

# Identification of Active Sites and Influence of Real Structure of Gold Catalysts in the Selective Hydrogenation of Acrolein to Allyl Alcohol

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## Abstract

We have successfully employed oxide supported gold catalysts in the gas-phase hydrogenation of acrolein, the  $\alpha,\beta$ -unsaturated aldehyde being most difficult to hydrogenate at the carbonyl group. The relation of structural characteristics and surface state of these catalysts with respect to their activity and selectivity have been studied by surface analytical techniques and high-resolution transmission electron microscopy which was carried out to elucidate the real crystal structures of gold particles. The performance of gold catalysts formed by various preparation and pretreatment procedures was strongly dependent on the reduction time: Increasing the latter resulted in a high number of multiple twinned gold particles which decrease both the selectivity to the desired product, allyl alcohol, and the turnover frequency. Furthermore, it has been demonstrated for the first time that the addition of a

second metal (indium) results in a selective decoration of the faces of nanosized gold particles leaving edges free. The active sites of supported gold catalysts, favoring the adsorption of C=O group of acrolein and subsequent reaction to allyl alcohol, have been identified as edges of gold nanoparticles. The zinc oxide supported bimetallic Au-In catalyst produced allyl alcohol with a selectivity of 63% which is comparable to the best hydrogenation catalysts for this reaction.

## Introduction

In recent years, supported gold catalysts with particle sizes smaller than 10 nm have attracted a lot of attention. While gold bulk metal is rather inert in chemical reactions and, thus, is of low interest for catalysis, highly dispersed gold particles supported on oxides as TiO<sub>2</sub> or ZrO<sub>2</sub> show surprisingly high activities in some reactions important for the chemical industry. The oxidation of carbon monoxide at low temperatures is mainly used as a model reaction to study the unusual properties of gold catalysts (1). Unfortunately, focusing on oxidation reactions masked the capabilities of gold in hydrogenation reactions. Therefore, to evaluate the catalytic potential of gold, other chemical reactions and in particular those which allow the control of selectivity have to be considered. The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to allylic alcohols is of both commercial relevance (e.g. in fine chemical and pharmaceutical intermediate production) and specific scientific interest (2). Note that thermodynamics favors hydrogenation of the C=C over the C=O group (stronger negative free reaction enthalpy of 35 kJ/mol), and for kinetic reasons the C=C bond is more reactive than the C=O group. Thus, in the presence of most of conventional monometallic hydrogenation catalysts, based on Pt, Rh or Pd, lower  $\alpha,\beta$ -unsaturated aldehydes such as acrolein and crotonaldehyde are hydrogenated predominantly to the saturated aldehydes and only to a minor extent to unsaturated alcohols. Therefore,

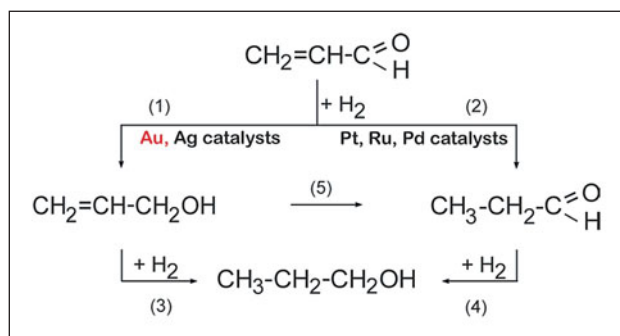


Figure 1

Reaction network of the hydrogenation of acrolein

it is desirable to find catalysts which are able to control the intramolecular selectivity by hydrogenation preferentially the C=O group while keeping the olefinic double bond intact.

In our group the hydrogenation of acrolein (Fig. 1) on supported gold catalysts has been used as test reaction to study several aspects of structure sensitivity, i.e. a dependence of activity and selectivity on the size of gold particles (3-5). Because of the lack of space-filling substituents (e.g. methyl, phenyl) at the C=C group acrolein is the  $\alpha,\beta$ -unsaturated aldehyde which is most difficult to hydrogenate to the unsaturated alcohol (allyl alcohol). The latter must be the criterion for the evaluation of the unusual properties of gold as hydrogenation catalyst. Moreover, from an industrial point of view allyl alcohol is much more important for the chemical industry (e.g. used for glycerol synthesis, allyl ester, epoxidation) than, for example, crotyl alcohol which can be obtained by selective hydrogenation of crotonaldehyde over supported gold catalysts (6-8). However, it must be kept in mind that in the case of crotonaldehyde (or higher  $\alpha,\beta$ -unsaturated aldehydes) the selectivities reported do not represent the intrinsic selectivity of the metal because a methyl (or phenyl) group as substituent on the C=C double bond contributes to the overall selectivity by steric repulsion of the olefinic group changing the adsorption configuration of the aldehyde as shown by a number of experimental data and theoretical calculations (2, 9-11). Note that beside gold on oxidic supports also silver catalysts are the only candidates to selectively produce allyl alcohol (12, 13) according to Fig.1.

