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Priority Communication

Increased methanation activity through passivation of the silica support

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ABSTRACT

Improvement of the catalytic performance of supported nanoparticles (NP) is an intense area or research, which involves modification of many different parameters on a nanoparticle (such as variation of particle size), support (e.g. its reducibility) and metal–support interactions. Here, we focus on the latter and show that the introduction of passivating groups ($-OSi(Me)_2$**R** with **R** = **Me** or **Bu**) at the interface between the support surface (silica) and RuNPs increases the rate of the reaction on RuNPs (per mole of surface Ru atoms) by a factor 5–6 compared to silica-supported RuNPs, whose surface is exposed to silanols. Chemisorption, IR spectroscopy and temperature-programmed desorption tests suggest that the rate increase likely originates from the difference in interaction between CO and RuNPs, which is influenced by the modification of the support surface functionality. It is also possible that the change in catalyst activity could be due to a modified electronic state of nanoparticles and/or their morphology.

1. Introduction

The prospective global energy challenges arising up from continuously increasing worldwide energy consumption create a demand for the development of alternative energy sources such as solar, wind or nuclear [1–3]. However, the intermittent nature of the energy production and demand, as well as the unequal geographical source distribution, requires the development of efficient technologies to store energy and convert its excess into energy carriers. In this respect, the production of chemicals/fuels such as methanol, syngas or CH_4 is of great interest [4,5]. Supported metal nanoparticles (NPs) are commonly used to catalyse the formation of these chemicals, and correspond to one of the largest classes of heterogeneous catalysts [6–9]. Numerous parameters influence the performances of such catalysts, such as the size and the distribution of the metallic nanoparticles [10], but also their interaction with the support surface [11–14]. Similar to what has been found for supported single-site catalysts (e.g. Ti- and Ta-based olefin epoxidation catalysts) [15–17], modification of the support by introducing passivating trimethylsilyl group can also improve the performances of supported metal NPs [18–22]. For instance, 2-nm Au nanoparticles (AuNPs) supported on passivated silica (silica covered with $-OSiMe_3$ groups) display much higher activity in the aerobic epoxidation of stilbene (0.12 mole (g of Au)$^{-1}$ h^{-1}) than the corresponding Au supported on standard oxide supports, including the usually best titania support (0.023 mole (g of Au)$^{-1}$ h^{-1}) [23]. In addition, AuNPs on passivated silica catalyse the preferential oxidation of CO by O_2 only when H_2 is present, in contrast to the corresponding AuNPs supported on normal silica. These data clearly point out the importance of the so-called metal–support or nanoparticle–interface interaction, which here refers most likely to the presence or not of surface Si–OH. In line with the above discussion, we decided to explore the effect of passivating groups ($-OSi(Me)_2$**R**; with **R** = **Me** or **Bu**) at the surface of silica, in place of silanols, on the reactivity of supported metal nanoparticles towards Water–Gas Shift (WGS) and methanation reactions (Eqs. (1) and (2), respectively).

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad (1)$$

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O \qquad (2)$$

Here, we describe the synthesis of supported Ru nanoparticles (RuNPs) on passivated silica and show that the modification of the metal–support interaction (interface between the nanoparticle and the support) by introducing trialkylsilyl group on the support increases the rates of methanation through the modification of the adsorption properties of the metallic particles.

2. Experimental

2.1. General procedure

All experiments were carried out under dry and oxygen-free Ar using either standard Schlenk or glove box techniques for

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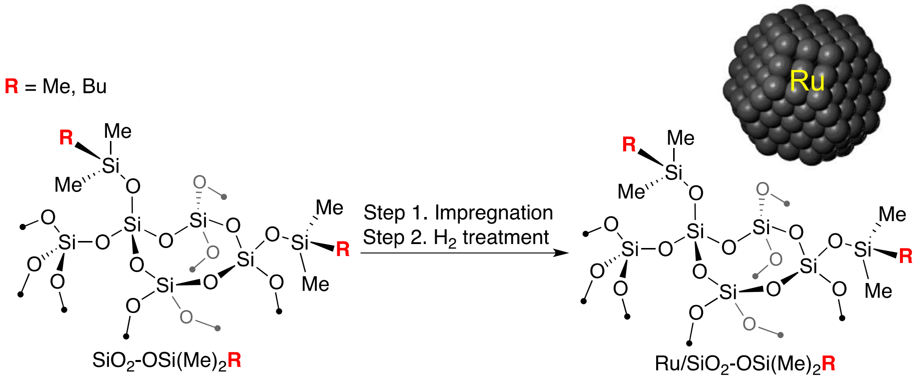

Fig. 1. Synthesis of RuNPs on passivated silica; Step 1: Impregnation of the THF solution of [Ru(COD)(COT)]; Step 2: Treatment under H_2 (1 bar, 38 mL min^{-1}), 300 °C (0.5 °C min^{-1}), 6 h.

organometallic synthesis. For the syntheses and the treatments of RuNPs, reactions were carried out using high vacuum lines (10^{-5} - mbar) and glove box techniques. Silica (Aerosil Degussa, 200 m^2/g) was compacted with distilled water, calcined at 500 °C under air for 2 h and treated under vacuum (10^{-5} mbar) at 500 °C for 12 h and then at 700 °C for 4 h (SiO_{2-700}). THF was distilled from sodium under Ar (benzophenone used as an indicator of dryness). H_2 were purified over R3-11 BASF catalyst/MS 4 Å prior to use.

