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Mononuclear Ruthenium Hydride Species versus Ruthenium Nanoparticles: The Effect of Silane Functionalities on Silica Surfaces

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The area of nanoparticle synthesis has gained interest in the past few years due to their potential and application in areas such as microelectronics and selective catalysis.[1] In the case of metal nanoparticles, their properties are often related to their size and shape, and therefore controlling their growth has been an area of active research for decades.[2] In the specific case of supported metal nanoparticles, some control is possible by changing the precursor, the method of impregnation, the nature of oxide support, and the final decomposition method. Using perhydrocarbyl complex precursors provides some advantages because of their ease of decomposition under H_2, which leads to metal surfaces free of strong ligands such as CO or Cl^-. The particle mean size can be somewhat controlled by the choice of the support, which directs the migration of the zero-valent ensembles in the process of the crystal growth, but the resulting particles are usually large (>1 nm). Even if the organometallic precursor is first grafted to the support to ensure a high dispersion, treatment under H_2 at high temperatures leads to the cleavage of the M−O bond and to aggregation, yielding large supported metal particles.[3] Controlling or even avoiding the aggregation process on oxide supports by surface organometallic chemistry tools would lead to smaller nanoparticles of a few atoms (<1 nm) or analogues of the early transition-metal surface hydrides,[4] which could be of great interest for catalytic applications. Recently, Pelzer et al. have shown that the treatment of a pentane solution of [Ru(cod)(cot)] (cod = cyclooctadiene, cot = cyclooctatriene) under 3 bars of H_2 in the presence of octylsilane yields soluble 2-nm nanoparticles stabilized by direct Ru−Si bonds.[5] Here, we show that tuning silica by adding surface Si−H bonds generates a support that avoids aggregation of the metal during the treatment under H_2 at high temperatures of grafted [Ru(cod)(cot)], yielding stable silica-supported mononuclear ruthenium hydride species **[Ru-H]** (Scheme 1). This system will be compared with what is usually obtained on silica support, namely Ru nanoparticles, **Ru_P/SiO_2**.[6]

The solid **[Ru-H]** is typically prepared by treatment under H_2 (2 × 55 equiv) at 300 °C for 24 h of solid **[Ru-L]** obtained by reaction of [Ru(cod)(cot)] (0.3–0.6 equiv/SiH) with a silica covered with surface silanes, [(≡SiO)SiMe$_2$H] (0.24 mmol per g or ca. 0.7 SiH per nm^2).[7] During the treatment under H_2 at 300 °C, about 10 ± 1 equivalents of CH_4/Ru are formed, in agreement with the hydrogenolysis of some hydrocarbon species. TEM analysis on the resulting light brown solid **[Ru-H]** does not show the presence of Ru particles, even for 0.85 wt % Ru loading (see Figure S1 in the Supporting Information). This is in sharp contrast with what is obtained by treating [Ru(cod)(cot)] adsorbed on silica under H_2 at 300 °C, which affords homogeneously dispersed Ru particles, **Ru_P/SiO_2** (0.73 wt %), with a mean size of 2.1 ± 0.3 nm (see Figure S2 and S3 in the Supporting Information). In fact, while [Ru(cod)(cot)] is only physisorbed on silica ($SiO_{2-(700)}$, ca. 0.7 OH per nm^2) and can be removed by simple washing with pentane, [Ru(cod)(cot)] reacts with [(≡SiO)SiMe$_2$H] (1.65 equiv) as evidenced by the disappearance of the yellow color of the solution during impregnation to yield an orange-brown solid **[Ru-L]**. This solid contains 1.52 wt % of Ru, that is 0.15 mmol of Ru per g of solid, in agreement with the grafting of all the [Ru(cod)(cot)] loaded.