In principle, there are two possible reaction pathways for acrolein hydrogenation. Adsorption, activation and subsequent hydrogenation of the C=O group results in production of allyl alcohol (propenol, reaction 1), which is the desired product. By hydrogenation of the C=C group in a parallel reaction propionaldehyde (propanal, reaction 2) can also be formed. Furthermore, the formation of n-propanol as a result of the subsequent hydrogenation of allyl alcohol and/or propionaldehyde is also possible (reactions 3 and 4). Note that propionaldehyde can be produced principally by isomerization of allyl alcohol (reaction 5), too. The present study was undertaken to focus on gaining more knowledge of how the unique catalytic behavior of gold can be controlled by the nanostructure of the catalyst.

## Experimental

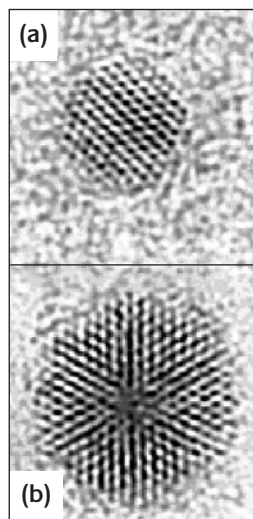
Gold particles were deposited on various oxidic supports ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{SiO}_2$ ) by applying different techniques such as impregnation, incipient wetness and deposition-precipitation. Details of the preparation procedures including pretreatment by calcination and reduction were recently

described (3-5, 14, 15). In the case of the bimetallic Au-In/ZnO catalyst, indium was added to the reduced gold sample by impregnation with  $\text{In}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ , corresponding to the pore volume of the support, followed by drying at 293 K for 12 hours and reducing in a flow of hydrogen at 573 K for 2 hours.

The catalysts were characterized by Conventional Transmission Electron Microscopy (CTEM, estimation of sizes and general morphology of the gold), High Resolution Transmission Electron Microscopy (HRTEM, estimation of the crystal structure of the gold particles as well as of the support), Energy Dispersive X-ray Spectroscopy (EDX, analysis of the composition of bimetallic particles), X-ray Photoelectron Spectroscopy (XPS, estimation of oxidation state of gold and surface composition) and Optical Emission Spectroscopy with Inductively Coupled Plasma (OES-ICP) to estimate the metal content of the catalysts. For some of the gold catalysts, transient experiments were carried out using a TAP (Temporal Analysis of Products) reactor to study gas ( $\text{H}_2$ , acrolein) – catalyst surface interactions (16).

The computer controlled fixed-bed micro reactor, coupled with on-line gas chromatographic analysis, used for the hydrogenation of acrolein was described earlier (17). This system enables us to carry out high-pressure gas phase hydrogenation of unsaturated organic compounds which are liquids with low vapor pressure under ambient conditions.

## Results and discussion

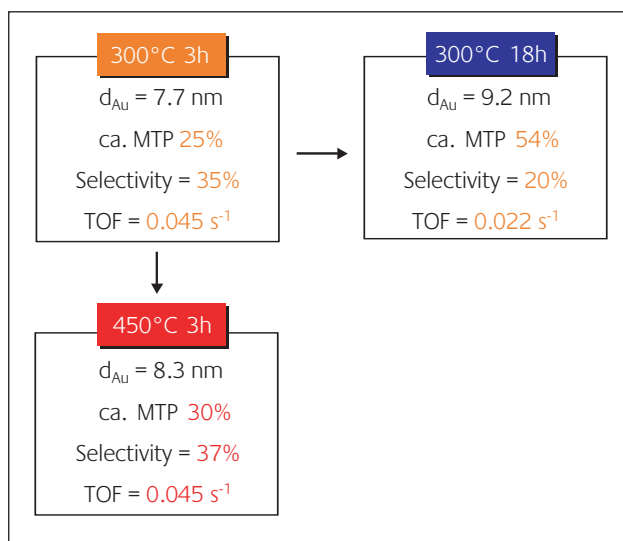


**Figure 2**  
HRTEM images of single crystalline (a) and multiple twinned particles (b)

In the first part of the experiments we focused our work on the influence of the geometrical configuration of the supported gold nanoparticles, namely the occurrence of multiple twinned particles (MTPs, Fig. 2) and the degree of rounding (real structure).

