

Low Temperature-High Selectivity Process over Supported Pd Nanoparticles in Partial Oxidation of Methanol

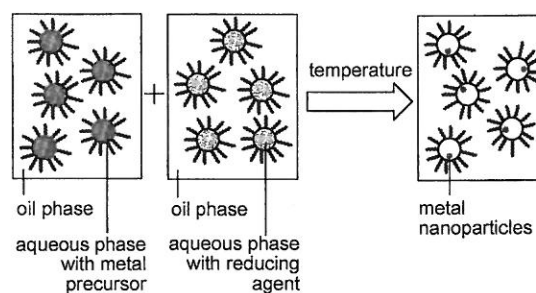
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The most important challenge in gas phase heterogeneous catalysis is to reach high selectivity in a desired process. Many efforts are made at present to improve selectivity in high temperature reactions (> 350 °C); however, under high temperature, it seems very difficult to reach a very high (about 100%) selectivity. The main reason for this is probably the difficulty (and maybe the impossibility) to separate the reactivity of the selective and non-selective active sites of the catalyst. In general, both sites form a part of the same structure of the active phase and they are located in a near proximity. Then, under the reaction conditions, the dynamic phenomena (oxidation and reduction rates, acid and base properties, restructuring of active sites and phases, formation of new phases, migration and reactivity of chemical species, formation of intermediates etc.) on which selectivity depends, are simultaneously involved and concern selective and non-selective sites. For these reasons, it could be stated that probably the only way to get high selectivity in gas phase heterogeneous catalysis is to work under "low temperature conditions".

It is well known that the nanosize of the catalytic particles could play an important role in the design of new catalytic processes. The decrease in size increases the catalytic activity. The small size can provide a large amount of surface atoms, which results in the high catalytic activity per unit amount of metal. Because surface atoms tend to be coordinatively unsaturated, there is a large energy associated with this surface. The smaller the nanoparticles, the larger the contribution made by the surface energy to the overall energy of the system will be. On the other hand, when the particles are too small, quantum effects prevail over the classical size effect giving the particles new and unexpected properties. Therefore, it is absolutely necessary to use synthesis techniques capable of producing nanoparticles of the catalytic active phases with a tailored-size distribution. In contrast, the partial oxidation of methanol (POMeOH) is usually performed at a relatively high temperature (above 250 °C), but the selectivity of the reaction is very low. Several reaction products, such as formaldehyde and dimethoxymethane (on the redox sites) and dimethyl ether and carbon oxides (on the basic and acidic sites), can be obtained.^[1–3] We report that methyl formate (MF) could be produced directly from methanol under the oxidation reaction conditions, with a very high selectivity, in a one step reaction

performed on catalysts formed by Pd nanoparticles supported on TiO₂ at low temperature and under atmospheric pressure.

The Pd/TiO₂ catalysts were prepared by using the water-in-oil microemulsion method (Scheme 1). This method is interest-



Scheme 1. Preparation of the catalysts by means of the water-in-oil microemulsion method.^[5]

ing because the chemical reduction and then the precipitation from solutions is a highly versatile and simple method to perform the synthesis of small supported particles. It is well recognized that the size control of nanoparticles can be achieved by changing the chemical composition of the primary microemulsion formed.

The synthesis of nanoparticles in microemulsions allows one to obtain size mono-disperse particles and to control the size of the particles by varying the size of the microemulsion droplet radius and of the precursor concentrations.^[4] The objective of the work was to study the catalytic activity of Pd-supported catalysts over a small size range at the nanometer level.

The hydrazine was chosen as appropriate reducing agent, as it can be used at low temperature and decomposes to NH₃ and/or N₂ after the reduction takes place. Analysis of the TEM images in Figure 1 confirmed the presence of metallic nanoparticles of palladium for AOT/1-butanol (Figure 1A) and Brij30/1-decanol (Figure 1C) catalysts. The average particle size of about 4 and 8 nm respectively was confirmed by XPS analysis.^[5] In case of the AOT/cyclohexane (Figure 1B) catalyst the palladium nanoparticles were not visible on TEM images although the EDS surface analysis confirmed the presence of palladium on the surface. In this case it could be supposed that, after the reduction with the hydrazine, the palladium particles formed are very small (< 2 nm). The differences in sizes observed for the different catalysts could be explained by the use of different solvents and surfactants.

