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Catalytic Materials by Design

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Abstract. Recent activities of our group in the design of catalytic materials are briefly surveyed. Special attention is given to sol-gel-derived mixed oxide aerogels and organic-inorganic hybrid gels, and to supported noble metals with controlled particle size. Examples discussed embrace: organically modified titania-silica aerogels for the epoxidation of bulky olefins, Ru-containing silica hybrid gels for the synthesis of formic-acid derivatives, and colloid-derived supported gold catalysts with controlled metal particle size.

hybrid gels [5][6], grafted oxides [7], perovskites [8], and pillard clays [9]. Metal-based catalysts of interest are bimetallic systems [10], chirally modified noble metals [11][12], and glassy metal alloys [13]. A discussion of our activities in all these areas is beyond the scope of this short research description, the reader is referred to the pertinent references which may provide an entry to the class of materials of interest.

In order to illustrate our research strategy and methodology, three recent examples of catalyst design are briefly discussed, organically modified mixed oxide aerogels, hybrid gels, and supported metal catalysts with controlled metal particle size.

1. Introduction

The design of novel catalytic materials is one of the most challenging areas of heterogeneous catalysis. Although most of the solid catalysts presently used in industry have been the result of empiricism and experience, there is a steadily increasing number of catalysts which have been designed on a rational basis. Rigorous rational design, as opposed to empirical design of a catalyst, requires not only some understanding of the reaction mechanism, but also knowledge and control of the crucial structural and chemical properties of the solid catalyst. Major advances in several fields essential for catalysis, such as surface science, organometallic chemistry, theoretical techniques, solid-state chemistry, material science, surface-analytical instrumentation, and reaction engineering, have led to a drastic reduction in the level of empiricism in catalyst design and moved it closer to the ultimate goal of rational design [1].

Our activities in catalyst design embrace various metal oxides and metals used as catalysts in the synthesis of fine chemicals and also in environmental catalysis [2]. Oxidic materials which are currently in focus include aerogels and xerogels of pure and mixed oxides [3][4],

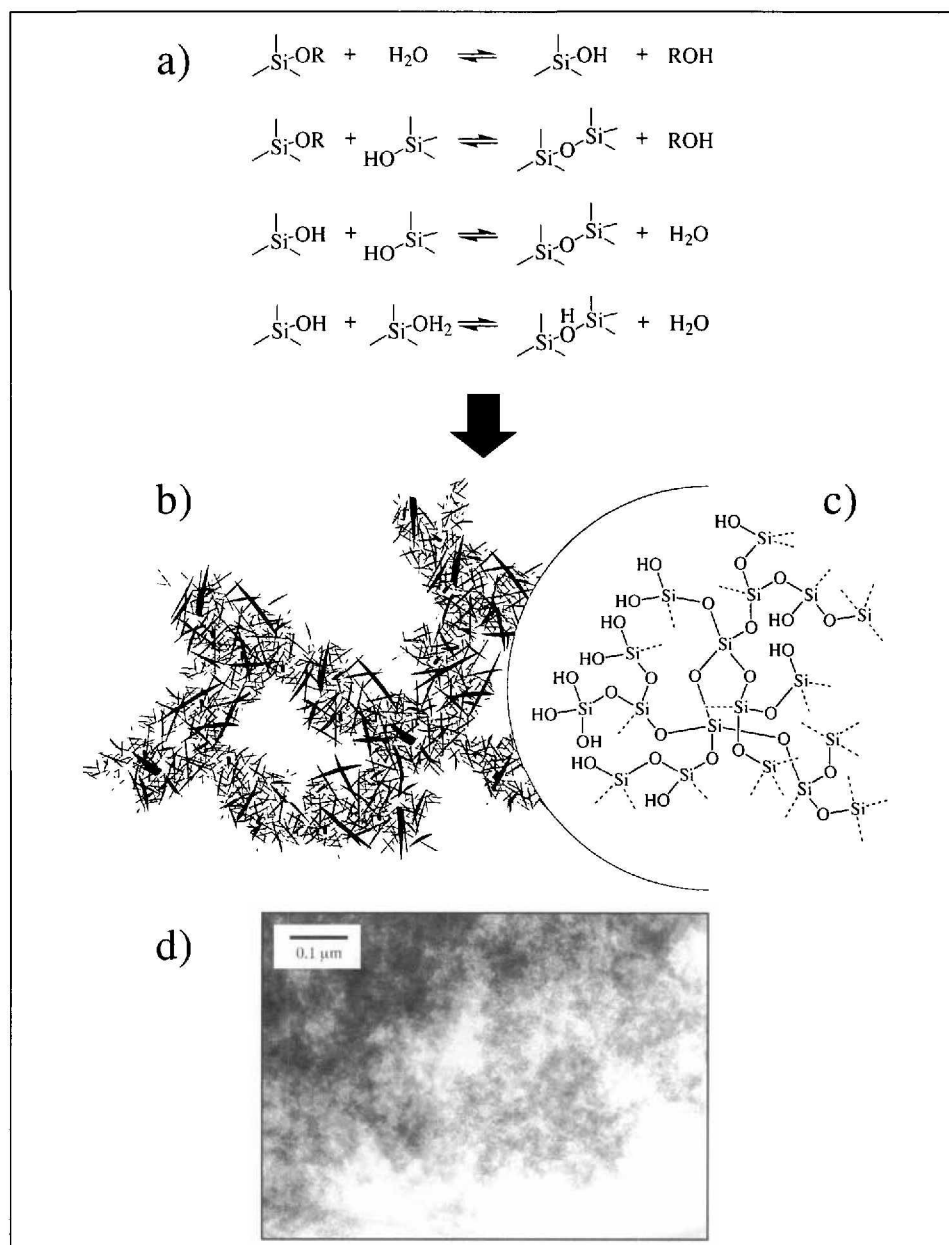


Fig. 1. Schematic illustration of the sol-gel process. a) Sol-gel reactions (hydrolysis and condensation reactions), b) schematic representation of sol-gel network, c) sol-gel linkages, d) transmission electron micrograph (TEM) of a modified titania-silica gel after supercritical drying.

