Novel, Spongelike Ruthenium Particles of Controllable Size Stabilized Only by Organic Solvents**

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In materials science there is considerable current interest in controlling the structure of a material at both the microscopic and mesoscopic levels and thus to influence its physical properties and reactivity. A recent method involves transferring the structure of surfactant aggregates to inorganic solids by calcination to give materials of controlled porosity.[1] Similarly, metal nanoparticles are attracting increasing interest because of the novel physical properties displayed by nanosized objects and the chemical properties exhibited by colloidal particles in solution.[2] In this case, the structure of surfactant aggregates is transferred by synthesizing ordered nanoparticles of metals, metal oxides, or metal sulfides in "nanoreactors" such as inverse micelles.[3] A drawback of this method is the presence of surface contaminants resulting from the reaction conditions, such as water, salts, organic residues, or even an oxide shell. This problem can be solved by decomposing an organometallic precursor under mild conditions in a polymer.[4] The physical properties of the resulting nanoparticles resemble those of free clusters in the gas phase (e.g., lattice-parameter contraction[4a] and enhanced magnetization[4d,e]). The disadvantage here is the presence of the polymer, which makes the material unsuitable, for example, for applications involving electron transfer and catalysis. Ligands have been used to stabilize metal particles,[4a,c] but they strongly modify their physical and chemical properties.[4e] However, we have shown that a combination of CO and THF, both weakly coordinated, allows the synthesis of monodisperse platinum particles.[4c] Similar titanium particles, weakly protected by THF, were recently reported by Bönnemann et al.[5]

We looked for similar effects, avoiding CO, which modifies the electronic configuration of the surface, by employing weakly coordinating polar solvents. The stabilization of the particles could then result from coordination or from the electrostatic repulsion that results from solvent-induced polarization of the surface. As the metal precursor, we chose [Ru(cod)(cot)][6] (**1**; cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene), which is readily decomposed by dihydrogen at or below room temperature and which leads to well-defined nanoparticles in polymer matrices.[7] Here we report on the synthesis of spongelike ruthenium nanoparticles of adjustable uniform size which are soluble in organic solvents and protected only by weakly coordinating solvents.

The reactions of **1** (50 mg, 1.54×10^{-4} mol) dissolved in 50 mL of various solvents with 3 bar of H_2 were carried out at 21 °C in a closed pressure bottle for 45 min (standard conditions). In THF, a black precipitate formed almost immediately. However, in pure methanol or THF/methanol (90/10, 95/5, or 99/1), the initial yellow solution rapidly became dark brown, after which it remained unchanged and stable for at least several days. Addition of pentane gave a black precipitate consisting of particles, the size of which depends upon the methanol content of the reaction mixture (Table 1). The isolated particles cannot be redissolved; they are very air sensitive and burn in the open air. However, an oxide passivation layer can be formed by bubbling a few milliliters of air through the reaction solution.

Table 1. Mean particle size as a function of reaction conditions.

THF/MeOH	[**1**] [mol L^{-1}]	T [°C]	Mean size [nm]
0/100	3.53×10^{-3}	21	70
90/10	3.65×10^{-3}	21	16
95/5	3.8×10^{-3}	21	24
99/1	3.67×10^{-3}	21	80–100
–[a]	3.65×10^{-3}	21	> 500
90/10	3.2×10^{-2}	21	54
90/10	1.6×10^{-1}	21	40–70; 230–280
90/10	3.2×10^{-3}	0	35–45
90/10	3.2×10^{-3}	41	12
90/10[b]	3.2×10^{-3}	21	24
90/10[c]	3.2×10^{-3}	21	35

[a] A stoichiometric quantity of methanol was used. [b] With addition of 2 equiv of cyclooctane. [c] With addition of 20 equiv of cyclooctane.

The products were analyzed by microanalysis, transmission electron microscopy (TEM), high-resolution electron microscopy (HR-EM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Preliminary wide-angle X-ray scattering (WAXS) and atomic force microscopy (AFM) studies were also performed.