The results of ICP analysis (Table 1) revealed that the Pd mass% varies between 1.6 and 1.8, which was smaller than expected (2 wt.%). Small differences are attributed to the method of preparation. Indeed, after chemical reduction with

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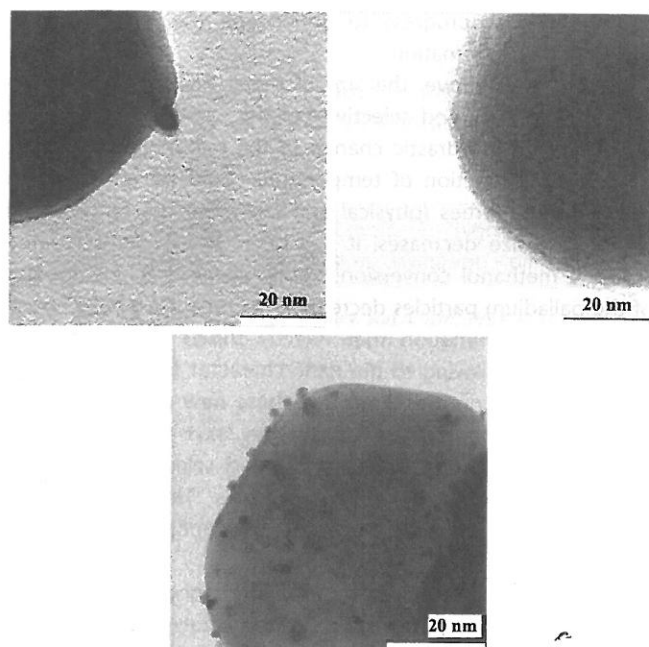


Figure 1. TEM images of the Pd/TiO₂ catalysts: A) AOT/1-butanol, B) AOT/cyclohexane, C) Brij30/1-decanol.

^a Catalyst (surfactant/solvent)	Pd wt. % ^[a]	Dispersion [%]	Particle size ^[b] [nm]	SSA ^[c] [m ² g ⁻¹]
AOT/1-butanol	1.8	14	7.7 (8.6)	8.0
AOT/cyclohexane	1.7	85	1.3 (1.5)	8.3
Brij30/1-decanol	1.6	28	3.9 (4.4)	8.2
TiO ₂ support	–	–	–	8.0

[a] from ICP. [b] from XPS. [c] Specific Surface Area (SSA) from BET N₂ physisorption.

hydrazine, the palladium precipitated onto TiO₂ surface. It could be expected that some palladium stabilized by the organic surfactants stayed in the solution. This also applies for the support because a loss of weight of about 8% was observed for all catalysts after filtration and drying. The specific surface area did not change significantly after chemical reduction as showed by the BET results in Table 1.^[6–7]

The highest dispersion (85%), namely the distribution of the palladium particles on the TiO₂ surface, was observed for AOT/cyclohexane catalyst (Table 1), which is in good accordance with literature data.^[8] The range of the particles size is between 1 to 8 nm (Table 1). As the size of particles was very small, a size estimation of the particles was not possible by XRD (Scherrer equation) or TEM analysis.^[9] The size of the palladium particles was estimated by using two XPS models.^[5] The change in the particle size for the AOT/1-butanol (about 8 nm) catalyst could be explained by the different polarity of the 1-butanol as compared to the higher alcohols (1-decanol) and other sol-

vents (cyclohexane). As the polarity of an *n*-alcohol becomes stronger with a decreasing carbon number, 1-butanol has a stronger affinity for the positively charged palladium particles.^[6–7] During reaction the sintering of particles was nearly negligible. Size of particles after reaction are presented in parenthesis, in Table 1. The limited sintering of the particles is coherent with the low reaction temperature used.