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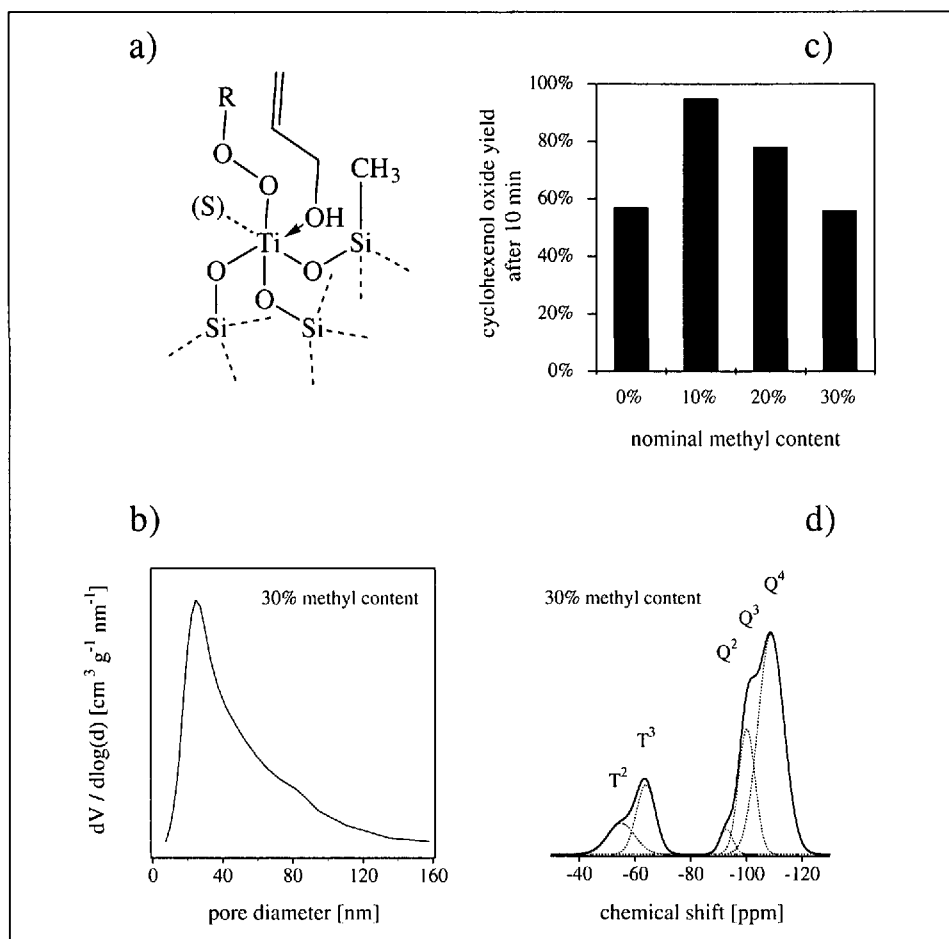


Fig. 2. Properties of titania-silica aerogels prepared with methyl-substituted silane precursors. a) Hypothetical structure of catalytic site, ((S) represents possible ligand introduced by solvent. This ligand may be strongly bound resulting in deactivation), b) pore-volume distribution of a modified aerogel, c) activities of modified aerogels with varying methyl content for cyclohexenol epoxidation, d) ²⁹Si CP-MAS NMR spectrum of a modified aerogel with T sites resulting from the methyl incorporation via modified precursor.

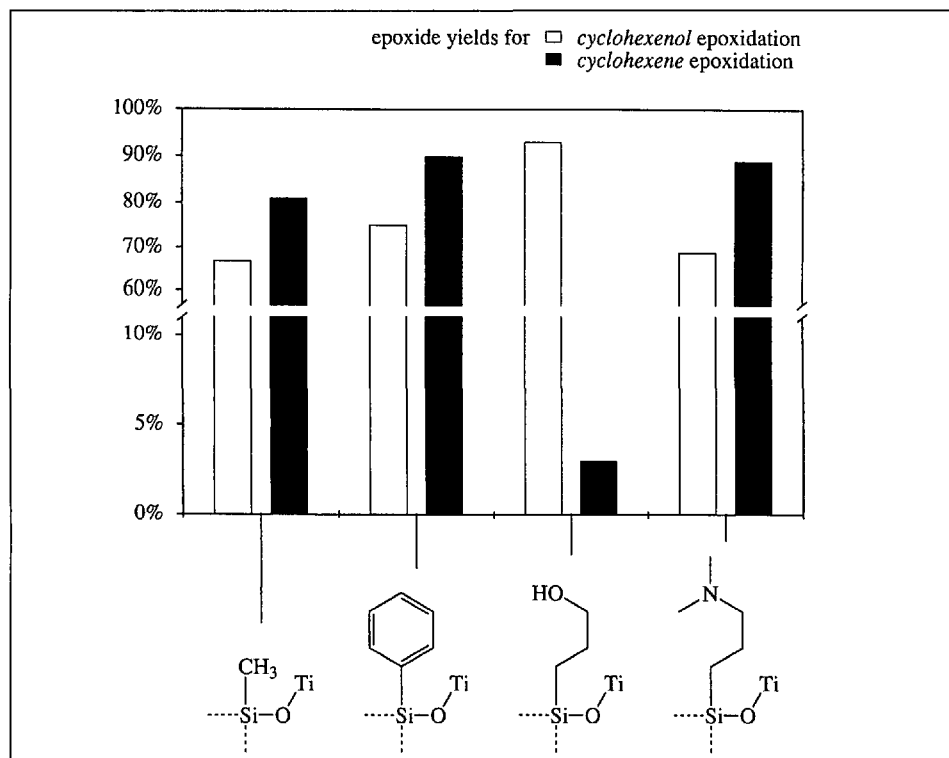


Fig. 3. Epoxide yields for the epoxidation of cyclohexenol and cyclohexene of titania-silica aerogels derived from different silicon precursors containing either methyl, phenyl, hydroxypropyl, or dimethylaminopropyl groups

2. Mixed Oxide Aerogels

Mixing metal oxides on a nanoscale affords unique opportunities for tailoring the chemical and structural properties of multicomponent, oxide-based catalysts. An attractive route for pursuing this aim is the solution-sol-gel (SSG) method, which has been extensively studied [14]. The principle of this method is based on the formation of an oxidic network through several reaction steps. The main wet-chemical reactions are hydrolysis (formation of hydroxy groups) of the metal-oxide precursor, and condensation (formation of bridging bonds), illustrated in Fig. 1, a for a Si-alkoxide. As precursors, inorganic salts in aqueous solution, aggregates of colloidal subunits, and organometallic compounds in mainly organic solution can be used. Among the organometallic precursors, metal alkoxides are applied most frequently.