2.2. WGS/methanation kinetic study

Supported RuNPs were loaded into a plug flow reactor (PFR) and reduced in pure H_2 (50 sccm) at 400 °C (5 °C min^{-1}) for 5 h, followed by a pretreatment at the standard WGS/methanation conditions (7% CO, 22% H_2O, 8.5% CO_2, 37.5% H_2 and balance Ar) with a flow rate of 75.4 sccm at 300 °C for 20 h. After this pretreatment, the temperature was lowered to reach conversion to be less than 10% in order to determine WGS/methanation rates and reaction orders under kinetic conditions (275 °C for Ru/SiO_2–OH and to 260 °C for RuNPs supported on passivated silica). Rate of the methanation reaction was calculated per mole of Ru surface atoms by taking into account the dispersion of supported RuNPs calculated from TEM study; reaction orders with respect to H_2, CO, H_2O and CO_2 were studied by varying one gas concentration at the time. Apparent activation energy (E_{app}) was measured by changing the temperature within a range of 40 °C.

3. Results and discussion

Passivated silica (SiO_2–OSi(Me)$_2$**R**) was prepared by the reaction of silica partially dehydroxylated at 700 °C (SiO_{2-700}) [24] with different alkyldimethylchlorosilanes (**R**(Me)$_2$SiCl with **R** = **Me** or **Bu**) in the presence of pyridine (Scheme S1, Fig. S1) [25]. Then, the supported Ru nanoparticles (Ru/SiO_2–OSi(Me)$_2$**R**) were obtained by impregnation of a THF solution of Ruthenium(1,5-cyclooctadiene)(1,3,5-cyclooctatriene), [Ru(COD)(COT)], targeting a final loading of 1 wt.% Ru, followed by a thermal treatment in a flow of H_2 (300 °C, 6 h) (Fig. 1).

During passivation, all silanols (–OH) of SiO_{2-700} were converted into (–OSi(Me)$_2$**R**) functionalities as evidenced by IR spectroscopy (Fig. S1). During the treatment at 300 °C under H_2, impregnated [Ru(COD)(COT)] decomposed, the production of methane was evidenced as the result of the hydrogenolysis of the ligand attached to Ru, namely cyclooctadiene and cyclooctatriene. This hydrogenolysis step took place without affecting the surface organosilane functionalities as evidenced by IR spectroscopy (Figs. S3–S5). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of RuNPs, which were exposed to ambient air prior microscopy study (Fig. 2) corresponds to RuO_2 nanoparticles (as evidenced by XPS; Figs. S9–S11), whose mean size diameters are 1.5 ± 0.3, 1.5 ± 0.2 and 1.6 ± 0.3 for Ru/SiO_2–OSi(Me)$_2$**Me**, Ru/SiO_2–OSi(Me)$_2$**Bu** and Ru/SiO_2–OH, respectively. Correcting for the difference of molar volume ratio between RuO_2 and Ru(0) (2.35), the calculated mean diameter of Ru(0) nanoparticles is thus 1.3 ± 0.3, 1.3 ± 0.2 and 1.4 ± 0.3 nm for Ru/SiO_2–OSi(Me)$_2$**Me**, Ru/SiO_2–OSi(Me)$_2$**Bu** and Ru/SiO_2–OH (Table 1). Transmission electron microscopy (TEM) images of RuNPs exposed to ambient air prior microscopy study are presented in Fig. S6.

All catalysts were evaluated in WGS/methanation as follows: the supported Ru nanoparticles were loaded into a plug flow reactor [27] and then reduced in pure H_2 (50 mL min^{-1}) at 400 °C (5 °C min^{-1}) for 5 h, followed by a pretreatment at the standard WGS/methanation conditions (7% CO, 22% H_2O, 8.5% CO_2, 37.5% H_2 and balance Ar) with a flow rate of 75.4 mL min^{-1} at 300 °C for 20 h [28]. After this pretreatment, the temperature was lowered to reach conversion less than 10% in order to determine WGS/methanation rates and reaction orders under kinetic conditions (275 °C for Ru/SiO_2–OH, and to 260 °C for RuNPs supported on passivated silica).

Under these reaction conditions, both methanation and WGS reactions are favored, but all supported RuNPs show very high selectivity (>90%) towards methanation, which is consistent with the ease of CO dissociation on Ru surface [29]. Post-catalytic TEM characterization showed that the mean diameter of supported RuNPs does not change during the kinetic test (Fig. S7, Table S1), and X-ray photoelectron spectroscopy after reduction or after reaction indicates that RuNPs remain metallic under reaction conditions (Figs. S9–S11, Table S2), similar to what was previously observed by the groups of Robert J. Davies [30] and Alexis T. Bell [31], under reducing conditions in the presence of water. It is noteworthy that >70% of the passivating group remains on Ru/SiO_2–OSi(Me)$_2$**Bu** and Ru/SiO_2–OSi(Me)$_2$**Me**, respectively, after 20 h at 270 °C under a flow of H2, CO, CO_2 and H_2O (Fig. S8). It is noteworthy that RuNPs supported on passivated silica present much higher rates (per mole of Ru) or turnover frequencies (per mole of surface Ru), and lower E_{app} (by ca. 40–50 kJ mol^{-1}) (Table 2, Fig. S12) than the corresponding particles supported on silica.[1] Measuring reaction orders for H_2, CO, H_2O and CO_2 shows, however, only minor differences between the catalysts, indicating similar reaction pathway and active sites. Nonetheless, it also suggests that the energetics of some of the elementary steps involved in the reaction are perturbed

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[1] The reaction rate per mole of surface Ru for RuNPs supported on silica is consistent with the previously reported activity of RuNPs on SiO_2 towards methanation, see: I.G. Bajusz, J.G. Goodwin Jr., J. Catal. 169 (1997) 157.