Feasibility of Methyl Mercaptane as Probe Molecule for Supported Gold Nanoparticle Surface Area Determination

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Abstract: Gold nanoparticles supported on TiO_2 were probed by adsorption of methyl mercaptane (MM), and the process was quantified gravimetrically. This method allowed discrimination between weakly adsorbed (physisorbed) and strongly bound (chemisorbed) methyl mercaptane. Strong adsorption of MM occured on exposed Au faces, while low-temperature pre-treatment (30 °C) completely suppressed adsorption of MM on the TiO_2 support. The thus obtained high selectivity of MM adsorption on Au enabled characterization of the gold surface area and the resulting values are comparable with other noble metal systems of similar average particle size. The estimated adsorption stoichiometry indicates that the entire Au surface is probed.

Keywords: Au/TiO_2 · Chemisorption · Methyl mercaptane · Surface area

Introduction

Surfaces of condensed matter play an important role in nature and many technical devices, because it is at their interface with the environment where most crucial processes occur. Examples are photosynthesis, solid catalyzed reactions, corrosion, photovoltaic devices, batteries and sensors.

In heterogeneous catalysis, the catalyst is usually a solid in a surrounding fluid phase, with reactants adsorbing and reacting on the solid surface and products desorbing from it. These processes are normally strongly affected by various properties of the solid, such as elemental composition and distribution, textural and structural properties (surface area, pore size distribution, particle size, crystallinity). The exposed total surface area is usually estimated by nitrogen adsorption using the well-known BET method, which is assumed to be insensitive to the chemical composition of the surface.[1]

Since many catalytic systems consist of a well-dispersed active phase (mostly a noble metal) deposited on a metal oxide support, determining the surface area of the active component is a necessary requirement for understanding structure–performance relationships. Here, nitrogen physisorption will not yield data on the available noble metal surface and thus a highly selective adsorption method is required. This is usually performed by chemisorption of a suitable probe molecule.

Prerequisite for a suitable probe molecule is the formation of a monolayer of adsorbate on the surface of interest, *i.e.* probing the entire surface. For the traditionally used noble metals, H_2 and CO are most useful and normally fulfill this requirement. However, chemisorption of these molecules on Au is often limited to adsorption on low-coordinated atoms only,[2] and has to be carried out at low temperature.[3]

In the past two decades gold, previously considered to be inactive, has attracted ever growing interest in the heterogeneous catalysis research community. It has been found to exhibit excellent activity in numerous reactions.[4] A peculiar characteristic of Au is the strong dependence of the activity on its particle size.[5,6] Therefore, for supported Au catalysts knowledge on and control of the particle size is very important. Due to the limitations of H_2 and CO chemisorption described above, qualitative, or semi-qualitative analysis of the Au surface area is generally obtained only by TEM or STEM analysis. This might yield reasonable information in situations where sufficiently large contrast between support and Au is available; inevitably, very small Au particles or Au particles supported on 'heavy' metal oxide supports will yield poorer data.

Therefore, it was our goal to search for a new potential probe molecule for chemisorption on Au surfaces and evaluate the viability of Au surface area determination from these chemisorption measurements. We drew our inspiration from the various literature on self-assembled monolayers (SAMs),[7] where Au surfaces are covered with a monolayer of long-chained thiols. The binding between the thiolate and Au surface is feasible at room temperature and rather strong. Additionally, large Au facets are covered, and not only low coordinated atoms, an important feature in surface area determination. We choose the smallest thiol, methyl mercaptane (MM), as probe molecule due to its high vapor pressure at room temperature and relatively low toxicity (compared to *e.g.* H_2S). Gold supported on titania, one of the most frequently used Au-catalysts,[4] was chosen as model system in this investigation. The rather good contrast between Au and TiO_2 allowed good quality STEM data to be obtained. We have reported our detailed investigations recently.[8] Here we extended our investigations to some commercially available Au/TiO_2 reference samples which further support the viability of the surface area measurement of Au nanoparticles supported on titania.

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Experimental

Gold nanoparticles were prepared by a colloidal synthesis route and deposited on TiO_2 (P25, Degussa) by a method developed in our group,[9] which allows for control of the average Au particle size.[6] Hydrogen tetrachloroaurate trihydrate (Alfa Aesar, 99.99%) served as Au precursor. This method was used to prepare 1.1, 2.6, 5.2, 7.6 and 9.9 wt% Au/TiO_2 catalysts (gold loading checked by AAS, for more details, see ref. [8]). One batch of TiO_2 was subjected to the same treatment as the Au/TiO_2 catalysts, with the exception of the addition of Au particles. Additionally, two commercially available catalysts, a 1 wt% Au/TiO_2 (AuTEK) and 1.5 wt% Au/TiO_2 (World Gold Council) were used as reference materials.