The chemical reactions create a voluminous inorganic network (gel) which is stabilized by entrapped liquid (solvent). Structural properties of the gels can be controlled by the reaction conditions. Important reaction parameters are: temperature, precursor concentration, type of acid or base used as a catalyst, hydrolysis level, and precursor type. For most applications, the gel has to be freed from the solvent in which the sol-gel process was carried out. The methods usually applied are evaporative drying (leading to xerogels or alcogels), freeze-drying (cryogels), and supercritical drying (leading to aerogels). Depending on the drying method applied, the resulting gels exhibit different textural properties. Evaporative drying usually leads to a significant loss of the porous structure due to detrimental capillary stress. This interfacial stress can be greatly reduced by applying supercritical conditions. The high-temperature supercritical drying is based on transferring the solvent into its supercritical state, whereas the low-temperature method uses supercritical CO₂ to extract the solvent continuously. Fig. 1, b and c illustrates the typical structure of a silica aerogel, in which the tenuous gel network is retained after drying. The morphology of a low-temperature supercritically dried titania-silica aerogel as seen by TEM is illustrated in Fig. 1, d. The voluminous material contains predominantly mesopores, as corroborated by gas adsorption measurements.

The catalytic potential of these materials was demonstrated for the epoxidation of bulky olefins with alkylhydroperoxides [15–17]. The pronounced mesoporosity, the high dispersion of titania in the silica

matrix, and the appropriate treatment preceding the reaction were identified as the most crucial factors for superior catalytic activity of these materials over those conventionally applied [16–18].

An interesting opportunity of the SSG method is the use of organically modified alkoxide precursors which allows tuning of the surface polarity. The Si–C bond is thermally and chemically stable, and thus can be employed to prepare organically modified inorganic materials [19]. Applicability of this method has been demonstrated for titania-silica-based epoxidation catalysts [20][21], albeit with moderate catalytic results. Recently, we adapted the technique in an attempt to combine the previously optimized sol-gel method with the usage of modified silane precursors for the synthesis of an organically modified hydrophobic aerogel. The target structure is depicted in Fig. 2, a, presenting an ideally dispersed titania site within a silica matrix that is partially modified by a methyl group. The appropriate tuning of the sol-gel parameters leads to a titania-silica mixed oxide with a mesoporous structure (Fig. 2, b), wherein the methyl group is covalently incorporated, as evidenced by the presence of different methyl-containing silicon structural units (T² and T³ sites) in the ²⁹Si-NMR spectrum given in Fig. 2, d. The T (triplet) site represents a silicon nuclei with one adjacent carbon atom, the exponent designates the number of neighboring Si–O–Si linkages (as opposed to Si–OH bonds). The modification has a significant influence on the epoxidation of cyclohexenol to cyclohexenol oxide as illustrated in Fig. 2, c. With increasing methyl content, a maximum yield is observed for 10% nominal methyl content. A positive influence of the modification on the epoxidation reaction has been demonstrated for a series of allyl alcohols, whereas for olefins the methyl incorporation had a negative influence. Allyl alcohols are assumed to adsorb on the titanium site in contrast to olefins, which do not interact with titanium [22]. It is assumed that the steric hindrance induced by the methyl group leads to a favorable arrangement of the titanium-bound allyl alcohol and the oxidant, whereas with olefins the absence of adsorption on titanium sites precludes this.

Recently, the investigations have been extended to several other modifiers. The aim was to incorporate functional groups in order to study their influence on the catalytic behavior. Methyl-modified catalysts have been compared with catalysts modified by phenyl, alcohol, or amino groups. The catalytic behavior of these

