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 of 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 ($-\text{OSi}(\text{Me})_2\mathbf{R}$ with $\mathbf{R} = \mathbf{Me}$ or $\mathbf{Bu}$) 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.

Keywords

Ruthenium nanoparticles, passivated silica, metal/support interaction, methanation, CO adsorption

1. Introduction

The prospective global energy challenges arising up from continuously increasing worldwide energy consumption creates 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 CH₄ 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 -OSiMe₃ 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 most performant titania support (0.023 mole.(g of Au)⁻¹.h⁻¹) [23]. In addition, AuNPs on passivated silica catalyze the preferential oxidation of CO by O₂ only when H₂ 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 (eq. 1 and 2, respectively).

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 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 m²/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 (SiO₂₋₇₀₀). THF was distilled from sodium under Ar (benzophenone used as an indicator of dryness). H₂ 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 H₂ (50 sccm) at 400°C (5°C.min⁻¹) for 5h, followed by a pretreatment at the standard WGS/methanation conditions (7% CO, 22% H₂O, 8.5% CO₂, 37.5% H₂, and balance Ar) with a flow rate of 75.4 sccm at 300°C for 20 h. After this pre-treatment, 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/SiO₂-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 H₂, CO, H₂O and CO₂ 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 (SiO₂-OSi(Me)₂R) was prepared by the reaction of silica partially dehydroxylated at 700 °C (SiO₂₋₇₀₀) [24] with different alkyldimethylchlorosilanes (R(Me)₂SiCl with R = Me or Bu) in the presence of pyridine (Scheme S1, Figure S1) [25]. Then, the supported Ru nanoparticles (Ru/SiO₂-OSi(Me)₂R) 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 H₂ (300 °C, 6h) (Figure 1).

Figure 1. Synthesis of RuNPs on passivated silica; Step 1: Impregnation of the THF solution of [Ru(COD)(COT)]; Step 2: Treatment under H₂ (1bar, 38 mL.min⁻¹), 300°C (0.5°C.min⁻¹), 6h.

During passivation, all silanols (-OH) of SiO₂₋₇₀₀ were converted into (-OSi(Me)₂R) functionalities as evidenced by IR spectroscopy (Figure S1). During the treatment at 300 °C under H₂, impregnated [Ru(COD)(COT)] decomposed, and 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 (Figure S3-S5). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of RuNPs, which were exposed to ambient air prior microscopy study (Figure 2) corresponds to RuO₂ nanoparticles (as evidenced by XPS; Figure S9-S11), whose mean size diameters are 1.5 ± 0.3 , 1.5 ± 0.2 and 1.6 ± 0.3 for Ru/SiO₂-OSi(Me)₂Me, Ru/SiO₂-OSi(Me)₂Bu and Ru/SiO₂-OH, respectively. Correcting for the difference of molar volume ratio between RuO₂ 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/SiO₂-OSi(Me)₂Me, Ru/SiO₂-OSi(Me)₂Bu and Ru/SiO₂-OH (Table 1.) Transmission electron microscopy (TEM) images of RuNPs exposed to ambient air prior microscopy study are presented in Figure S6.

Table 1. Particle size and metal dispersion of as-synthesized supported RuNPs (1 wt.% Ru) according to HAADF-STEM.

Materials	<i>Ru/SiO₂-OSi(Me)₂Me</i>	<i>Ru/SiO₂-OSi(Me)₂Bu</i>	Ru/SiO ₂ -OH
RuO ₂ [nm] ^a	1.5 ± 0.3	1.5 ± 0.2	1.6 ± 0.3
Ru(0) [nm] ^b	1.3 ± 0.4	1.3 ± 0.3	1.4 ± 0.3
Dispersion ^c	0.75	0.75	0.73

^aParticle size of the samples exposed to ambient air (RuO₂)

^bCalculated particle size of Ru(0) assuming bulk-like molar volume of RuNPs.

^cDispersion calculated based on the particle size of Ru(0).

Figure 2. Respective HAADF-STEM and particle size distribution of Ru/SiO₂-OSi(Me)₂Me: a) and b); Ru/SiO₂-OSi(Me)₂Bu: c) and d); and Ru/SiO₂-OH: e) and f).

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 H₂ (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% H₂O, 8.5% CO₂, 37.5% H₂, and balance Ar)

with a flow rate of 75.4 mL.min⁻¹ at 300 °C for 20 h [28]. After this pre-treatment, 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/SiO₂-OH, and to 260 °C for RuNPs supported on passivated silica).

Table 2. Methanation kinetic study for supported RuNPs: rates, apparent activation energies and reaction orders in H₂, CO, H₂O and CO₂.