The adsorption of MM was monitored gravimetrically on either a Netzsch STA 449 C or a Netzsch STA 409 thermoanalyzer using the PulseTA technique.[10] This technique is based on the injection of a known amount of gas in an inert carrier stream and monitoring incremental changes in sample mass and gas composition. A description of the application of this method to monitor adsorption processes can be found in ref. [11]. The exhaust gas was analyzed by an Omnistar (Pfeiffer Vacuum) mass spectrometer connected by a heated (*ca.* 200 °C) stainless steel capillary. The experiments were carried out as follows: the as-prepared sample was heated with a rate of 10 K/min in flowing He (50 ml/min) up to a chosen pre-treatment temperature (*vide infra*). Subsequently, the sample was cooled down to the adsorption temperature (generally 35 or 90 °C) and was subjected to a series of MM pulses (MM obtained from Linde AG as a 5.26 wt% mixture in He at *ca.* 10 bar pressure). The adsorption was monitored by recording mass changes resulting from the adsorption of the probe molecule. Injection of MM was stopped when the difference in mass uptake during two following pulses were negligible after total desorption of the physisorbed MM.

The number of Au surface atoms required for the determination of the stoichiometric factor (MM/Au_{SURF}) was estimated using a simple geometric model adapted from Van Hardeveld and Hartog.[12] We assumed cuboctahedral particles (cuboctahedral symmetry is common for unsupported Au nanoparticles[13,14]) with an identical number for height (amount of Au layers) and length of the sides of the hexagon. See refs [8,15] for a more detailed description.

Results and Discussions

Optimization of Experimental Settings

The first step in this investigation was the determination of proper experimental conditions, *i.e.* temperatures of pre-treatment and adsorption. Since some supports can contribute to the adsorption of probe molecules,[16] the adsorption of MM on bare TiO_2 was evaluated. A typical adsorption experiment is shown in Fig. 1A. After obtaining a stable TG baseline, MM was injected resulting in an irreversible mass increase of the sample, due to strong adsorption (chemisorption) of the probe molecule on the sample. Further injections resulted in only partial irreversible adsorption of MM, with the other part of the probe molecules slowly desorbing, resulting in a slow mass loss of the sample after initial increase. Pre-treatment at temperatures above 90 °C caused considerable adsorption of MM on bare TiO_2 (Fig. 1B), whereas after pre-treating the sample at 30 °C, no MM was adsorbed (within experimental accuracy). Pre-treatment at temperatures above 30 °C led to desorption of surface hydroxyl groups, water and carbon dioxide (as evidenced by MS, not shown), apparently freeing up TiO_2 surface sites for MM adsorption. The temperature of adsorption did not have a large influence on the amount of adsorbed MM. No measurable difference was observed between adsorption performed at 80 or 35 °C on 9.9 wt% Au/TiO_2. Therefore, to suppress the influence of the titania surface, all experiments were performed at 30 °C (both pre-treatment and adsorption).

