Experimental report

14/09/2023

Proposal:	**7-05-568**	**Council:**	10/2022

Title: Metal hydrides formation and hydrogen spillover over Ru/Al_2O_3 and Ru/AC catalysts

Research area: Chemistry

This proposal is a new proposal

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Samples:
Ru/AC
Ru/Al_2O_3
AC

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	5	07/06/2023	12/06/2023

Abstract:

Supported ruthenium nanoparticles are a promising alternative to more noble metals such as Pt or Pd as catalysts for hydrogenation and oxidation reactions. With this experiment we aim to investigate the nature of the Ru-H species formed upon dosing H_2 onto highly dispersed Ru catalysts supported on transition alumina and activated carbon supports, as well as the occurrence of hydrogen spillover from the metal surface onto the support. The experiment is part of a collaboration with our industrial partner Chimet S.p.A. The catalysts were already investigated and tested in catalysis in our labs, and Inelastic Neutron Scattering (INS) will provide fundamental insights on the nature of the Ru-H species formed at the metal nanoparticles surface in the presence of H_2, as well as on the (possible) occurrence of H-spillover phenomena involving the supports. Previous INS experiments on supported Pt and Pd catalysts (7-05-466, 7-05-514, 7-05-493) demonstrated that this approach is very valuable for better understanding the behavior of this typology of catalysts under hydrogenation conditions, and we are thus confident that fundamental results could be obtained for Ru as well.

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Characterization of surface Ru-hydrides and spillover on industrial Ru/Al_2O_3 and Ru/AC catalysts

1.Introduction

In this experiment, we investigated the INS spectra of the RuH species in three Ru based catalysts: one supported on Al_2O_3, and two others supported on two different industrial active carbons (AC). Ru based catalysts are already widely spread in catalysis for oxidation and hydrogenation reactions, however literature lacks a detailed characterization of RuH surface species by means of spectroscopic techniques. The observation itself of such species constitutes an experimental challenge due to the occurrence of spillover [1].

In our labs it was possible to follow the formation of linear RuH surface species upon dosing H_2 with FTIR spectroscopy. Hower RuH species are often reported to be mostly stable in the bridged form, which have characteristic signals that cannot be observed with FTIR because of support signals interference. We believe that these species can be easily observed with INS measurements, as we previously obtained good results with similar Pt based samples [2]. In particular, we expected to measure very weak Ru-H intensities at the limit of sensitivity of LAGRANGE spectrometer, meaning that good statistics (i.e. long scans) were fundamental, especially to work with difference spectra. Moreover, the samples the samples differed only in the support material, meaning that the metal loading was always fixed at 5 wt% in all three samples, allowing direct comparisons between the effects induced by the different supports. We were also interested in observing and correlate with the different supports the spillover phenomenon in presence of excess H_2, as it is a crucial aspect of hydrogenation reactions.

2.Experimental

The activation procedure was performed at our home university and consisted in: 1) outgassing the sample at RT; 2) further outgassing at 200°C (~ 470 K); 3) reduction in 100-200 mbar of H_2 at 200°C (~ 470 K) (three repetitions); 4) final outgassing up to a final pressure < 10-3 mbar at 200°C. The procedure was intended to remove all the physisorbed water on the sample and the weakliest bounded fraction of the hydroxyl groups at the alumina surface, as well as to reduce the nanoparticles to their metallic state. Any further manipulation was performed within a glove-box in order to avoid contaminations with atmospheric moisture and the re-oxidation of the sample. About 10 of samples were charged in the gas injection cell inside the glove-box. Prior to the experiments, the samples were outgassed with the available pumps at the beamline for about 6 hours.

The samples were measured at 25K as such and in the presence of H_2 excess (equilibrium pressure of about 500 mbar) that was instead dosed at RT. In addition to the metal supported catalysts, we also performed an experiment dosing excess H2 onto an AC support, which are themselves relevant for several applications. Bare samples and cells measurements were carried out to allow the difference treatment of data in the analysis.

3.Results and Discussion

The Ru nanocatalysts were measured at 25 K as such and after dosing excess of H_2 at RT, obtaining the spectra shown in Figure 1. The spectrum of the bare catalyst was then subtracted to the others, in order to highlight the spectral contributions attributed to the hydrogenous species formed and the spillover phenomenon (Figure 1C).

