on the external MCM-48 surface. The ionic gold undergoes autoreduction at room temperature in Ar even under dark conditions, which can be effectively suppressed by storing the samples at lower temperature (273 K). The catalysts exhibit 50 % CO conversion between 262 and 282 K, with good reproducibility. Significant CO

conversion – with very low activation energy – was obtained at much lower temperatures. This low-temperature activity, which has been related to Au sites not in contact with the TiO₂ component in the literature, was less reproducible. From the data one may suggest that further modification of the synthesis aiming at the conservation of the pore system still bears promise for improvement.

Acknowledgements

We acknowledge financial support by the Deutsche Forschungsgemeinschaft in the frame of the Sonderforschungsbereich “Metal-support interactions in heterogeneous catalysis”, SFB 558 (Projects B3 and A3). The authors are grateful to Dr. A. Birkner and Dr. M. K. Schröter for TEM measurements, and to Ms. Susanne Buse for nitrogen physisorption measurements. We also thank Prof. C. Louis (Paris) for allowing usage of Au(OH)₃ XAFS data measured in her group.

References

- [1] G.C. Bond, D.T. Thompson, *Catal. Rev. Sci. Eng.* 41 (1999) 319.
- [2] M. Valden, X. Lai, D.W. Goodman, *Science* 281 (1998) 1647.
- [3] J.A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, M. Perez, *Science* 318 (2007) 1757.
- [4] B. Hammer, J.K. Norskov, *Nature* 376 (1995) 238.
- [5] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* (1987) 405.
- [6] M. Haruta, N. Yamada, T. Kobayashi, S. Ijima, *J. Catal.* 115 (1989) 301.
- [7] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, *J. Catal.* 144 (1993) 175.
- [8] M. Haruta, *Gold Bull.* 37 (2004) 27.
- [9] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, *J. Catal.* 182 (1999) 430.
- [10] E. Seker, E. Gulari, *Appl. Catal. A* 232 (2002) 203.
- [11] J. Hua, K. Wei, Z. Qi, X. Lin, *Appl. Catal. A* 259 (2004) 121.
- [12] P. Claus, S. Schimpf, R. Schödel, P. Kraak, W. Mörke, D. Hönicke, *Appl. Catal. A* 165 (1997) 429.
- [13] C. Bianchi, F. Porta, L. Prati, M. Rossi, *Top. Catal.* 13 (2000) 231.
- [14] B.S. Uphade, Y. Yamada, T. Akita, T. Nakamura, M. Maruta, *Appl. Catal. A* 215 (2001) 137.
- [15] R.J.H. Grisel, P.J. Kooyman, B.E. Nieuwenhuys, *J. Catal.* 191 (2000) 430.
- [16] M. Okumura, S. Nakamura, S. Tsubota, T. Nakamura, M. Azuma, M. Haruta, *Catal. Lett.* 51 (1998) 53.
- [17] M. Bowker, A. Nuhu, J. Soares, *Catal. Today* 122 (2007) 245.
- [18] A. Wolf, F. Schüth, *Appl. Catal. A* 226 (2002) 1.
- [19] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J. B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [20] A. Corma, *Chem. Rev.* 97 (1997) 2373.
- [21] C.M. Yang, M. Kalwei, F. Schüth, K.J. Chao, *Appl. Catal. A* 254 (2003) 289.
- [22] D.T. On, D. Desplantier-Giscard, C. Danumah, S. Kaliaguine, *Appl. Catal. A* 222 (2001) 299.
- [23] E. Sacaliuc, A. M. Beale, B.M. Weckhuysen, T.A. Nijhuis, *J. Catal.* 248 (2007) 235.
- [24] J.P. Gabaldon, M. Bore, A.K. Datye, *Top. Catal.* 44 (2007) 253.
- [25] H. Gies, S. Grabowski, M. Bandyopadhyay, W. Grünert, O.P. Tkachenko, K.V. Klementiev, A. Birkner, *Microporous Mesopor. Mater.* 60 (2003) 31.
- [26] O.P. Tkachenko, K.V. Klementiev, E. Löffler, I. Ritzkopf, F. Schüth, M. Bandyopadhyay, S. Grabowski, H. Gies, V. Hagen, M. Muhler, L. Lu, R.A. Fischer, W. Grünert, *Phys. Chem. Chem. Phys.* 5 (2003) 4325.
- [27] M.W.E. van den Berg, S. Polarz, O.P. Tkachenko, K.V. Klementiev, M. Bandyopadhyay, L. Khodeir, H. Gies, M. Muhler, W. Grünert, *J. Catal.* 241 (2006) 446.
- [28] M. Bandyopadhyay, A. Birkner, M.W.E. van den Berg, K.V. Klementiev, W. Schmidt, W. Grünert, H. Gies, *Chem. Mater.* 17 (2005) 3820.
- [29] M. Bandyopadhyay, O. Korsak, M.W.E. van den Berg, W. Grünert, A. Birkner, W. Li, F. Schüth, H. Gies, *Microporous Mesopor. Mater.* 89 (2006) 158.
- [30] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.