Mode of Adsorption

Raman spectroscopy was performed on Au/TiO_2 samples previously saturated with MM. Fig. 2 shows the spectra of 5.2, 7.6 and 9.9 wt% Au/TiO_2, with the spectrum of pure TiO_2 subtracted. Samples with an Au loading lower than 5.2 wt% did not show any clear MM-related Raman signals and are therefore not presented. The contribution of MM is visible at 636 (S–C) and 273 cm^{-1} (Au–S).[17] The presences of both of these signals are a strong indication that MM is chemisorbed intact on the Au surface. This is in line with SAM literature,
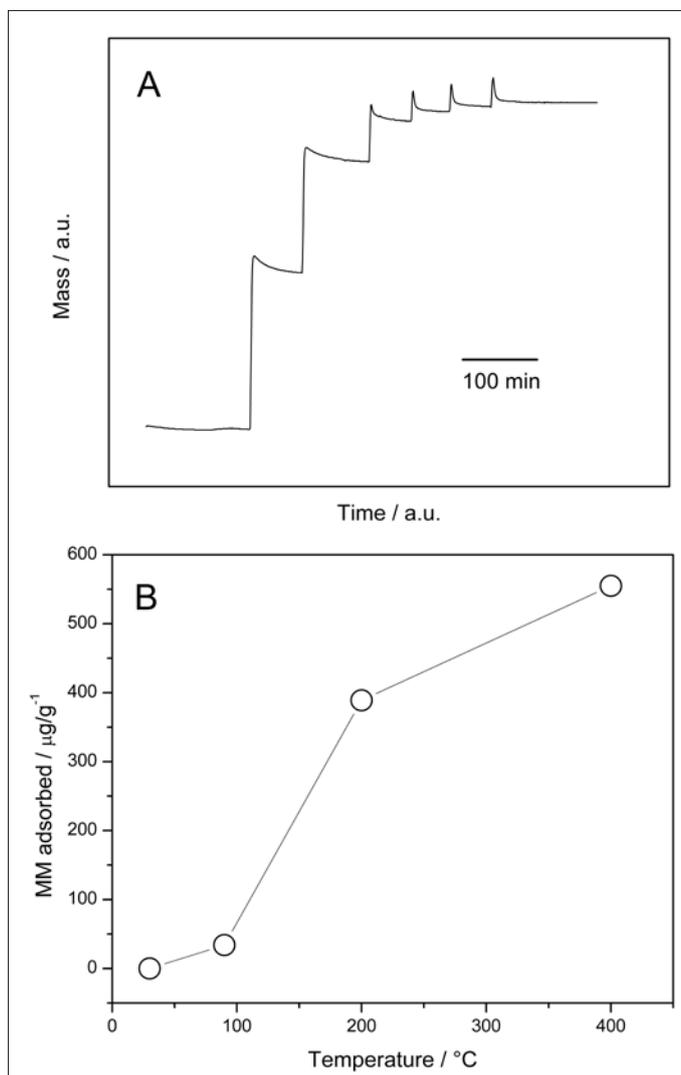
Fig. 1. Mass uptake resulting from the adsorption of MM injected over 9.9 wt% Au/TiO_2 catalyst at 30 °C (A); Effect of pre-treatment temperature on MM adsorption on bare TiO_2 (B).
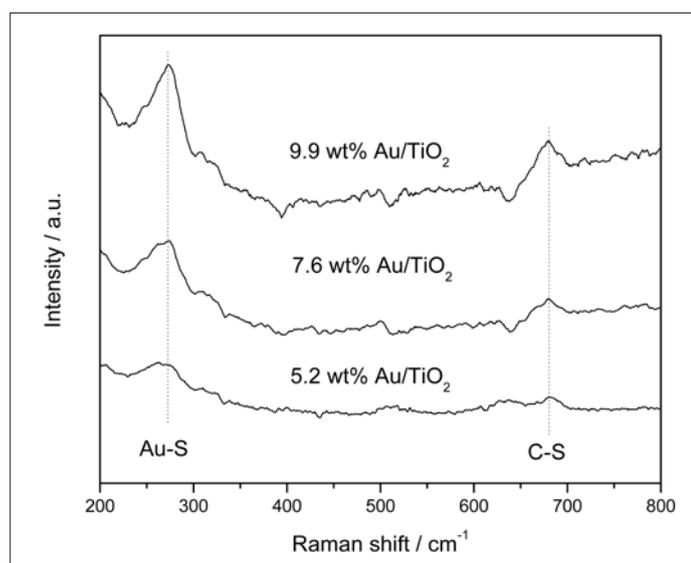
Fig. 2. Raman difference spectra of MM saturated 5.2, 7.6 and 9.9 wt% Au/TiO$_2$ samples.
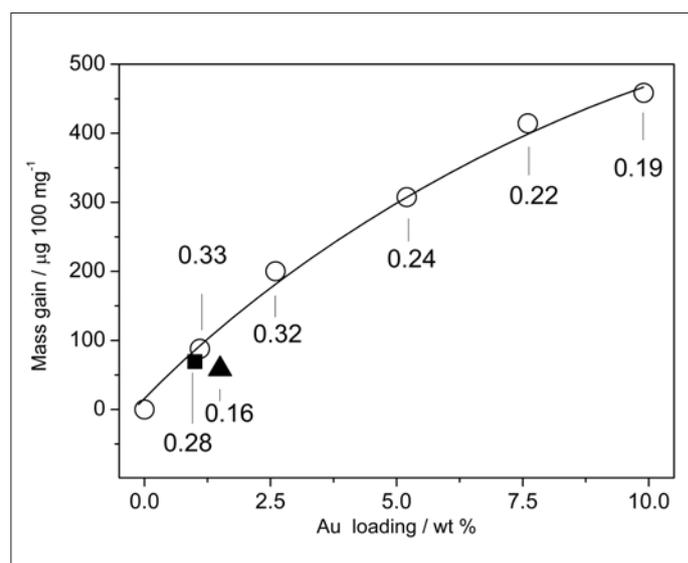
Fig. 3. MM uptake as function of Au loading, numbers indicate the MM/Au$_{TOT}$ ratio.