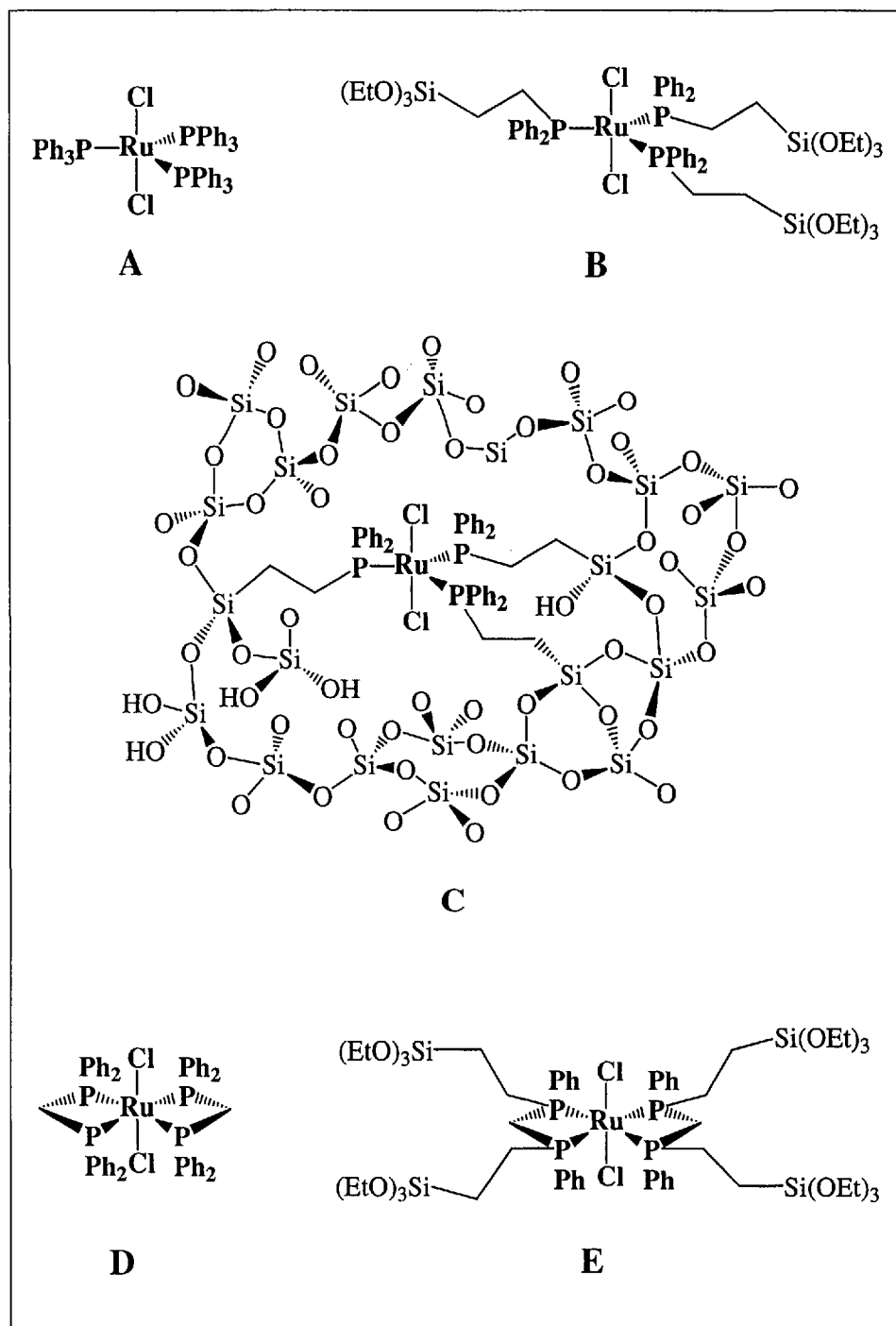


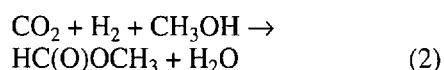
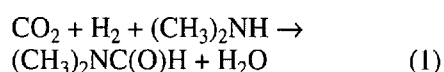
Fig. 4. Concept of hybrid catalysts: functionalization of the homogeneous Ru complex A leads to B, which is used as a precursor suitable for anchoring into a silica matrix via a sol-gel process C. Bidentate ruthenium complexes of the type D and E which exhibits higher activity and improved stability compared to the monodentate complex A.

materials for the epoxidation of cyclohexenol and cyclohexene is summarized in Fig. 3. Compared to the catalyst modified with methyl groups, improved yields were observed with other substituents. The hydroxypropyl-modified catalyst showed best results for the allyl-alcohol (cyclohexenol) oxidation, whereas for cyclohexene epoxidation superior catalytic behavior was achieved with a phenyl-modified material. It should be noted that the best olefin selectivity was reached for both reactions with the amino substituent.

3. Hybrid Gels

Hybrid gels, consisting of metal complexes or organometallic compounds which are anchored on an oxide network, allow to merge advantageous features of both homogeneous and heterogeneous catalysts [23][24]. The basic idea is to maintain the favorable catalytic properties of the homogeneous catalysts while making them insoluble and thus easier to separate from the products. The design of organic-inorganic hybrid-gel catalysts is

illustrated using the preparation of catalysts for the synthesis of *N,N*-dimethylformamide and methyl-formate from carbon dioxide.



Transition-metal complexes are efficient homogeneous catalysts for these reactions [25–28], and among them $\text{RuCl}_2[\text{P}(\text{CH}_3)_3]_4$ [29][30] and other ruthenium-phosphine complexes [31] are particularly suitable.

The strategy for the heterogenization of two homogeneous ruthenium catalysts is illustrated in Fig. 4. The corresponding preparation processes have been described in detail elsewhere [6]. The homogeneous complexes (Fig. 4, A, D) are functional-

ized by introducing silylether groups. In the acid-catalyzed sol-gel process, these silylether groups and the added tetraethoxysilane (TEOS) are hydrolyzed and co-condensed forming a silica network with covalently bonded active sites (Fig. 4, C).

The resulting xerogels are micro- to mesoporous and have BET (Brunauer, Emmett, Teller) surface areas between 190 to 880 m^2/g , depending on group VIII transition-metal content and preparation conditions. The surface area decreases with increasing content of transition-metal complex.

The structure of the silica matrix was investigated by ^{29}Si -NMR applying single-pulse excitation. In Fig. 5, the original (a) and a deconvoluted spectra (b) are shown for the hybrid gel prepared from $\text{RuCl}_2[\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3]_3$ and TEOS. Signals originating from two different groups of structural units can be identified: silicon species originating from tetra-

alkoxysilane with four oxygen neighbors (Q-group) and silicon species arising from silylether complexes with three oxygen neighbors (T-group). The various species resulting from different degrees of condensation are also summarized in Fig. 5. Quantification of the degree of condensation revealed that a high percentage of the structural units do not undergo complete condensation. A typical spectrum, shown in Fig. 5, a, indicates the following contribution of the various structural units: 46% Q^4 $\{\text{Si}(\text{OSi})_4\}$, 34% Q^3 $\{(\text{HO})\text{Si}(\text{OSi})_3\}$, 4.6% Q^2 $\{(\text{HO})_2\text{Si}(\text{OSi})_2\}$, 7.4% T^3 $\{\text{RSi}(\text{OSi})_3\}$, 5.4% T^2 $\{\text{R}(\text{HO})\text{Si}(\text{OSi})_2\}$, and 2.0% T^1 $\{\text{R}(\text{HO})_2\text{SiOSi}\}$.

To gain further information on structure and state of the organometallic complexes, EXAFS measurements were carried out [6]. Fig. 6 shows extended X-ray absorption fine structures (left) of a hybrid gel made from $\text{RuCl}_2[\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3]_3$. It can be concluded from the