- [31] K. V. Klementiev, *VIPER for Windows (Visual Processing in EXAFS Researches)*, freeware, www.desy.de/~klmn/viper.html.
- [32] O.P. Tkachenko, K.V. Klementiev, M.W.E. van den Berg, N. Koc, M. Bandyopadhyay, A. Birkner, C. Wöll, H. Gies, W. Grünert, *J. Phys. Chem. B* 109 (2005) 20979.
- [33] J.J. Pireaux, M. Liehr, P.A. Thiry, J.P. Delarue, R. Caudano, *Surf. Sci.* 141 (1984) 221.
- [34] A.I. Kozlov, A.P. Kozlova, H.C. Liu, Y. Iwasawa, *Appl. Catal. A* 182 (1999) 9.
- [35] Y.Z. Yuan, A.P. Kozlova, K. Asakura, H.L. Wan, K. Tsai, Y. Iwasawa, *J. Catal.* 170 (1997) 191.
- [36] J. Radnik, C. Mohr, P. Claus, *Phys. Chem. Chem. Phys.* 5 (2003) 172.
- [37] S. Schimpf, M. Lucas, C. Mohr, U. Rodemerck, A. Brückner, J. Radnick, H. Hofmeister, P. Claus, *Catal. Today* 72 (2002) 63.
- [38] A. Zwiijnenburg, A. Goossens, W.G. Sloof, M.W.J. Crajé, A.M. van der Kraan, L.J. de Jongh, M. Makkee, J.A. Moulijn, *J. Phys. Chem. B* 106 (2002) 9853.
- [39] S. Arrii, F. Morfin, A.J. Renouprez, J.L. Rousset, *J. Am. Chem. Soc.* 126 (2004) 1199.
- [40] M.G. Mason, *Phys. Rev. B* 27 (1983) 748.
- [41] S.B. DiCenzo, G.K. Wertheim, *J. Electron Spectrosc. Relat. Phenom.* 43 (1985) C7.
- [42] F. Parmigiani, E. Kay, P.S. Bagus, C.J. Nelin, *J. Electron Spectrosc. Relat. Phenom.* 36 (1985) 257.
- [43] C.C. Chusuei, X. Lai, K. Luo, D.W. Goodman, *Top. Catal.* 14 (2001) 71.
- [44] R. Zanella, S. Giorgio, C.H. Chin, C. Henry, and C. Louis, *J. Catal.* 222 (2004) 357-367.
- [45] M. Haruta, *Cattech* 6 (2002) 102.
- [46] M.W.E. van den Berg, W. Grünert, H. Gies, O. Korsak, in preparation (2008).
- [47] M. Comotti, C. Weidenthaler, W.C. Li, F. Schüth, *Top. Catal.* 44 (2007) 275.
- [48] U. Ciesla, F. Schüth, *Microporous. Mesopor. Mat.* 27 (1999) 131

Table 1. Experimental parameters used for the structure refinement of gold nanoparticles inside TiO₂/MCM-48

Diffractionmeter	Siemens D 5000
Sample holder	capillary
Wavelength [Å]	1.54053
2θ range [°]	35 - 85
Step size [° 2θ]	0.0079
Number of points	6329
Total no. of reflections	5
Fwhm (2θ=38.000(7) °)	0.74
Peak profile	TCH-Pseudo-voigt
Space group	Pca2 ₁ (29)
Lattice parameter	
a [Å]	4.0971(3)
Number of parameters	3
R _{wp}	73.4
R _{exp}	66.1
χ ²	1.23