where thiols are found to chemisorb as thiolates on Au surfaces.[18]

Effect of Au Loading on MM Adsorption

The adsorption of MM on Au/TiO$_2$ with different Au loading is presented in Fig. 3. As expected, the uptake of MM increases with Au loading. This dependence slowly flattens at higher loadings, suggesting that less MM adsorbs per mol Au with increasing Au loading. This is better visible when expressing these uptakes as the molar ratio of chemisorbed MM per mol Au in the sample (MM/Au$_{TOT}$). These values are given beside their corresponding data point in Fig. 3 and decrease from 0.33 (1.1 wt%) to 0.19 (9.9 wt%, WGC). In chemisorption measurements, a decrease in the ratio of probe molecule to total metal atoms usually indicates a reduced dispersion of the metal under investigation or a change in the stoichiometric factor of the adsorption process.[16] Although the synthesis method should have resulted in comparable average particle size distributions in the supported Au systems, the data shows a decrease in MM/Au$_{TOT}$, suggesting an increase in average particle size with increasing Au loading.

The reference materials from AuTEK (1 wt% Au, square) and WGC (1.5 wt% Au, triangle) are also included in Fig. 3, and have MM/Au$_{TOT}$ ratios of 0.28 and 0.16, respectively. Based on these values, the sample from AuTEK seems to have a dispersion comparable to the colloidal-based samples. The WGC sample however has a MM/Au$_{TOT}$ value of 0.16, much lower than samples with comparable weight loadings, and even lower than the 9.9 wt% Au sample.

Effect of Particle Size on MM Adsorption Stoichiometry

As the decrease in MM/Au$_{TOT}$ ratio might indicate an increase in average Au particle size with increasing Au loading, STEM analysis on the colloid-derived samples was performed and more than 600 particles over four or more different STEM images were counted. The thus derived number averaged particle sizes are listed in Table 1 and increases slightly from 1.9 nm for the 1.1 wt% Au sample, to 2.3 for the 9.9 wt% Au sample. Apparently, the particle size is not completely constant during synthesis, and agglomeration of Au particles occurs, resulting in a slight increase of average Au particle size with increasing Au loading.

As mentioned in the introduction, any suitable chemisorption probe molecule should preferably cover the entire surface of the particles under investigation. Additionally, since generally dispersion values (surface atoms to total amount of atoms)

are reported, information on the adsorption stoichiometry (MM/Au$_{SURF}$) is also required.

We assumed a cuboctahedral gold particle shape,[13–15] and calculated the average ratio Au$_{SURF}$/Au$_{TOT}$ (i.e. dispersion) based on the STEM-derived histograms and the geometrical considerations (for more information, see ref. [8]). Combining the thus-derived dispersion value with the Au molar MM uptake (MM/Au$_{TOT}$), an estimate for the MM/Au$_{SURF}$ ratio was obtained (Table 1). The values for the thus estimated stoichiometry factor decrease from 0.55 to 0.35 with increasing particle size. In SAM literature, it is well established that (long-chained) thiols have a stoichiometry factor of 0.33[18–20] on large Au surfaces, i.e. every thiol molecule covers three Au atoms on adsorption. Hostettler et al. found that for average Au particle sizes below 6 nm, an increase in the stoichiometry factor is observed with decreasing particle size.[18] A maximal value of 0.66 was

Table 1. Adsorption uptake of MM over Au/TiO$_2$ samples with different Au loading and corresponding derived Au surface areas.

Sample [wt%]	d$_{average}$[b] [nm]	MM uptake [μg / 100 mg]	Au$_{SURF}$/Au$_{TOT}$	MM/Au$_{SURF}$	Au surface area [m^2 g$_{catalyst}$$^{-1}$]
1.1 [a]	1.9	88	0.60	0.55	2.4
2.6 [a]	2.0	200	0.59	0.54	5.5
5.2 [a]	2.1	308	0.56	0.44	8.5
7.6 [a]	2.2	414	0.56	0.40	11.5
9.9 [a]	2.3	459	0.55	0.35	12.7
1 [c]		69			1.9
1.5 [c]		59			1.6

[a]Data taken from ref. [8]; [b]average Au particle size estimated as described in text; [c]according to supplier.