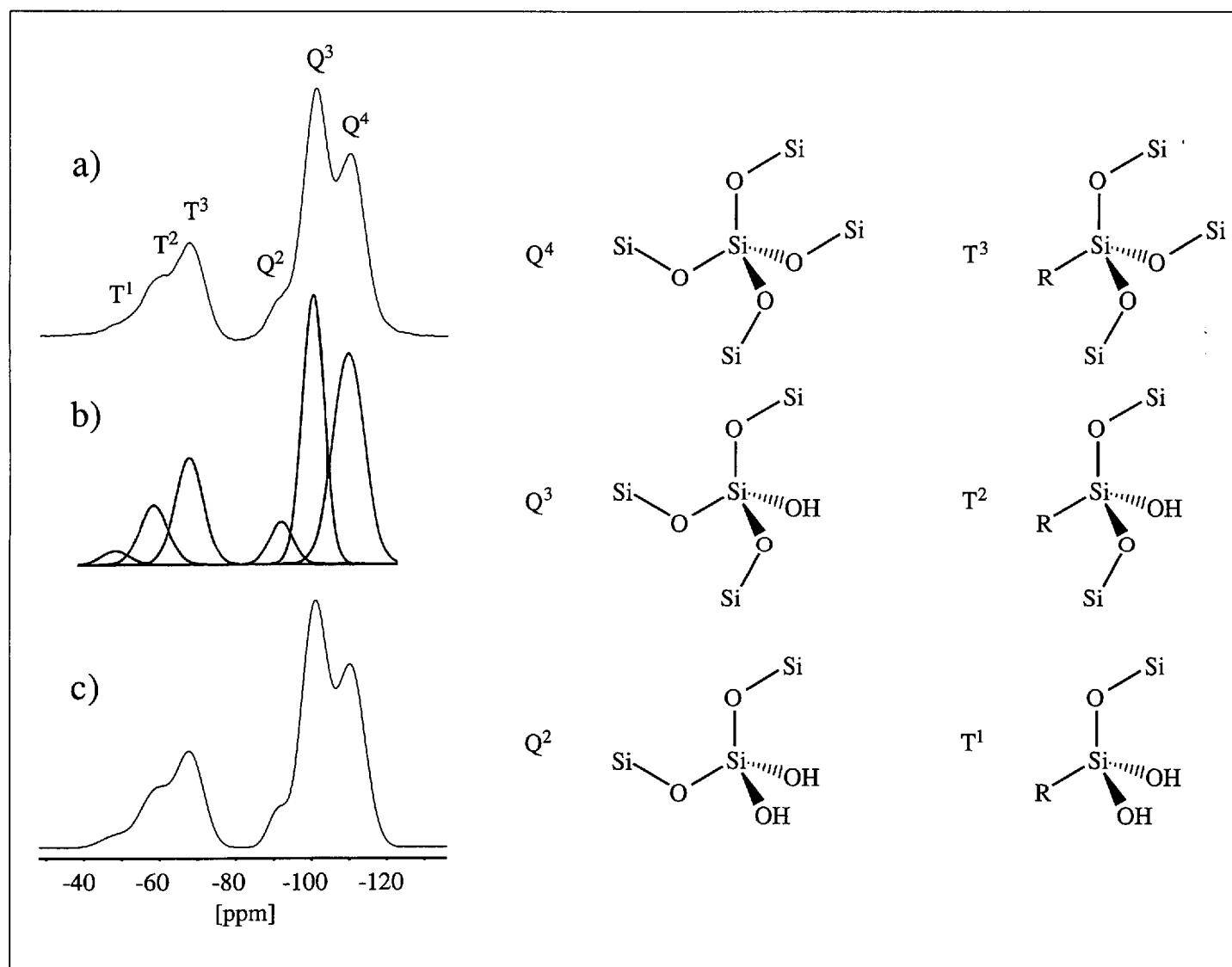


Fig. 5. a) ^{29}Si -NMR spectrum of the hybrid catalyst prepared from $\text{RuCl}_2[\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3]_3$ and TEOS (complex:TEOS = 1:20), b) deconvoluted spectrum revealing the contribution of differently condensed species shown on the right side, c) spectrum constructed from deconvoluted peaks (sum of deconvoluted peaks)

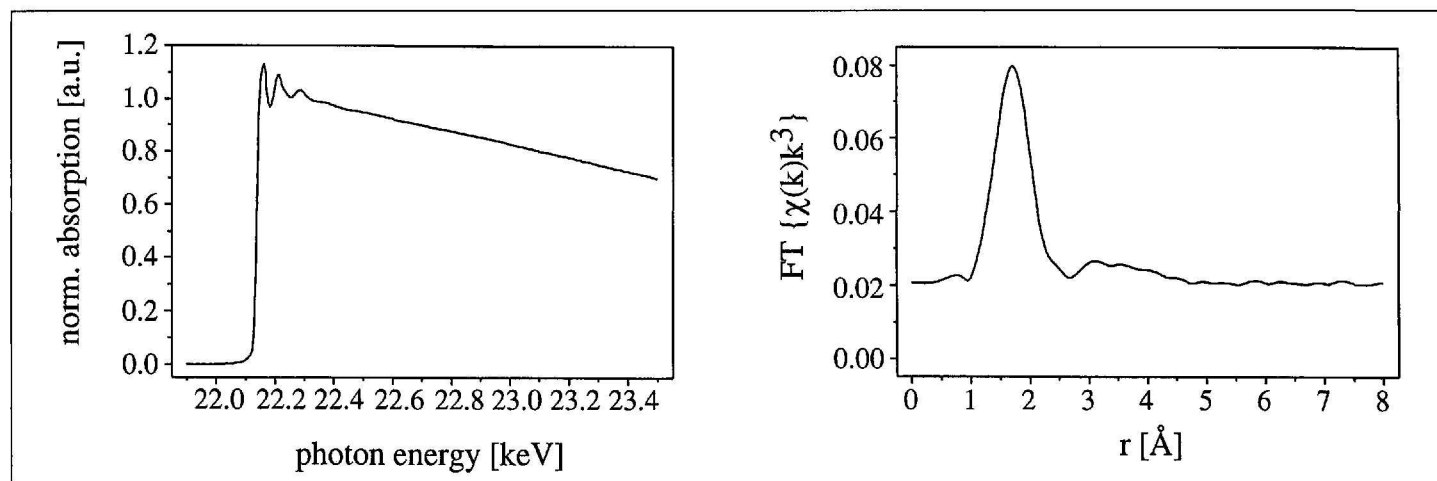


Fig. 6. Extended X-ray absorption fine structures (EXAFS) of the hybrid catalyst prepared from $\text{RuCl}_2[\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3]_3$ and TEOS (complex:TEOS = 1:20). The Fourier transforms (right) indicate that the Ru complexes are incorporated as single isolated entities. Data taken from [6].

presence of only one peak in the Fourier-transformed spectrum that the ruthenium atom exhibits only one coordination shell. Consequently, Ru-Ru interactions can be excluded, indicating that neither dimerization nor oligomerization of the Ru complex occurs during the sol-gel process. This proves that all complexes in the silica matrix are isolated, an important property for catalysis. The high dispersion of Ru was corroborated by transmission electron microscopy which showed neither the existence of ruthenium particles nor crystalline regions of silica. Furthermore, X-ray diffraction exhibited only broad signals and no distinct reflections, characteristic for amorphous materials.

To check the immobilization of the complexes, ^{31}P -NMR measurements were carried out on both precursors and corresponding hybrid gels. Precursor samples were analyzed in solution, whereas hybrid gels were measured in solid state using cross-polarization and magic angle-spinning techniques. No additional peaks could be found in the spectra of hybrid gels indicating undestructed immobilization of the Ru complexes.

Catalytic tests, carried out in a stirred 500 ml autoclave at a total pressure of 21.5 MPa showed that among the different transition-metal silylether complexes tested [5][6], ruthenium complexes were most active and selective (100% selectivity to *N,N*-dimethylformamide). The highest turnover frequency (TOF, 1860 h^{-1} at 133°) was found for a hybrid catalyst prepared from $\text{RuCl}_2[\text{PMe}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3]_3$ with a molar ratio complex:TEOS of 1:50. This turnover frequency is 600 times greater than the highest TOF reported so far for the heterogeneous catalytic production of *N,N*-dimethylformamide [32].