Here are reported the spectra obtained for the bare samples, for the samples in contact with excess H_2 and the difference spectra obtained from the previous two. Already from a first analysis of the spectra of the catalyst supported on alumina (Figure 1A), it is possible to observe the appearance of a signal centred just below 2000 cm^{-1}, which is confirmed by FTIR to be associated with linear RuH species. In the catalysts supported on ACs (Figure 1B and 1C) the spectral profile is significantly different, dominated by the CH stretching signals of the supports. The bands around 1600 cm^{-1} and 1000 cm^{-1} [2] are too overlapped with signals due to the support to be resolved, however it is possible to appreciate in the difference spectra the presence of a band around 500 cm^{-1} in all three catalysts that could be assigned to a RuH species [1,2]. In order to propose an attribution for the exact RuH species observed, it will be necessary to employ a parallel DFT simulation work on model systems to further support the data analysis.

Moreover, considering the Ru/Al_2O_3 catalysts, the rising OH band centred around 800 cm^{-1} upon dosing H_2 suggests the occurrence of spillover. The same behaviour is observed also in the Ru/AC samples, where the increase in intensity due to spillover is affecting both the narrow bands associated to out-of-plane CH bending between 750 and 1020 cm^{-1} and the broad band associated to in-plane CH bending between 1050 e 1600 cm^{-1} [1,3,4].

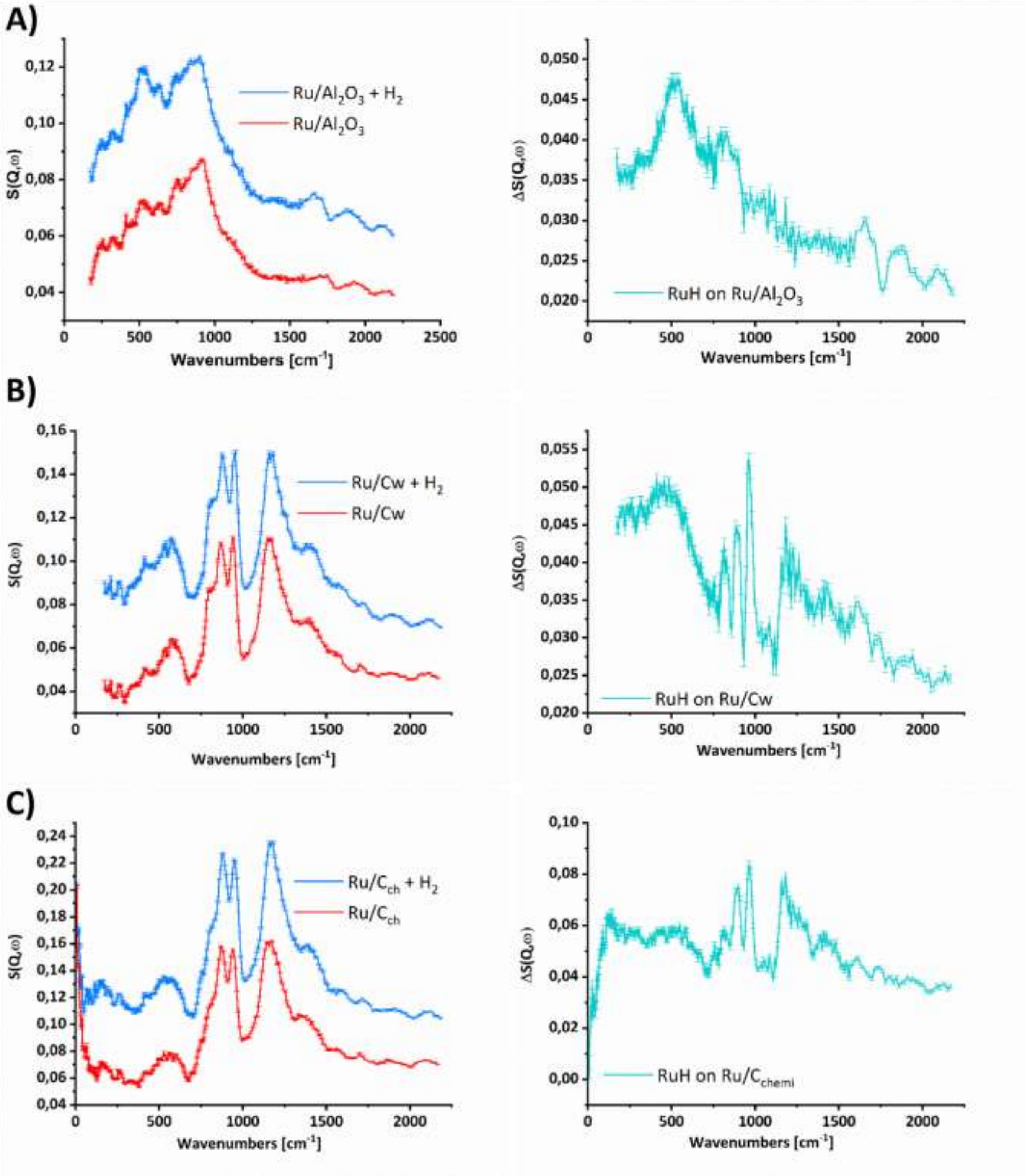

Figure 1. *A) Ru/Al$_2$O$_3$; B) Ru/Cw; C) Ru/Cch; Left: INS spectra of samples before (red) and after (blue) dosing excess H$_2$; right: INS difference spectra after dosing H$_2$.*