It was found that a higher amount of MTPs resulted in a lowering of selectivity to the desired product allyl alcohol as well as in a lowering of the turnover frequency (14) (Fig. 3). Therefore, the main demand for the catalyst synthesis is that supported gold catalysts with single crystalline gold particles must be prepared.

The higher turnover frequency of gold supported on  $\text{TiO}_2$  compared to  $\text{ZrO}_2$  is attributed to a higher degree of rounding of the former (14).



**Figure 3**

*Influence of catalyst (Au/ZrO<sub>2</sub>-DP) pretreatment in H<sub>2</sub> on the occurrence of multiple twinned particles (MTPs) and on the selectivity to allyl alcohol and turnover-frequency (TOF) during acrolein hydrogenation (T = 513 K, p<sub>TOTAL</sub> = 2 MPa, molar ratio H<sub>2</sub>/Ac = 20, W/F<sub>Ac,0</sub> = 15.3 g h mol<sup>-1</sup>). The increase of the reduction time increases not only the portion of MTPs by a factor of 2, but also slightly the mean particle size (7.7 nm to 9.2 nm). The influence of the latter can be ruled out since an increase of the reduction temperature (from 573 K to 723 K) led also to a slight increase of d<sub>Au</sub>, but the allyl alcohol selectivity and TOF remained constant*

After the recent finding that this hydrogenation reaction preferentially occurs on single crystalline particles rather than multiple twinned ones, the second part of our investigation reports on a new approach to distinguish different features of

**Table 1**

*Results of catalytic hydrogenation of acrolein over zinc oxide supported mono- and bimetallic gold catalysts (15)<sup>1</sup>*

| catalyst  | r<br>[μmol/g <sub>Au</sub> s] | AyOH | PA   | n-PrOH | HC   | d <sub>Au</sub><br>[nm] | D    | TOF<br>[1/s] |
|-----------|-------------------------------|------|------|--------|------|-------------------------|------|--------------|
| Au/ZnO    | 83.4                          | 34.0 | 46.9 | 10.0   | 11.6 | 9.0 ± 0.3               | 0.17 | 0.103        |
| Au-In/ZnO | 42.3                          | 63.3 | 30.4 | 3.5    | 4.4  | 10.1 ± 0.2              | 0.16 | 0.052        |

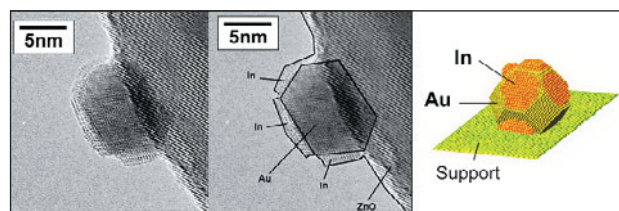
<sup>1</sup>Catalytic activities are expressed in terms of a rate related to the mass of the gold (abbreviated as r) as well as related to the surface area of gold (turnover-frequency, TOF). Selectivity to reaction products allyl alcohol (abbreviated as AyOH), propionaldehyde (PA), n-propanol (n-PrOH) and C<sub>2</sub> and C<sub>3</sub> hydrocarbons (HC). d<sub>Au</sub> = gold particle size, D = dispersion. Reaction conditions: T = 593 K, p<sub>TOTAL</sub> = 2 MPa, W/F<sub>Ac,0</sub> = 15.3 gh mol<sup>-1</sup>, molar ratio H<sub>2</sub>/Ac = 20. Catalyst composition: 1.59 wt%Au, 0.13 wt%In.

**Table 2**

*Results of catalytic hydrogenation of acrolein over zirconia supported gold and platinum catalysts (3)<sup>1</sup>*

| catalyst            | d <sub>M</sub><br>[nm] | r<br>[μmol/g <sub>M</sub> s] | AyOH | PA   | n-PrOH | HC  |
|---------------------|------------------------|------------------------------|------|------|--------|-----|
| Au/ZrO <sub>2</sub> | 3.8                    | 58                           | 41.5 | 53.9 | –      | 0.7 |
| Pt/ZrO <sub>2</sub> | 3.3                    | 4300                         | 3.9  | 91.5 | –      | 4.1 |

<sup>1</sup>Selectivities were compared at nearly identical conversion (X = 3.6% and 3.9% for Au/ZrO<sub>2</sub> and Pt/ZrO<sub>2</sub>, respectively, obtained by systematical variation of W/F<sub>Ac,0</sub>). T = 513 K, p<sub>TOTAL</sub> = 2 MPa, molar ratio H<sub>2</sub>/Ac = 20. Catalyst compositions: 1.2 wt%Au, 0.15 wt%Pt. For abbreviations of reaction products, s. Table 1.