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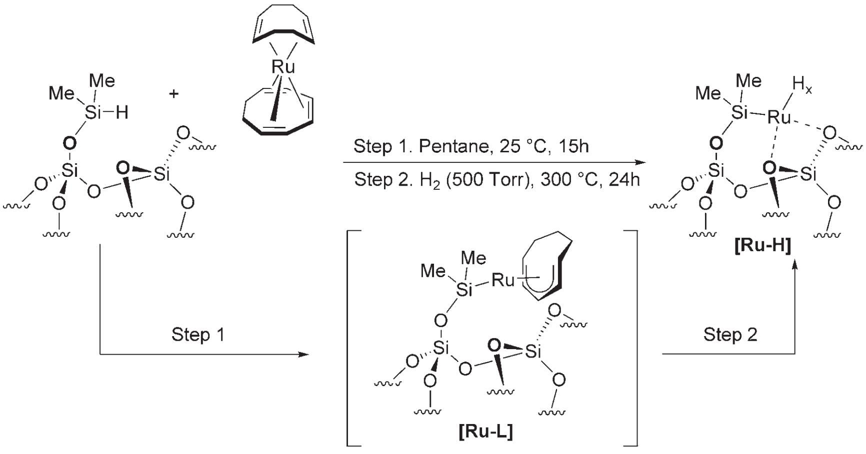

Scheme 1. Preparation of **[Ru-H]** surface species.

Furthermore, monitoring this reaction sequence by IR spectroscopy shows the following: the Si–H are consumed upon contacting [Ru(cod)(cot)] with [(≡SiO)SiMe$_2$H], as evidenced by the disappearance of its characteristic IR band at 2158 cm^{-1}, and the appearance of new bands associated with $\nu(\mathrm{C_{sp^2}/_{sp^3}\text{-}H})$ and $\delta(\mathrm{C_{sp^2}/_{sp^3}\text{-}H})$ (see Figure S4 in the Supporting Information). This is consistent with chemical grafting of the Ru complex on the modified silica surface in **[Ru-L]**. After treatment of this solid under H$_2$ at 300 °C, the $\nu(\mathrm{C_{sp^2}\text{-}H})$ bands have disappeared, and the $\nu(\mathrm{C_{sp^3}\text{-}H})$ bands have been mostly consumed (this process is accompanied by the formation of methane, vide supra). The initial Si–H bands are not regenerated during the formation of **[Ru-H]**, and no Ru–H band is detected.[8]

The hypothesis of chemical grafting of the Ru complex on [(≡SiO)SiMe$_2$H] and the absence of aggregation of the metal under H$_2$ is supported by Ru K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy. First, the EXAFS spectrum of **[Ru-L]** is consistent with the presence of 1 Si at 2.40 Å and 5 C at 2.19 Å, even if a structure having 1 Si at 2.40 Å plus 3.7 O at 2.16 Å around Ru cannot be excluded (Table 1, and Table S1 and S2, and Figure S5 in the Supporting Information).[9,10] However, on the basis of the reactivity of [Ru(cod)(cot)][11] and solid-state NMR spectroscopy (see Figure S6 and Table S3 in the Supporting Information),[9,12,13] we propose that **[Ru-L]** is a ruthenium attached to the support by one covalent Si–Ru bond[14,15] with its coordination sphere probably completed by a η^5-cyclooctadienyl ligand (Scheme 1).[16] Nevertheless, because of the low concentration of surface species and the difficulty to access ^{13}C-labeled enriched compounds, other coordination of the C$_8$ ligand can also be proposed, such as Ru(1-3:5-6-η-C$_8$H$_{11}$),[17] Ru(1-5-η-C$_8$H$_9$), and Ru(1-3:5-6-η-C$_8$H$_9$).[18] Second, after treatment of **[Ru-L]** under H$_2$ at 300 °C, the Ru center in **[Ru-H]** still possesses one Si at 2.40 Å, confirming the stability of the Ru–Si bond of this system under these conditions, which is in full agreement with TEM and IR data (no aggregation, no formation of initial Si–H). The EXAFS fit is improved by including either 2 O at 2.20 Å or 2.7 C at 2.23 Å in the coordination sphere of Ru in **[Ru-H]**. Although the presence of 2.7 C at 2.23 Å cannot be rigorously excluded, the fit with the 2 O at 2.20 Å is better, and we propose a surface species coordinated to two adjacent surface siloxane bridges (Scheme 1).[19] Note that no Ru–Ru contributions are found at 2.64–2.67 Å (representative of Ru nanoparticles). Contribution of 0.3 Ru at 2.95 Å can be included in the fit, to take into account the possible presence of Ru clusters, but without significant improvement as evidenced by the Hamilton test, about 0.14 (Table 1, and Tables S4 and S5, and Figure S7 in the Supporting Information).[20] Again, this is in sharp contrast with the EXAFS data for **Ru$_\mathrm{P}$/SiO$_2$** (0.8 wt % Ru), which are fully consistent with TEM analysis (vide supra) and which show the presence of small Ru nanoparticles (contribution of 10 Ru neighbors at 2.64–2.67 Å) with an estimated particle size of (2.2 ± 0.7) nm (Table 1, and Table S6 and Figure S8 in the Supporting Information).[21] The difference between **[Ru-H]** and **Ru$_\mathrm{P}$/SiO$_2$** is also clearly shown in Figure 1: the low signal amplitude in *k* and *R* space for mononuclear Ru species **[Ru-H]** surrounded by light atoms in contrast to the high amplitude for **Ru$_\mathrm{P}$/SiO$_2$**, composed of ruthenium atoms surrounded by several heavy Ru atoms.