TiO₂ was inert at low temperature. At higher temperature (200 °C), the support alone produced only traces of methyl formate, CO₂ and water. All catalysts showed high conversion in partial oxidation of methanol reaction conditions (50–150 °C, Table 2, Figure 2). However, no hydrogen production was ob-

Table 2. Results of the catalytic test at 80 °C (100 mg of catalyst, gas mixture containing 5 vol. % of methanol and 2.5 vol. % of O₂ with a total flow rate of 100 cm³ min⁻¹. The catalytic test was performed at various temperatures (50–300 °C))

Catalyst (surfactant/solvent)	Methanol conversion [%]	Yield methyl formate [%]	Selectivity methyl formate [%]
AOT/1-butanol	67	55	82
Brij30/1-decanol	54	43	79
AOT/cyclohexane	78	40	52
TiO ₂ -support	0	0	–

served. Interestingly, for all catalysts, at very low temperature (50–100 °C), the direct formation of methyl formate was observed (Figure 2). At 50 °C, MF is produced with a high selectivity (100% for AOT/1-butanol catalyst, and 81 and 91% for Brij30/1-decanol and AOT/cyclohexane catalysts respectively). Under the limit of detection of the analysis, only CO₂ as carbon containing secondary product was observed. No other product was observed. The maximum of MF production was found for catalysts prepared from the AOT/1-butanol microemulsion and at 80 °C the MF yield is as high as 55%. Catalysts prepared from AOT/cyclohexane showed the smaller selectivity to MF at 80 °C (52%). At high temperature (> 150 °C), the conversion of methanol is complete, but methyl formate is now not formed at all. At above 150 °C, the total methanol conversion was observed and only CO₂ is produced. Traces of CO were observed at high temperature (300 °C). Notably, this catalyst is the most active sample. For Brij30/1-decanol catalyst the yield and selectivity decrease with temperature, but they still remained high at 80 °C (43 and 79% respectively). Clearly, depending on the synthesis conditions of the catalysts and on the reaction conditions, there is an optimal temperature at which the selectivity for methyl formate is very high. Catalytic tests as a function of time on stream at 80 °C were also performed. In all cases the selectivity to methyl formate and methanol conversion stay unchanged after 24 h of reaction. Moreover any carbon deposit was observed on the catalysts surface in XPS after the stability tests.

The reaction resulting in methyl formate formation involves a C–O–C coupling. There is still no consensus on the role of the nature of the active phase, the role of the support and the reactant molecules, nor on the rate determining step for this re-

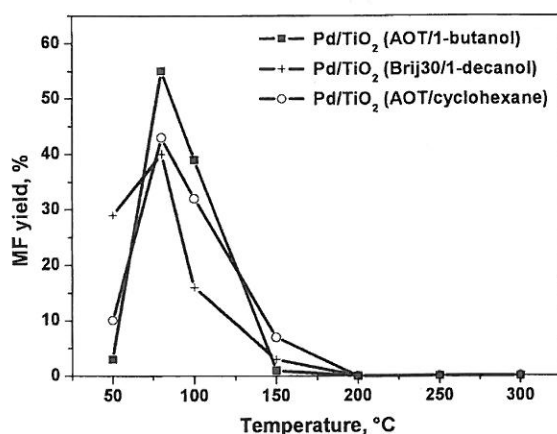


Figure 2. Methyl formate yield versus temperature.