Under standard conditions, the mean size of the particles varies from 16 nm (10 vol% methanol) to 24 nm (5 vol% methanol) and 80–100 nm (1 vol% methanol; Figure 1). Addition of one molar equivalent of methanol with respect to ruthenium leads to the precipitation of unorganized material, whereas in pure methanol a mean particle size of 70 nm was obtained (Figure 2). Other parameters that influence the size of the particles are the temperature (for MeOH/THF 10/90: ca. 40 nm at 0 °C and 12 nm at 41 °C), the precursor concentration (for MeOH/THF 10/90: [Ru] = 3.2×10^{-2}, 54 nm; [Ru] = 1.6×10^{-1}, bimodal, ca. 50 and ca. 250 nm), and the presence of an excess of cyclooctane (for

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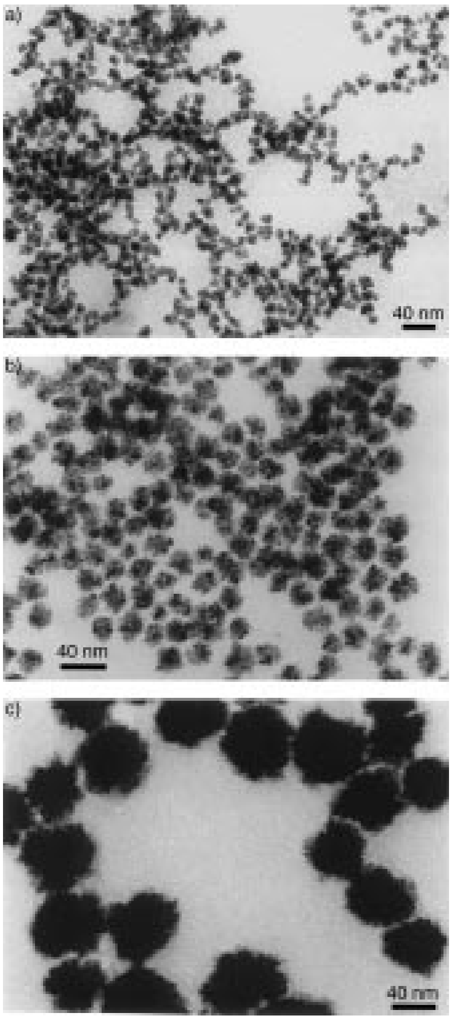

Figure 1. Micrographs of ruthenium particles prepared at room temperature in mixtures of methanol/THF: a) 10/90, b) 5/95, c) 1/99.

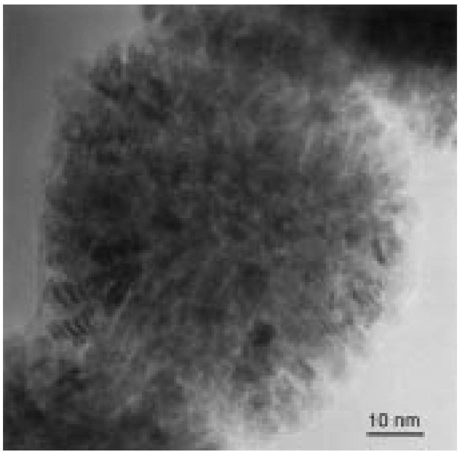

Figure 2. High-resolution micrograph of a ruthenium particle prepared at room temperature in pure methanol.

MeOH/THF 10/90: $[C_8H_{16}]/[Ru] = 2$, 24 nm; $[C_8H_{16}]/[Ru] = 20$, 35 nm).

For each preparation, the particles have a narrow size distribution and a porous, polycrystalline aspect. The XRD experiments on passivated particles showed that they consist of hexagonal close packed (hcp) ruthenium. A very weak peak was attributed to the passivating RuO_2 layer, no evidence of which was obtained in WAXS experiments in an air-free Lindemann capillary. Only peaks corresponding to well-crystallized hcp ruthenium particles were observed. These results are also confirmed by XPS on a passivated sample; the spectrum displays peaks due to oxidized ruthenium and oxygen. However, the disappearance of almost all oxygen peaks after argon bombardment to remove the external layers of the material shows that only a thin external passivation layer is present.

The polycristallinity of the particles was deduced from HR-EM studies; the size of the individual crystallites is on the order of a few nanometers. The fact that the particles consist of a uniform spongelike structure rather than an agglomerate of small crystallites was indicated by application of the Scherrer equation to the XRD data (using the (101) diffraction line for particles prepared at 10 vol% MeOH in THF gave a calculated size of 16–18 nm); by preliminary AFM experiments, which showed that 16-nm particles keep their integrity when moved by the tip; and by reactivity studies (see below). Precedents for such porous structures are known and have been discussed by Antonietti and Göltner.[8] The particle morphology is referred as "raspberry" or "cauliflower" according to the growth mechanism of the particles, that is, whether individual particles aggregate in a single micelle or form in a micelle and aggregate after their formation because of a lack of stabilization by the block copolymer. However, such structures were always obtained in the presence of a protective layer (block copolymers that form micelles).