Table 1. EXAFS parameters for solids **[Ru-H]**, **[Ru-L]**, and **Ru$_\mathrm{P}$/SiO$_2$**.

Neighbor	No. of neighbors	Distance [Å]	σ^2 [Å^2]	Hamilton Test[a] (p)
		[Ru-H]		
O	2	2.198(7)	0.0030(6)	0.0004
Si	1	2.40(1)	0.007(2)	0.023
Ru	0.3(1)	2.95(2)	0.008(fixed)	0.14
		[Ru-L]		
C	5.0(9)	2.19(2)	0.007(2)	0.004
Si	1	2.40(1)	0.005(1)	0.000004
		Ru$_\mathrm{P}$/SiO$_2$[b]		
Ru	4.95[c]	2.634(2)	0.0058(2)	–
Ru	4.93[c]	2.679[d]	0.0058[d]	–

[a] The likelihood that adding additional parameters does not more accurately fit the data. In general, a value of <0.05 is needed to state that including this set of atoms significantly increases the quality of the fit.[23] [b] Only the two first shells are included in this table. The first shell of the HCP structure of Ru contains two sets of six atoms, which have slightly different bond distances. [c] Determined by using the formula for nanoparticles.[21] [d] Parameter constrained to change with the preceding shell.

Moreover, the presence of H atoms in the coordination sphere of Ru in **[Ru-H]** has been shown by 1) the formation of 1.5 ± 0.5 HD per Ru upon contacting **[Ru-H]** with D$_2$ (see Figure S9 in the Supporting Information)[22] and the

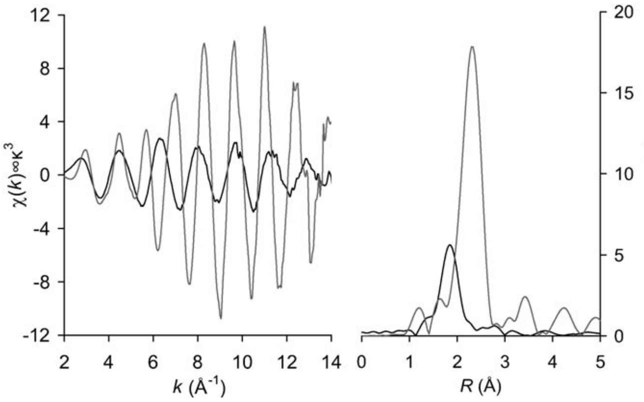

Figure 1. EXAFS spectrum (at the Ru K-edge) and Fourier transform of **[Ru-H]** (dark) and **Ru_p/SiO_2** (gray).

presence of a sharp signal at $\delta -8.3$ ppm in the ^1H MAS solid-state NMR spectrum recorded at 24 KHz (see Figure S10 in the Supporting Information).[15] Furthermore, **[Ru-H]** can reversibly desorb and adsorb H_2. In fact, after desorption of **[Ru-H]** at 300 °C for 3 h, 1.8–2.0 H per Ru are adsorbed, which is again different from what is observed for particles (0.9–1.0 H adsorbed per total Ru atoms for **Ru_p/SiO_2**; see Figure S11 in the Supporting Information). Overall, based on IR, NMR, EXAFS, and TEM data, we propose that the major species of **[Ru-H]** have the following average structure $[(\equiv SiO)(Me)_2Si-Ru(H)_x(\equiv SiOSi\equiv)_2]$ (Scheme 1).