Materials		<i>Ru/SiO₂-OSi(Me)₂Me</i>	<i>Ru/SiO₂-OSi(Me)₂Bu</i>	Ru/SiO ₂ -OH
Rate (10 ⁻² mole CH ₄ (mole Ru) ⁻¹ s ⁻¹ ^a		7.0	6.7	1.4
	TOF (10 ⁻² mole CH ₄ (mole Ru _{surf.}) ⁻¹ s ⁻¹) ^b	9.3	8.9	1.9
E _{app} (kJ/mol)		78 ± 1	70 ± 2	121 ± 3
Reaction orders ^c	H ₂	1.19 ± 0.02	1.23 ± 0.03	0.89 ± 0.04
	CO	-0.44 ± 0.04	-0.47 ± 0.04	-0.53 ± 0.07
	H ₂ O	0.03 ± 0.01	0.01 ± 0.02	-0.20 ± 0.06
	CO ₂	0.07 ± 0.02	0.01 ± 0.01	0.08 ± 0.02

^a Reported rate with respect to methane at 300 °C, 7% CO, 22% H₂O, 8.5% CO₂, 37.5% H₂.

^b TOF with respect to methane reported at 300°C (s⁻¹) and calculated per mol of surface Ru atom by taking into account the fresh catalyst dispersion obtained from HAADF-STEM (Table 1.)

^c Orders of the reaction were measured at 260°C for Ru/SiO₂-OSi(Me)₂Me and Ru/SiO₂-OSi(Me)₂Bu and at 275 °C for Ru/SiO₂-OH.

Under these reaction conditions, both methanation and WGS reactions are favored, but all supported RuNPs shows 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 (Figure S7, Table S1), and X-ray photoelectron spectroscopy after reduction or post reaction indicates that RuNPs remains metallic under reaction conditions (Figure S9, S10, S11, Table S2.), similarly 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/SiO₂-OSi(Me)₂**Bu** and Ru/SiO₂-OSi(Me)₂**Me** respectively after 20 h at 270 °C under a flow of H₂, CO, CO₂ and H₂O (Figure 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, Figure S12) than the corresponding particles supported on silica.[‡] Measuring reaction orders for H₂, CO, H₂O and CO₂ 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 by the presence of passivating groups, thus leading to a difference in the reaction rate. The reaction orders with respect to H₂ (Table 2, Figure S13) are 0.89 (for non-passivated), 1.19 and 1.23 for passivated supports (SiO₂-OSi(Me)₂**Me** and SiO₂-OSi(Me)₂**Bu** respectively), indicating that hydrogen pressure has a slightly more positive effect on methanation rate on passivated samples. Interestingly, for RuNPs on passivated supports, the order of the reaction with respect to H₂ is higher than one, which can be explained by the fact, that H₂ and CO compete for the same adsorption sites [33]. The orders with respect to CO (Table 2, Figure S14) are negative and similar (ca. -0.5) for all catalysts, which is in agreement with an inhibiting effect of CO on methanation rates [34]. For H₂O (Table 2, Figure S15), the reaction order is close to 0, showing that water does not inhibit the methanation

[‡] The reaction rate per mole of surface Ru for RuNPs supported on silica is consistent with the previously reported activity of RuNPs on SiO₂ towards methanation, see: I. G. Bajusz, J. G. Goodwin Jr. J. Catal, 169 (1997) 157.

reaction.[§] Note the slightly negative value for the silica supported catalyst, indicating its small inhibitory effect, probably because of slower desorption of H₂O from the more hydrophilic silica surface. The CO₂ order for all the catalyst is 0, since it is not involved in methanation reaction (Figure S16).^{**}

While the study of the reaction orders did not reveal any significant difference between the catalysts, chemisorption studies outlined major differences. Indeed, the H₂ and CO chemisorption differ particularly from passivated to non-passivated silica supported RuNPs (Table 3, Figure S17, S18).

Table 3. H₂ and CO chemisorption for supported RuNPs.^a

Materials	<i>Ru/SiO₂-OSi(Me)₂Me</i>	<i>Ru/SiO₂-OSi(Me)₂Bu</i>	Ru/SiO ₂ -OH
Q _{max} (μmol _{H₂} ·g _{cat} ⁻¹)	54	49	54
Q _{max} (μmol _{CO} ·g _{cat} ⁻¹)	90	109	144
Dispersion (H ₂) ^b	0.71	0.64	0.71

^aAll samples are treated at 350°C (10⁻⁶ mbar) prior the chemisorption measurement, which is performed at 25°C. The chemisorption data are fitted with a dual dissociative (H₂) and non dissociative (CO) adsorption Langmuir model to estimate the quantity of adsorbed gas at saturation (Q_{max}) [32].

^b Calculated assuming 2H/Ru_{surf} adsorption [26].