For the synthesis of methyl formate from supercritical carbon dioxide, hydro-

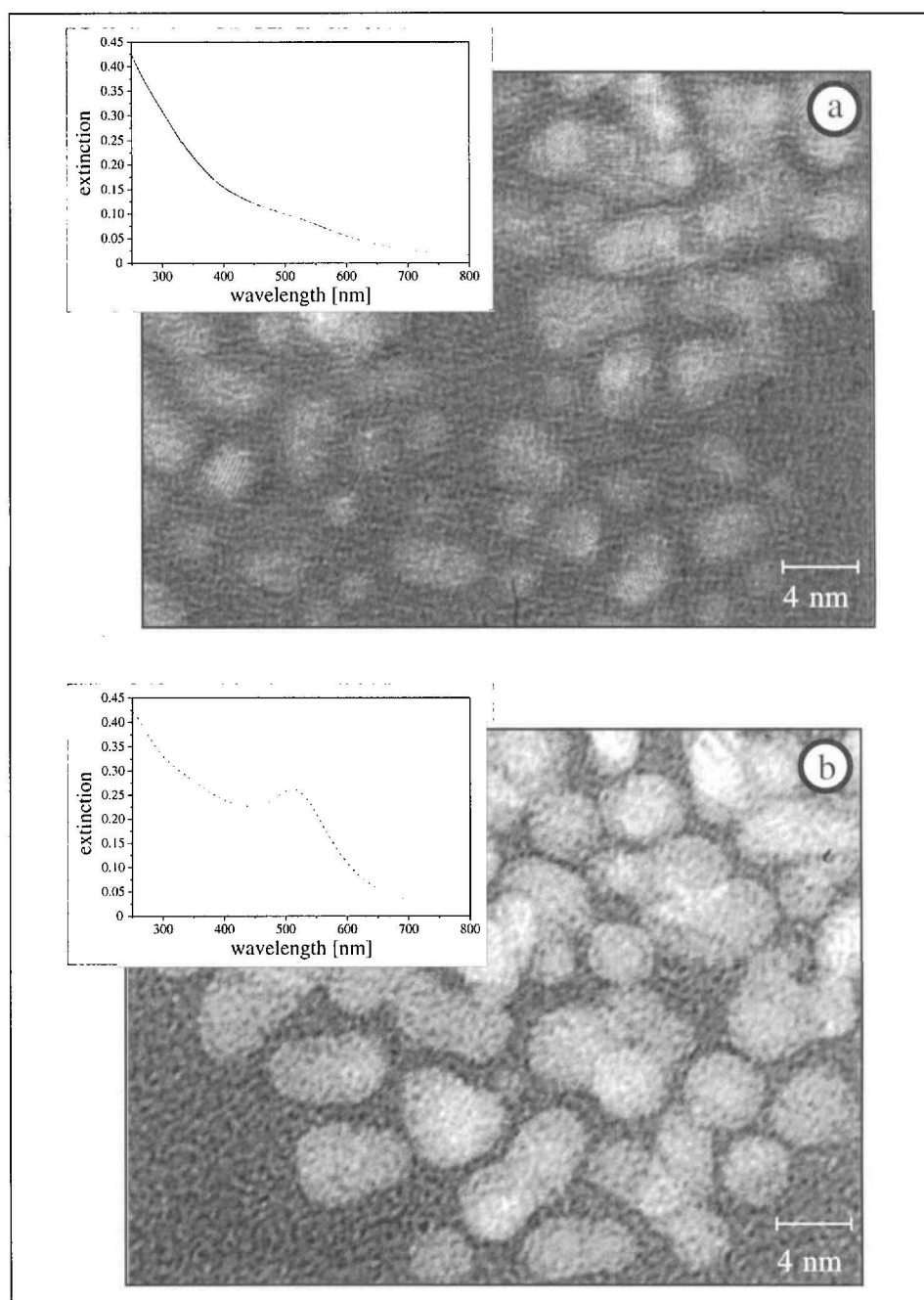


Fig. 7. HRTEM image of gold colloids in solution (gold sol directly transferred to the carbon grid) after a) one day, b) one month. Corresponding UV-VIS spectra are shown as insets.

gen, and methanol, the addition of base (triethylamine) had a crucial influence due to stabilization of the intermediate formic acid. With a selectivity of 100% to methyl formate, a turnover frequency of 115 h^{-1} could be reached with the same catalyst as used for *N,N*-dimethylformamide production. Strikingly this activity is more than two times greater than that of the best homogeneous catalyst reported so far [31]. Thus, this represents one of the rare examples, where heterogenization of an active homogeneous catalyst affords improved activity.

More recently, we have synthesized bidentate ruthenium complexes to improve the stability of the precursors under atmospheric conditions. The complex shown in Fig. 4, **D** exhibits extremely high activity for the homogeneously catalyzed reaction with a selectivity to *N,N*-dimethylformamide of 100%. At 100° , $\text{RuCl}_2[\text{PPh}_2(\text{CH}_2)\text{-PPh}_2]_2$ exhibits a turnover frequency of 232900 h^{-1} , whereas the precursor with silylether groups (complex **D**, Fig. 4) reaches 4430 h^{-1} . The preparation, characterization, and testing of a corresponding hybrid catalyst is presently undertaken.

Further improvement of the textural properties of the hybrid gels seems possible by applying a supercritical drying procedure, which should preserve the gel structure and afford catalysts with higher pore volume and better accessibility of the active sites.

4. Supported Metals with Controlled Particle Size

Conventional preparation procedures for supported metal catalysts [33] (im-

pregnation, precipitation, ion exchange, etc.) consist of several steps connected with immobilization of the metal precursors and formation of the metal particles by activation (calcination, reduction) at elevated temperature. Consequently, the metal particle size is strongly dependent on the wetting ability of the oxide and the activation procedure.

An alternative strategy, which we have applied for the preparation of supported noble metals, is based on the use of metal colloids [34] which can be deposited on metal oxides [35]. We will outline here in more detail some of the recent findings concerning gold/metal-oxide catalysts. Gold as bulk metal is known to be rather inert in heterogeneous catalysis. However, finely dispersed on different oxides (e.g., TiO_2 , ZrO_2 , $\alpha\text{-Fe}_2\text{O}_3$) [36–39], it has excellent catalytic properties for several reactions such as CO oxidation [36–39], partial oxidation of hydrocarbons [40], and NO_x reduction [41]. To understand the influence of the support and the particle size, it is useful to prepare size-controlled gold particles (smaller than 5 nm) on different metal oxides. We recently succeeded in preparing small gold colloids and supporting them on TiO_2 and ZrO_2 .