action. The only agreement that comes out from the literature data is that the surface reaction sequence changes in a wide range with the reaction conditions. Methanol oxidation reactions may lead to formaldehyde (HCHO), dimethoxymethane ($\text{CH}_3\text{OCH}_2\text{OCH}_3$, DMM), and methyl formate (HCOOCH_3 , MF) products. Oxidative routes to HCHO are practiced on silver-based and iron-molybdate catalysts.^[10] Methyl formate is produced through (nonoxidative) CH_3OH dehydrogenation on CuO or carbonylation using liquid bases^[10–12] and DMM can be produced in a two-step process involving methanol oxidation to HCHO followed by acetalization of $\text{HCHO-CH}_3\text{OH}$ mixtures with liquid or solid acids.^[10] The decomposition of methanol on TiO_2 starts with the formation of methoxide species upon the adsorption at room temperature. On the TiO_2 surface the scission of both, C–O and O–H bonds is equally probable.^[13–14] When methanol is adsorbed on the surface of Pd, its OH bond weakens, formation of Pd–O bonds prevails, chemisorbed methoxy species CH_3O are formed, then undergoing successive dehydrogenation to formaldehyde CH_2O and then to chemisorbed CO and H_2 .^[13] It could be argued that in the first step, methanol adsorbed on Pd promotes the formation of CO at the interface of the TiO_2 surface with the palladium particles. At that same time, the dehydrogenation of water occurs to give both OH and O adsorbed species. It was shown, in the case of Pd/ SiO_2 catalyst that the methanol adsorbs and reacts at 25 °C on Pd and the dissociation of methanol via both O–H and C–O bond breaking is observed. The latter scission is only detected at 380 °C. At room temperature, adsorbed CH_3OH decomposes easily on the Pd crystallites, to give CO multicoordinated to the metal surface. Formyl species have also been found at this temperature, but they promptly disappear when the catalyst is heated and the formation of CO and H_2 prevails.^[13,15] Methyl formate can form through the condensation of adsorbed methoxides with HCHO to form methoxymethanol intermediates ($\text{CH}_3\text{OCH}_2\text{OH}$) that then dehydrogenate to methyl formate.^[16] The esterification of formic acid (HCOOH) intermediates formed by HCHO oxidation is also possible but the high selectivities to methyl formate reported here indicate that fast reactions through condensation of HCHO to methyl formate occur. However, works using DRIFT in operando mode

are presently in progress to understand the mechanism of methyl formate formation.

As discussed above, the size of metal nanoparticles determines the activity and selectivity of the catalyst. It cannot be excluded that the drastic change of the nanoparticle catalytic properties as function of temperature could be attributed to their new properties (physical and chemical) that are created when their size decreases. It has been clearly demonstrated that the methanol conversion highly increases when the size of the palladium particles decreases (< 7 nm).^[7] We have no experimental confirmation that directly shows the creation of new properties, owing to the nano-character of palladium particles, but we cannot exclude that these new properties could have developed. If this is the case, they have to be taken into account to explain the high activity and selectivity in methyl formate formation of the nano-catalysts. The study of the chemical and physical properties of nanoparticles are in progress.

In summary, well dispersed palladium nanoparticles (ranged between 1–8 nm) can be highly active catalysts for the gas-phase reaction of methanol oxidation. The formation of methyl formate from methanol was observed. The reaction occurs at very low temperatures (50 °C–150 °C) with a very high selectivity, and, in some cases, with selectivity as high as 100%. The results strongly suggest that palladium nanoparticles induce the C–O–C coupling at low temperature.

Experimental Section

All catalysts were prepared as follows. The microemulsion was formed using 50 mL of organic solvent (cyclohexane, 1-butanol or 1-decanol), 1 mL of aqueous precursor solution (PdCl_2) and the appropriate quantity of organic surfactant (Brij30-ethylene glycol monolauryl ether or AOT-sodium bis(2-ethyl-hexyl)sulfosuccinate). The mixture was heated to 50 °C and then 2 g of TiO_2 was incorporated to the reactant flask under magnetic stirring before injection of the hydrazine. After 30 min, the appropriate quantity of hydrazine was injected. The reaction was performed under nitrogen atmosphere. As prepared catalyst was filtered, purged with water and acetone, and dried at 100 °C for 1 h under air atmosphere. The partial oxidation of methanol was performed in a metallic fixed-bed microreactor operating at atmospheric pressure. The catalytic bed was composed of 100 mg of catalyst diluted with 600 mg of glass spheres. The reactant gas mixture containing 5 vol.% of methanol and 2.5 vol.% of O_2 was passed through the reactor with a total flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$. The catalytic test was performed at various temperatures (50–300 °C). Methanol, oxygen and the reaction products were analyzed each 30 min using a CP3800 Varian gas chromatograph.

The sizes of the metallic particles was estimated from the XPS elemental intensity ratios using an adequate modeling of the XPS signal.^[5] Two XPS models were applied (Davis and Kerkhof–Moulijn). For very small palladium particles (smaller than 3 nm) a good accordance of the two models was found. The results obtained using XPS technique permitted also to understand the differences observed between XRD and TEM studies and their limitation to estimate the size of small particles. Dispersion was calculated from^[9] using particle size estimated from XPS.