To further study the role played by the AC supports, an experiment has been conducted dosing H$_2$ onto an AC support without metal phase supported, obtaining interesting results compared to previous similar experiments. By comparing the former INS spectra of the AC supports collected during the experiment 7-05-466 under high H-coverage conditions and the new spectrum measured after H$_2$ during this experiment, it is possible to observe to observe that they exhibit very different spectral profiles, especially in the range related to the rotational peak of H$_2$ (Figure 2). These changes were attributed to effects induced by the different active carbons' porosity on the solid-like phase of encapsulated H_2, which could be an interesting topic to develop for its relevance for both hydrogen storage and catalytic purposes.

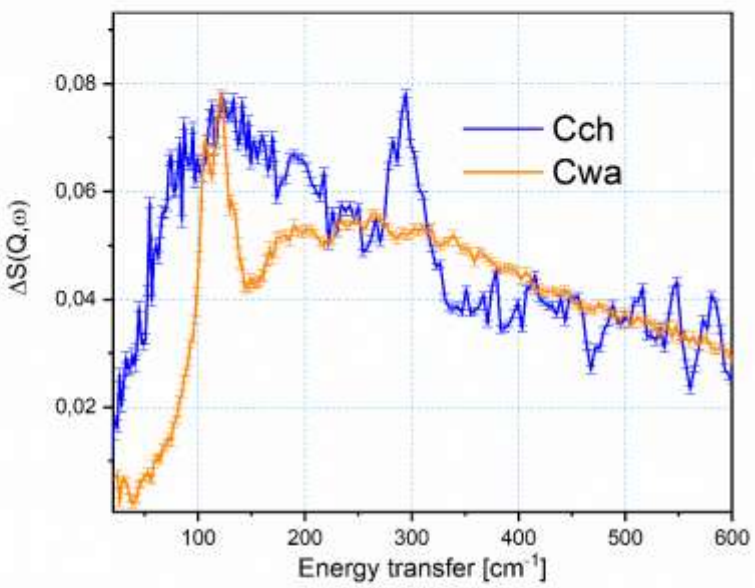

Figure 2. *INS difference spectra of AC supports Cw (blue) and Cch (orange) after dosing excess H_2*

Conclusions

To be able to characterize the adsorption species formed at a catalyst surface in the presence of H_2 as well as the occurrence of spillover phenomena is of fundamental importance in the field of hydrogenation catalysis. Among the available techniques, INS is sensible to all the vibrational modes of H-containing species, providing a complementary information to FTIR measurements on the vibrational frequencies of all Ru-H species formed in the sample and making it possible to compare their differences depending on the different support chosen. In this respect, with this experiment we managed to exploit the sensibility of the Lagrange instrument to measure very weak signals of the Ru-H bridged species formed in the presence of excess H_2. These results, paired with the ones of lab scale FTIR experiments, allow us to achieve better understanding of the surface interaction and phenomena occurring at Ru surface when exposed to H_2. The presence of H spillover onto the support, rarely seen on alumina supports, is also an interesting result of this experiment. Overall, the observation of this kind of dynamics of the catalyst is fundamental for understanding its behaviour under reaction conditions. Moreover, comparing observation made in this experiment on AC supports with results from experiment 7-05-466 (obtained under high H-coverage conditions), allowed to point out an interesting behaviour of the H_2 rotational band. It is known that the profile of such band can be correlated to the encapsulation of solid-like H_2 in AC micropores. This could be an interesting topic to develop for its relevance both for hydrogen storage and catalytic purposes.

References

[1] *Polo-Garzon, et al. ChemSusChem 12.1 (2019): 93-103.*

[2] *Vottero, et al. ACS Catalysis 12.10 (2022): 5979-5989.*

[3] *del Rosal, et al. The Journal of Physical Chemistry C 115.5 (2011): 2169-2178.*

[4] *Blackburn, et al. The Journal of Physical Chemistry C 116.51 (2012): 26744-26755.*