obtained, *i.e.* two thiol molecules sharing three Au atoms. The different adsorption of MM on smaller particles might be due to the increased fraction of low coordinated atoms in those systems, allowing for other adsorption geometries. Our estimated MM stoichiometry factors show a similar trend with particle size and lie between the values reported for bulk Au and small Au particles. This indicates that indeed the entire Au surface is probed by MM, an important improvement over other probe molecules.[2,3]

Gold Surface Area

With a basic understanding of the adsorption of MM on Au established, the Au surface area can be estimated. We used the MM 'footprint' on an Au(111) face, as determined by Nuzzo *et al.*, being 0.216 nm^2.[19] The Au surface areas obtained range between 1.6 and 12.7 m^2 g^{-1} and are presented in Table 1. These values are comparable with those obtained for other supported noble metal catalysts with similar average particle sizes.

Conclusions

The adsorption of methyl mercaptane on titania-supported Au particles has been examined. The results show that mild pretreatment of the samples is required in order to suppress the adsorption of MM on the titania support. On thus pre-treated samples, MM shows an excellent selectivity for adsorption on Au. However, the optimal pre-treatment procedure found for TiO$_2$ supported Au particles might be different for other supports and further research is required to assess the applicability of this method to differently supported Au catalysts. In this respect, using TG to monitor the adsorption is certainly an advantage, allowing easy discrimination between physisorption and chemisorption.

MM chemisorbs as thiolates on the Au surface and appears to have adsorption geometries similar to larger thiols on ideal Au surfaces or Au nanoparticles. The estimated adsorption stoichiometry lies between 0.55 and 0.35, implying adsorption of MM on the entire Au surface. This is a substantial advantage compared to other probe molecules such as H$_2$ and CO which on Au adsorb only on specific low coordinated sites.

[1] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309.
[2] E. Bus, J. T. Miller, J. A. van Bokhoven, *J. Phys. Chem. B* **2005**, *109*, 14581.
[3] F. Menegazzo, M. Manzoli, A. Chiorino, F. Boccuzzi, T. Tabakova, M. Signoretto, F. Pinna, N. Pernicone, *J. Catal.* **2006**, *237*, 431.
[4] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem., Int. Ed.* **2006**, *45*, 7896.
[5] G. C. Bond, D. T. Thompson, *Gold Bulletin* **2000**, *33*, 41.
[6] P. Haider, B. Kimmerle, F. Krumeich, W. Kleist, J. D. Grunwaldt, A. Baiker, *Catal. Lett.* **2008**, *125*, 169.
[7] P. E. Laibinis, G. M. Whitesides, D. L. Allara, Y. T. Tao, A. N. Parikh, R. G. Nuzzo, *J. Am. Chem. Soc.* **1991**, *113*, 7152.
[8] N. van Vegten, P. Haider, M. Maciejewski, F. Krumeich, A. Baiker, *J. Colloid Interface Sci.* **2009**, *339*, 310.
[9] J. D. Grunwaldt, C. Kiener, C. Wogerbauer, A. Baiker, *J. Catal.* **1999**, *181*, 223.
[10] M. Maciejewski, C. A. Müller, R. Tschan, W. D. Emmerich, A. Baiker, *Thermochim. Acta* **1997**, *295*, 167.
[11] F. Eigenmann, M. Maciejewski, A. Baiker, *Thermochim. Acta* **2000**, 359.
[12] R. Van Hardeveld, F. Hartog, *Surf. Sci.* **1969**, *15*, 189.
[13] A. S. Barnard, L. A. Curtiss, *ChemPhysChem* **2006**, *7*, 1544.
[14] M. J. Yacaman, J. A. Ascencio, H. B. Liu, J. Gardea-Torresdey, *J. Vac. Sci. Technol. B* **2001**, *19*, 1091.
[15] P. Haider, A. Urakawa, E. Schmidt, A. Baiker, *J. Mol. Catal. A: Chem.* **2009**, *305*, 161.
[16] J. J. F. Scholten, A. P. Pijpers, A. M. L. Hustings, *Catal. Rev.-Sci. Eng.* **1985**, *27*, 151.
[17] J. Noh, S. Jang, D. Lee, S. Shin, Y. J. Ko, E. Ito, S. W. Joo, *Current Applied Physics* **2007**, *7*, 605.
[18] M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans, R. W. Murray, *Langmuir* **1998**, *14*, 17.
[19] R. G. Nuzzo, B. R. Zegarski, L. H. Dubois, *J. Am. Chem. Soc.* **1987**, *109*, 733.
[20] G. E. Poirier, M. J. Tarlov, *Langmuir* **1994**, *10*, 2853.