**Figure 4**

*HRTEM image of Au-In/ZnO (left, (15)), and surface model (right)*

the gold particle morphology. By means of HRTEM, the crystal structure of individual gold particles prepared on ZnO (S<sub>BET</sub> = 15 m<sup>2</sup> g<sup>-1</sup>) was investigated (15). Most particles (d<sub>Au</sub> = 9.0 ± 0.3 nm) were single crystalline and practically no MTPs were found. This is an important result because elucidation of the active site issue cannot be simply done by varying the size of gold particles, since the effects of faceting and multiple twinned particles may interfere in other gold nanoparticle systems. In the next step, modification of the gold particle surface by indium has been used to vary the active site characteristics of a suitable catalyst, and a selective decoration of gold particle faces has been observed by detailed HRTEM analysis, leaving edges free (Fig. 4).

Statistical evaluation of appearance of indium on the cubooctahedral gold surfaces was undertaken which supports the selective face decoration by the second metal. EDX analysis revealed a homogeneous distribution of indium on the gold particles and no monometallic indium deposits were found. In Table 1 an overview of the catalytic properties is given. With the bimetallic Au-In/ZnO catalyst, the desired allyl alcohol is the main product formed with a selectivity of

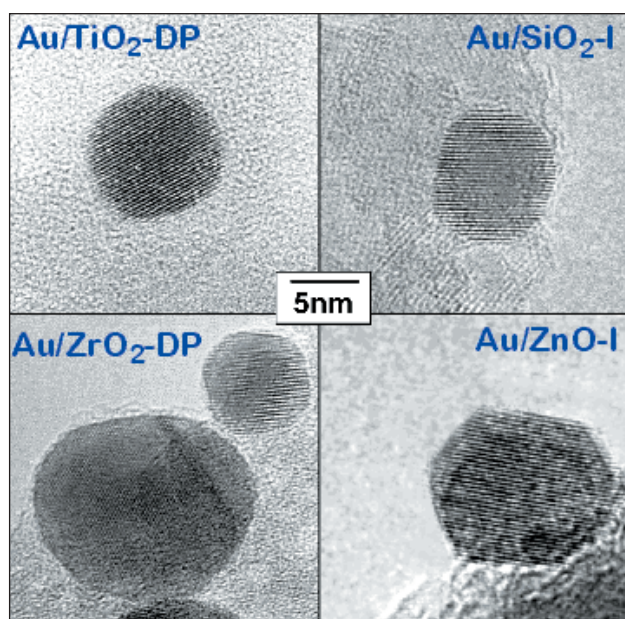
63% (at  $T = 593\text{ K}$  and  $p_{\text{total}} = 2\text{ MPa}$ ). Note that the Au-In system is the first example showing the important impact of a second metal for tuning the selectivity of a gold catalyst in selective hydrogenation of functional groups. The level of selectivity obtained with Au-In/ZnO is one order of magnitude higher compared with conventional mono- and bimetallic catalysts for acrolein hydrogenation (2) and comparable to our best catalyst for the selective hydrogenation of acrolein to allyl alcohol, Ag-In/SiO<sub>2</sub> (18,19). From the experimentally proven correlation between surface structure and catalytic behavior, the edges of single crystalline gold particles have been identified as active sites for the preferred C=O hydrogenation (15).