On the one hand, the maximum quantity of H₂ measured (Q_{max}) is very similar for all catalysts (49-54 μmolH₂·g_{cat}⁻¹) and are in line with the adsorption of ca. 2H/Ru (obtained comparing HAADF-STEM results) as found previously on silica-supported RuNPs [26]

[§] Based on the H₂O adsorption experiment (Figure S24) the calculated amount of H₂O monolayers at 260°C is 0.01ML for SiO₂-OH and 0.004ML for SiO₂-OSi(Me)₂Me.

^{**} Additionally, as shown by Panagiotopoulou et al. [35] who studied CO methanation reaction over Ru/Al₂O₃ at 250°C with co-fed CO₂ and H₂O, the rate of CO methanation is higher than the rate of CO₂ methanation by a factor of 14. The partial pressure of CO₂ used in abovementioned study (15%) was 15 times higher than the partial pressure of CO (1%). Thus, even in excess of CO₂, the rate of methanation was lower by an order of magnitude for CO₂. In our kinetic measurement the CO₂/CO ratio was 1.25. Hence, we believe that the extent of CO₂ methanation was significantly lower than the one for CO methanation.

In addition, the similar values of $Q_{\max}$ obtained by H_2 -chemisorption indicate similar accessibility of Ru surface atoms in all samples. Since the dispersions evaluated by both HAADF-STEM and H_2 -chemisorption are very similar (Table 1, Table 3), the number of subnanometer particles is probably small and does not contribute significantly to the observed rate difference between passivated and unpassivated silica surface.[35] On the other hand, the CO adsorption properties vary greatly, Ru/SiO₂-OSi(Me)₂**Me** and Ru/SiO₂-OSi(Me)₂**Bu** adsorbing 37% and 24% less CO than on the non-passivated system, Ru/SiO₂-OH. In addition, the linear fitting of the data points from the Henry Law regime of CO isotherm (Figure S19) shows that the shape of the isotherm varies for RuNPs on passivated and nonpassivated SiO₂. The higher slope for silica-supported RuNPs ($a = 1.42$) compared to RuNPs supported on passivated silica (0.64 and 0.51 for Ru/SiO₂-OSi(Me)₂**Bu** and Ru/SiO₂-OSi(Me)₂**Me** respectively) indicates that CO binds more strongly on RuNPs supported on the former, consistent with a higher affinity of CO. The IR spectra of supported RuNPs contacted with an excess of CO are consistent with this observation, with a decrease of the intensity of the CO bands by 41% and 38% for Ru/SiO₂-OSi(Me)₂**Me** and Ru/SiO₂-OSi(Me)₂**Bu** compared to Ru/SiO₂-OH.^{††} However the nature of the CO adsorbed species does not seem to be dramatically perturbed as the CO bands are similar for all samples (Figure S20). Furthermore, the CO-TPD (Temperature Programmed Desorption) study of catalysts, previously exposed with CO, barely shows any evolution of CO (Figure S21), while significant amount of CO₂ is observed, presumably arising from Boudouard reaction (CO disproportionation) or WGS (with residual adsorbed water). The main CO₂ peak is observed at 480°C, 485°C and

^{††} IR spectra were normalized with respect to siloxane bridge (Si-O-Si) region of the IR spectra.

560°C for Ru/SiO₂-OSi(Me)₂**Me**, Ru/SiO₂-OSi(Me)₂**Bu** and Ru/SiO₂-OH, respectively (Figure S22), consistent with the easier product formation and/or desorption for Ru particles on passivated support. In addition, the amount of CO₂ evolved during the CO-TPD experiment was significantly lower for RuNPs on passivated silica than on RuNPs supported on SiO₂. For Ru/SiO₂-OSi(Me)₂**Me** and Ru/SiO₂-OSi(Me)₂**Bu** the amount of CO₂ evolved during CO-TPD was 28% and 23% lower on the non-passivated system, Ru/SiO₂-OH, which is consistent with the CO chemisorption experiments (Table S3). However, while we have no direct evidence for it, the observed change of adsorption properties of supported RuNPs upon modification of the nanoparticle-support interaction (interface between the nanoparticle and the support) might be due to a change of the particle morphology (e.g. change of shape) or their electronic state.

4. Conclusions

The increase in methanation rate observed for RuNPs supported on passivated silica is likely arising from the lower adsorption affinity for CO on RuNPs in view of the inhibition of the reaction by CO (negative order). While the similar kinetic parameters for all catalysts indicate that the mechanism of the reaction remains unchanged for studied RuNPs, the observed difference of rates suggests that the energetics of some of the elementary steps are likely perturbed by the change of interface, i.e. the presence of the organosilane functionality. Overall, the observed change of adsorption properties and reactivity of supported RuNPs clearly results from the modification of the interface, and it could be due to a change of Ru particle morphology (shape) and/or their electronic state. We are currently further exploring this approach to tune the activity and selectivity

of supported metal nanoparticles, where the interface between the particle and the support can play an important role.

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