Table 2. Porosity data of MCM-48, TiO₂/MCM-48, and Au-TiO₂/MCM-48

Sample (n ^a)	Surface area, m ² / g	Pore volume, cm ³ / g	Most abundant pore diameter ^b , nm
MCM-48 (4)	1080 ± 30	1.09 ± 0.04	2.26 ± 0.07
TiO ₂ /MCM-48 (3)	965 ± 45	0.96 ± 0.01	2.22 ± 0.07
Au-TiO ₂ /MCM-48 (3)	820 ± 150	0.73 ± 0.09	< 2.0

^anumber of samples studied ^b average pore size underestimated by BJH method below 3 nm [48], data to be used only for comparison between samples.

Figure Captions:

- Figure 1.** Schematic representation of the preparation of Au/TiO₂-MCM-48 catalyst.
- Figure 2.** Small and wide angle powder X-ray diffractograms of pristine MCM-48, TiO₂-MCM-48, and Au/TiO₂-MCM-48 (all reference batch). While there are no reflections due to TiO₂, weak Au signals can be discerned.
- Figure 3.** Results of Rietveld analysis of the diffractogram of an as-prepared Au/TiO₂-MCM-48 catalyst. For parameters of the model used see Table 1
- Figure 4.** Pore-size distributions from N₂ physisorption experiments (BJH method) of original MCM-48, TiO₂-MCM-48, and Au/TiO₂-MCM-48 (reference batch). Porosity parameters obtained (BET surface area, pore volume), MCM-48 – 1080 m²/g, 1.09 ml/g, TiO₂-MCM-48 – 967 m²/g, 0.96 ml/g, Au/TiO₂-MCM-48 – 930 m²/g, 0.81 ml/g. Inset – 3 batches of Au/TiO₂-MCM-48, porosity parameters, ◇ - as in main panel, * - 870 m²/g, 0.78 ml/g, ★ - 650 m²/g, 0.60 ml/g. The BET surface area Au/TiO₂-MCM-48 may be affected by microporosity effects.
- Figure 5.** TEM images of as-synthesized Au/TiO₂-MCM-48. Contrast variation shows the periodic ordering over the grains and the presence of heavy matter in the pores. The presence of Au and Ti was confirmed by EDX. In b (reference batch), a large extra-zeolite particle can be seen, together with concentrations of very small particles, probably located at pore entrances.
- Figure 6.** Au 4f XP spectra of Au/TiO₂-MCM-48 catalysts after different storage – 5 months at 277 K (reference batch) or 8 months at room temperature (all in the dark).

Figure 7. X-ray absorption spectra (Au L3 edge at 11919.0 eV) of three different Au/TiO₂-MCM-48 batches, compared with spectra of reference substances. a) XANES, b) EXAFS, Fourier-transform of the k^2 -weighted spectra, $4.50 \text{ \AA}^{-1} < k < 14 \text{ \AA}^{-1}$. The asterisk denotes the spectrum used for the analysis shown in Fig. 8.

Figure 8. Superposition of the EXAFS spectra of Au(OH)₃ and Au metal to reproduce that of an initial Au/TiO₂-MCM-48 catalyst. The spectra are presented in k^3 weighing to emphasize the contributions of the Au-Au coordinations. The arrows indicate the higher shells of bulk gold (cf. reference spectrum in Fig. 7), the larger of which clearly seen. The spectrum of the catalyst was best reproduced with 8 % Au(0).

Figure 9. Temperature dependence of CO conversion for two different Au/TiO₂-MCM-48 batches. 1 % CO in synthetic air at 67 ml/min, 50 mg catalyst (80,000 ml/h g_{cat}). Three successive temperature ramps are shown. Regime A – as-prepared (dried) catalyst cooled to 230 K, subsequently heated in the feed mixture, data shown are from reference batch, regime B – as-prepared (dried) catalyst contacted with the feed at room temperature, cooled to 210 K, then ramped to 310 K.

Figure 1,

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9