Finally, **[Ru-H]** catalyzes the selective hydrogenation of styrene into ethylbenzene, even at high conversions (>99.9 % selectivity at 100 % conversion), in contrast to **Ru_p/SiO_2**, which gives a selectivity of 96.0 % in ethylbenzene at 96.7 % conversion; higher conversions lead to a worse selectivity because of the competitive subsequent hydrogenation of the benzene ring (see Figure S12 in the Supporting Information). In fact, in the hydrogenation of benzene, the initial rate is 0.01 mol benzene per mol Ru per min @ 40 min for **[Ru-H]**, whereas it reaches 8 mol benzene per mol Ru_s per min @ 30 min for **Ru_p/SiO_2** under similar reaction conditions (see Figure S13 in the Supporting Information). This is again consistent with the absence of Ru particles in **[Ru-H]** as shown by EXAFS and TEM.[24] Furthermore, **[Ru-H]** efficiently catalyzes the hydrogenation of propene (see Figure S14 in the Supporting Information) in a continuous flow reactor (H_2/propene/Ru: 40/40/1 per min), with a much higher stability than **Ru_p/SiO_2**, which more rapidly deactivated by coke formation.

In conclusion, we have shown that a silica covered with surface Si–H reacts at room temperature with [Ru(cod)(cot)], and that the resulting surface species treated under H_2 at 300 °C provides a highly unsaturated mononuclear ruthenium hydride species [**Ru-H**]. Thus, a simple modification of a silica support, replacing surface hydroxyl groups by Si–H, leads to the formation of a stronger Ru–Si bond rather than Ru–O bond upon grafting with [Ru(cod)(cot)]. The stronger Ru–Si interaction prevents aggregation and the growth of metal particles during treatment under H_2 at high temperatures. This highly unsaturated mononuclear ruthenium hydride species [**Ru-H**] displays a very different spectroscopic and reactivity profile compared to that of silica-supported Ru particles **Ru_p/SiO_2**, which, in turn, allows the selective hydrogenation of alkene over aromatic compounds. We are currently carrying out detailed studies on the process of formation of [**Ru-H**] and its reactivity.

Experimental Section

Preparation of [Ru-L] by impregnation of [Ru(cod)(cot)] onto $(\equiv SiO)SiMe_2H$: A mixture of [Ru(cod)(cot)] (91 mg, 0.29 mmol, 0.6 equiv) and $(\equiv SiO)SiMe_2H$ (2.0 g, 0.48 mmol SiH) in pentane (15 mL) was stirred at 25 °C for 15 h. The solid initially turned orange, then orange-brown, while the yellow color of the solution totally vanished. The reaction mixture was filtered off. The solid was washed with pentane (3 × 15 mL), and finally dried under vacuum (10^{-5} mbar) at 25 °C for 1 h to yield **[Ru-L]**.

Preparation of solid [Ru-H] by treatment of [Ru-L] under H_2: The solid **[Ru-L]** (1.54 g, 0.23 mmol) was loaded in a 470-mL reactor flask at 25 °C, H_2 (666 mbar, 12.6 mmol, 55 equiv) was added, and the reactor was heated at 300 °C for 24 h. After the sample was cooled to room temperature, the gas phase was analyzed by GC to quantify the CH_4 formed during this operation. After evacuation of the gas phase, a second loading of H_2 was performed, and this procedure was repeated. Finally, the reactor was evacuated under vacuum (10^{-5} mbar) for 30 min, to yield the solid **[Ru-H]**.

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