A further example for the importance of gold as hydrogenation catalyst is illustrated in Table 2 where gold is compared to platinum, both supported on zirconia, in acrolein hydrogenation (3). Preliminary hydrogenation experiments showed that over Pt/ZrO<sub>2</sub> the selectivity to allyl alcohol was always very low (ca. 2%). In order to ensure that this was not due to the high catalyst activity (acrolein conversion of 43% at 473 K) and the related secondary reactions of allyl alcohol (s. Fig. 1), the modified space time  $W/F_{\text{Ac,O}}$  was varied in such a way that a comparison of selectivities for the catalysts Au/ZrO<sub>2</sub> and Pt/ZrO<sub>2</sub> was possible with almost the same acrolein conversion. Even under these experimental conditions propionaldehyde was the main product with Pt ( $S > 90\%$ ). Selectivity to allyl alcohol was only 3.9%, i.e. only one-tenth of the selectivity obtained with Au/ZrO<sub>2</sub> (3). This finding clearly indicates that gold catalysts are more efficient than platinum catalysts in selective acrolein hydrogenation. If the  $\alpha,\beta$ -unsaturated

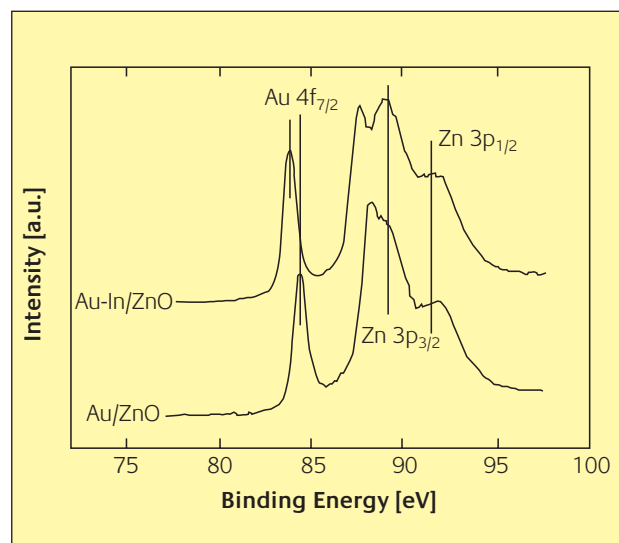
aldehyde as educt is changed from acrolein to, for example, crotonaldehyde, then monometallic Pt catalysts show high selectivity towards the allylic alcohol, e.g. Pt/ZnO (20).

Beside the catalyst characterization by TEM/HRTEM and EDX also XPS experiments were systematically carried out. In most cases, lower binding energies than the Au 4f<sub>7/2</sub> of 84.0 eV (the value of bulk gold atoms) were observed, as mentioned earlier for Au/TiO<sub>2</sub> (5), depending on the oxidic support as well as the pretreatment conditions (21). It is well known, that the Au 4f<sub>7/2</sub> electrons of surface Au atoms have a lower binding energy of 83.6 eV which is explained by the lower coordination number of surface atoms (22). In the present work the origin of the observed differences of the core level values is discussed in terms of different models like an electron transfer from support to the gold particles, size and geometric effects. Again, especially geometric factors like the particle shape seem to play an important role: After a pretreatment in hydrogen at 573 K, the gold particles on SiO<sub>2</sub> and TiO<sub>2</sub> are nearly spherical, whereas on the other supports extended facets of the gold surface are visible, in particular for Au/ZnO (Fig. 5).

On particles exhibiting surfaces with large facets, the amounts of atoms at edges, corners or steps are significantly lower than for rounded particles. Due to this fact, a lower binding energy of the Au 4f<sub>7/2</sub> electrons originating from the atoms of the nearly spherically-shaped particles on SiO<sub>2</sub> and TiO<sub>2</sub> supports can be expected, compared to the Au 4f<sub>7/2</sub> electron binding energy of the atoms from the gold particles supported on ZrO<sub>2</sub> and ZnO. This interpretation is strongly supported by characterizing the bimetallic Au-In/ZnO catalyst with XPS and discussing the results in terms of our knowledge from the in-depth characterization via HRTEM shown above. Due to the geometry of the Au-In particles in the sample Au-In/ZnO, the main part of Au 4f electrons



**Figure 5**  
Representative gold particles on different supports (21)

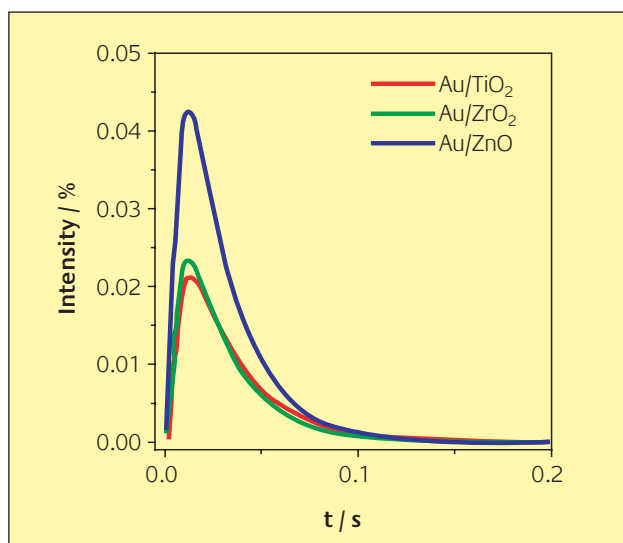


**Figure 6**  
Au 4f (and Zn 3p) spectra of the mono- and the bimetallic gold catalyst (Au/ZnO and Au-In/ZnO) after hydrogen pretreatment at 573 K (21)