The particles display interesting reactivity. For example, a solution prepared at 10 vol% MeOH in THF catalyzed the complete reduction of benzene to cyclohexane under mild conditions (20 bar, 80°C, 15 h, 1000 equiv). A black precipitate was observed at the end of the reaction but could be redispersed in solution, and micrographs of the particles before and after catalysis were essentially identical.

Since the solubility of these particles was astonishing, we observed their organization in solution by cryomicroscopy (Figure 3). The cryomicroscopy experiments were performed on a Philips CM-120 bioTWIN Cryo, which is equipped with a specially designed objective lens to enhance image contrast relative to a normal 120-kV microscope. The specimens were first frozen by fast immersion in liquid ethane. This freezes the solvent to amorphous ice fast enough to prevent any rearrangement of the particules in the solution. The sample was then transferred to a cryo-holder (Oxford CT-3500) cooled with liquid nitrogen to below −180°C. Microscopy was performed under low-dose conditions to prevent beam damage (especially transformation of the amorphous ice into cristalline ice). This type of sample preparation is particularly relevant for particles synthesized in solution, because it shows whether structural features observed after drying were already present in the liquid phase. We observed individual spongelike[8] particles, agglomerated in some cases, in complete agreement with the data obtained from samples deposited on a grid.

The intriguing properties of these particles—that is, 1) their solubility in organic solvents, 2) the size control induced by

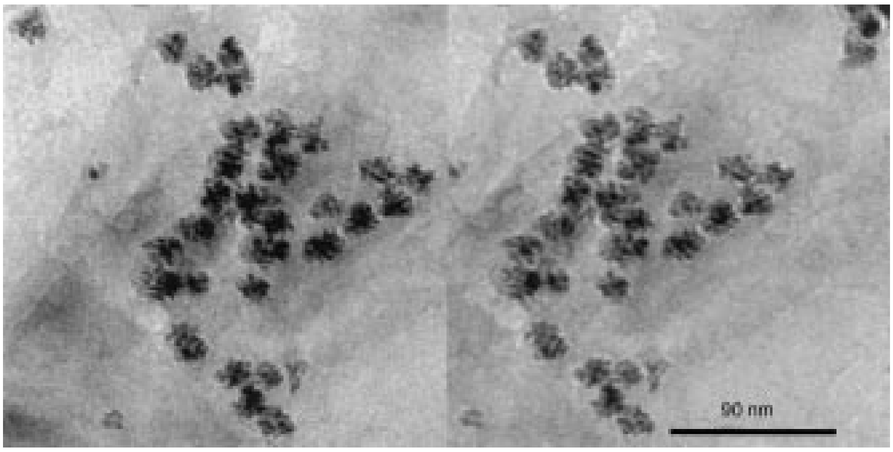

Figure 3. Stereoview of a TEM micrograph of ruthenium particles in a frozen solution of methanol/THF (10/90; cryomicroscopy technique).

the solvent composition, and 3) the influence of concentration, temperature, and excess cyclooctane—can be understood if one imagines the formation of a nanosized emulsion whose droplets act as nanoreactors. Methanol could be ordered around the particles by forming hydrogen-bonded networks with THF. These structures would be more stable when both solvents are present, since methanol is a good hydrogen-bond donor, and THF a good hydrogen-bond acceptor. The core of the droplets would be lipophilic, as can be deduced from the influence of as little as two equivalents of cyclooctane relative to ruthenium.

In conclusion, we have prepared novel ruthenium nanoparticles that are free of protective oxide or polymer layers, uncontaminated by ligands or impurities from the synthesis other than the solvent mixture, soluble in organic solvents, and controllable in size by means of the solvent composition. These highly porous particles are catalytically active and remain unchanged by the catalytic process.

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Broadening the Aldolase Catalytic Antibody Repertoire by Combining Reactive Immunization and Transition State Theory: New Enantio- and Diastereoselectivities**

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The aldol reaction is a C–C bond forming reaction that is key to the practice of synthetic organic chemistry.[1] As a result of its utility intensive effort has been applied to the development of catalytic enantioselective variants of this reaction. Catalytic enantioselective aldol reactions are typically accomplished with preformed enolates and chiral transition metal catalysts[2a–e] or with natural aldolase enzymes.[2f–h] The enantioselectivity of transition metal catalyzed aldol reactions is readily reversed by exchange of the chiral ligand that directs the stereochemical course of the reaction. However, a general approach to the reversal of enantioselectivity is not available with enzymes. To address the problem of the de novo

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