Gold colloids were prepared by reduction with tetrakis(hydroxymethyl) phosphonium chloride (THPC) in alkaline solution [42–45]. Two TEM micrographs are shown in Fig. 7. Immediately after preparation, the gold particle size is around 2 nm (Fig. 7, a). The particles are rather stable against aggregation – after one month, the particle size is ca. 3–4 nm (Fig. 7, b). These results are corroborated by small angle X-ray scattering (SAXS) and UV-VIS spectroscopy. UV-VIS spectra

of the gold sols are also shown in Fig. 7. The adsorption band around 500 nm, due to a plasmon excitation, is strongly dependent on the particle size and can be used for *in situ* monitoring of the gold particle size.

Such colloids are slightly negatively polarized [46] and can be immobilized on metal-oxide supports according to the scheme in Fig. 8, similar to anionic complex ions [47]. The surface oxide is protonated and positively charged at $\text{pH} < \text{IEP}$ (isoelectric point of the oxide), so that the colloids can be adsorbed on the surface by electrostatic interactions. In fact, we found high adsorption of the gold colloids on powders as well as on thin metal-oxide plates.

Typical HRTEM images of Au/TiO_2 and Au/ZrO_2 are depicted in Fig. 9, revealing a particle size of 2 nm for gold on both supports. Hence, the particle size is nearly preserved throughout all preparation steps. Catalytic tests indicated that after calcination in air at 300° both types of catalysts are active for CO oxidation at room temperature. However, a more detailed analysis of the catalytic activity revealed that there are significant differences between titania- and zirconia-supported catalysts. Au/TiO_2 is more active than Au/ZrO_2 at lower temperatures under the same conditions. Moreover, an uncalcined Au/TiO_2 catalyst is active for CO oxidation at room temperature, whereas a similarly prepared Au/ZrO_2 catalyst is inactive. The particle size of gold is preserved if the gold catalysts is heated to 300° . Heating to temperatures $> 400^\circ$ results in significant sintering of the gold particles and a concomitant decrease in CO oxidation activity. These observations demonstrate that both the particle size and the support have a strong influence on the catalytic activity. Investigation of the adsorptive properties by diffuse reflectance infrared spectroscopy (DRIFTS) and pulse thermal analysis (PTA) showed that CO adsorption on gold particles is weak on both Au/TiO_2 and Au/ZrO_2 , whereas the adsorption of oxygen seems to be stronger. Since gold does not appreciably adsorb oxygen, the adsorption and activation of O_2 is probably the crucial step in the synergism of gold and the metal-oxide support [48]. Oxygen can adsorb on vacancy defects of the metal-oxide support and migrate to the gold particles where the reaction takes place. This may explain why pure gold catalysts are virtually inactive as CO oxidation catalysts at room temperature.

The preparation route *via* gold colloids provides the opportunity to control gold

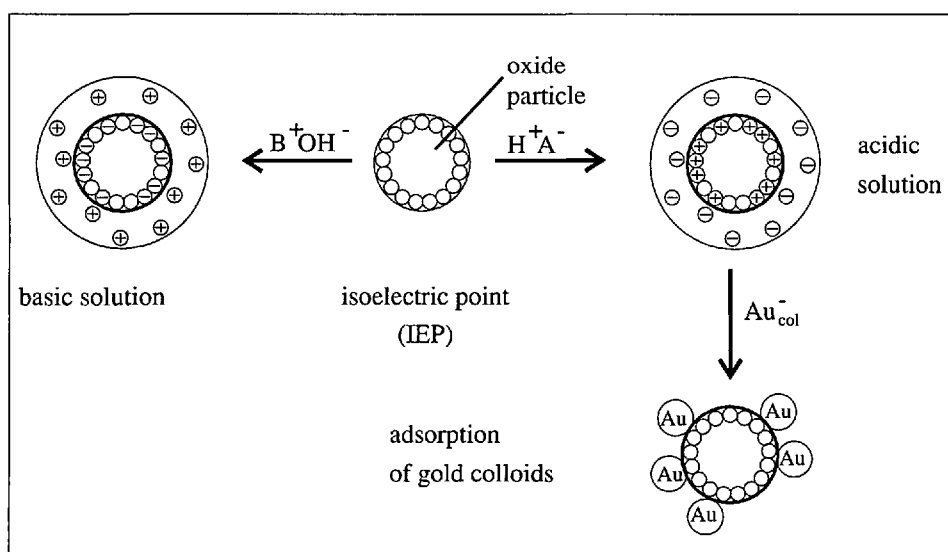


Fig. 8. Schematic representation of the adsorption of negatively charged gold colloids on a positively polarized oxide particle. BOH and HA denote a base and a mineral acid, respectively.

particle size independent of support type. Recently, we also immobilized gold colloids supported on alumina. This catalyst is difficult to prepare *via* impregnation methods, since the alumina support is more acidic, and aggregation to large particles occurs at low temperatures [49]. In addition, preparation of bimetallic catalysts *via* bimetallic clusters/colloids (*e.g.*, [50]) could be achieved *via* this way. The control of the metal particle size, almost independent of the support, opens interesting opportunities to study some fundamental aspects, such as structure sensitivity (dependence of catalytic activity on particle size), or the agglomeration of the metal particles on different supports.

Flat model catalysts suitable for fundamental studies with modern surface-analytical tools have been prepared using the colloidal route [48][51][52]. Albeit the best defined model is a gold or metal-oxide single crystal, for understanding the reaction at interfaces, multicomponent models are required. For this purpose, gold colloids were deposited on metal-oxide/Au(111)/mica films [48][52]. These model systems are structurally similar to the Au/MO₂ catalysts and catalytically active as evidenced by DRIFTS measurements. The conducting single-crystalline Au(111)/mica films proved to be particularly suitable for spectroscopic analysis and the study of adsorption phenomena.

5. Conclusions and Outlook

The performance of a heterogeneous catalyst is usually very sensitive to rather subtle changes of the nature and number of the catalytically active sites, their environment and accessibility. Consequently, control of the microstructure of the catalytically active materials is of paramount importance. Among the various techniques used in catalyst preparation [33], sol-gel processing of molecular precursors is gaining momentum due to some inherent advantages connected with control of structure, composition, purity, porosity, pore-size distribution, and specific surface area. Sol-gel processing combined with various methods for removal of the solvent entrapped in the gel network [3][4][14] facilitates the design of various multicomponent catalytic materials which are not easily accessible by the classical catalyst preparation techniques. The synthesis of new mixed oxides and hybrid organic-inorganic catalysts presented here are only two of the many opportunities sol-gel processing can provide [3][4][24][53–56].