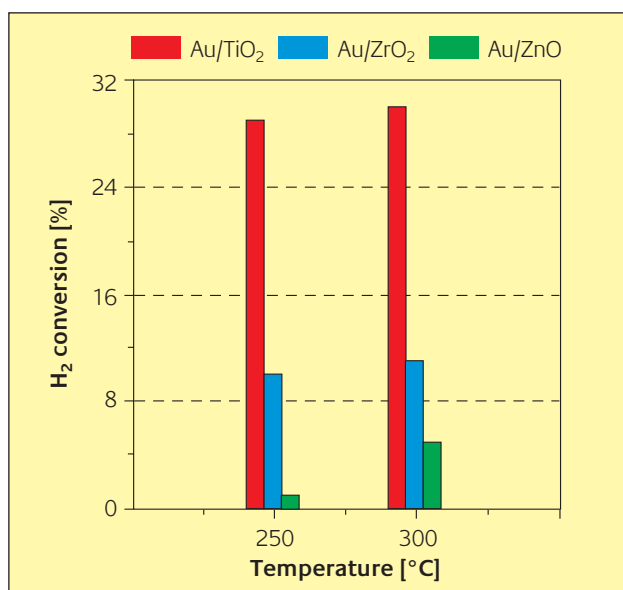


analyzed originates from atoms at edges and corners having low coordination numbers. In contrast, for the monometallic sample Au/ZnO, the majority of the electrons are ejected from atoms situated in the flat facets of the particles. For Au/ZnO, the binding energy of Au 4f electrons was significantly higher, compared to Au-In/ZnO (Fig. 6). This is in excellent agreement with the interpretation of the binding energy shift on the basis of the degree of rounding of the gold surface.

Actually, the activation of hydrogen on supported gold catalysts, a question which is still open, is investigated by our group. It is well-known that gold surfaces do not interact



**Figure 7**  
Typical hydrogen pulse profiles measured in the TAP reactor over gold supported on titania, zirconia and zinc oxide



**Figure 8**  
Hydrogen conversion over gold supported on titania, zirconia and zinc oxide

substantially with hydrogen, however, this might be different for low-coordinated gold-surface sites (edges). A detailed investigation of gold catalysts with the TAP reactor gave a similar transient behavior (an example of typical pulse profiles is shown in Fig. 7) like silver catalysts (16, 23).

For the latter, the response of the interaction of D<sub>2</sub> pretreated with H<sub>2</sub> produced HD which is indicative for the dissociation of molecular hydrogen, whereas pure silver and the support alone did not show H/D exchange in the temperature range 100-500°C. In the case of supported gold catalysts the hydrogen conversion depends on the support used (Au/TiO<sub>2</sub> > Au/ZrO<sub>2</sub> > Au/ZnO, Fig. 8) and corresponds to the catalyst activity during acrolein hydrogenation.

## Conclusions

In-depth characterization of oxide supported gold catalysts was coupled with reaction studies aimed at disclosing the nature of the active sites controlling the hydrogenation of C=O vs. C=C bonds of  $\alpha,\beta$ -unsaturated aldehydes. Elucidation of the active site issue and the structure-sensitivity cannot be simply undertaken by varying the size of gold particles because the latter may interfere with the portion of multiple twinned particles (MTPs) and the degree of particle rounding. Because a large portion of MTPs gave low allyl alcohol selectivity (product of C=O group hydrogenation), catalysts with single crystalline gold particles must be prepared by appropriate synthesis methods. The modification of gold particles by a second metal (indium) was not only a suitable tool to increase the intramolecular selectivity, but also essential to identify the active sites for this hydrogenation reaction. The present results, coupled with conclusions drawn from new *in-situ* EXAFS experiments with on-line product analysis from the catalytic reactor working at  $p \gg 1$  bar (24), will give deeper insight into kinetics and mechanism of gold catalyzed hydrogenations as a key toward future applications.

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