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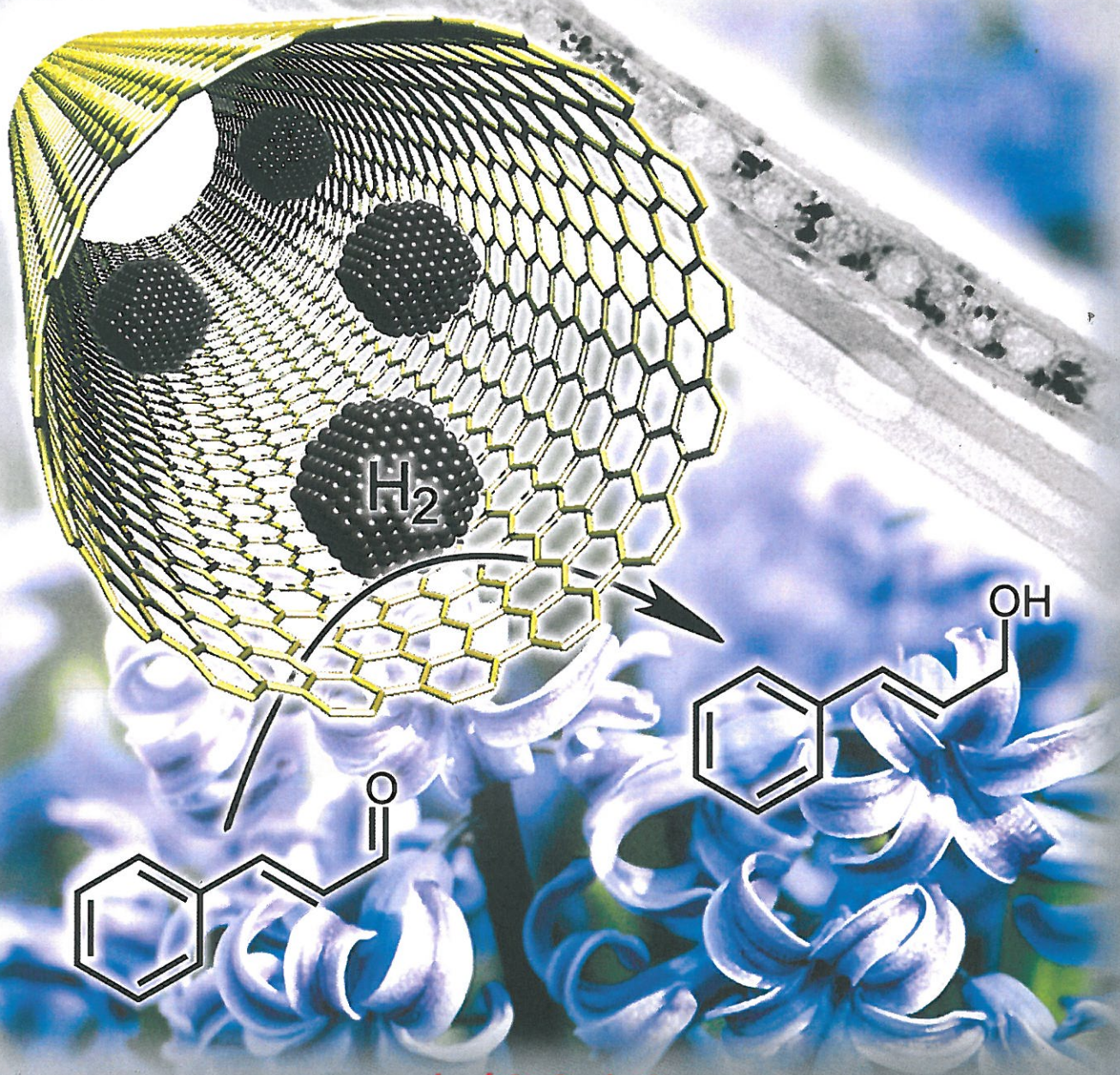
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