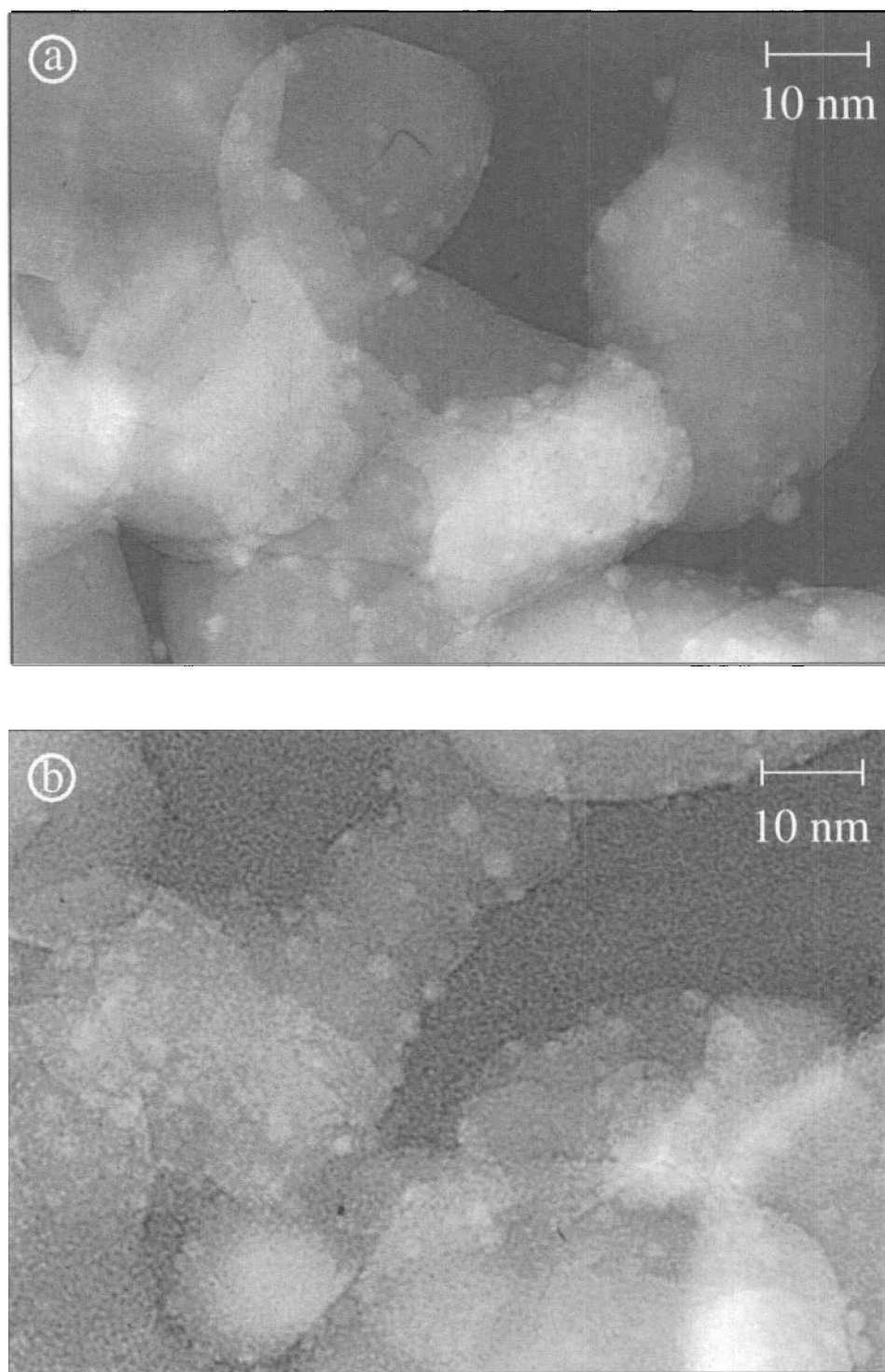


Fig. 9. High-resolution TEM micrographs of a) Au/ZrO₂ and b) Au/TiO₂ (gold loading 1.5 wt.-%)

Sol-gel processing and supercritical drying has been successfully applied for the structural and chemical tailoring of titania-silica mixed oxides modified by organic species *via* suitable precursors. The excellent catalytic behavior of these aerogels for the epoxidation of various bulky olefins is the result of an optimization of the crucial factors: Si–O–Ti connectivities, pore size, and hydrophobicity.

Sol-gel-derived oxide matrices can host a variety of catalytically active species, which can either be chemically anchored

or entrapped in the porous network. This provides the opportunity for heterogenizing highly active homogeneous catalysts as well as enzymes [57]. Compared to ‘surface heterogenization’ (fixation on support), ‘sol-gel heterogenization’ affords catalysts which are usually more resistant against mechanical abrasion and leaching, and can accommodate a higher number of active species per unit volume. In this way, organic-inorganic hybrid gels bear a great potential for merging the advantages of homogeneous and heterogeneous cata-

lysts. This merger is likely to gain importance in fine-chemical catalysis and applications where complex catalyst materials are necessary to meet catalytic requirements.

The ruthenium-containing hybrid gels described are the most active heterogeneous catalysts known so far for the synthesis of *N,N*-dimethylformamide and methyl formate. Although the development of hybrid-gel catalysts is still in its infancy, the present result show that they provide interesting opportunities for catalyst design. Further development in the sol-gel technique for catalyst preparation requires addressing of several fundamental aspects of sol-gel science. A crucial impetus is likely to come from the exploration of the molecular structure of nanometer-scale interfaces which are of particular importance for catalysis.

As regards the size control of dispersed noble metals, the colloidal route described for the preparation of supported gold catalysts seems to be attractive. Its main advantage is that the size of the colloidal gold particles is virtually maintained after immobilization. This is in contrast to other wet-chemical preparation methods, where the final metal particle size is determined by many parameters which are often difficult to control. The preparation of other supported metal catalysts with controlled particle size using similar strategy seems feasible. Colloid-derived catalysts are likely to provide valuable insight into the functioning of supported noble-metal catalysts which is inevitable to reach the ultimate goal of rational design of these materials.

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