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Cite this: *Chem. Sci.*, 2024, **15**, 12369

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Understanding the role of supported Rh atoms and clusters during hydroformylation and CO hydrogenation reactions with *in situ*/*operando* XAS and DRIFT spectroscopy†

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Received 2nd May 2024
Accepted 29th June 2024

DOI: 10.1039/d4sc02907k

rsc.li/chemical-science

Supported Rh single-atoms and clusters on CeO_2, MgO, and ZrO_2 were investigated as catalysts for hydroformylation of ethylene to propionaldehyde and CO hydrogenation to methanol/ethanol with *in situ*/*operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray absorption spectroscopy (XAS). Under hydroformylation reaction conditions, *operando* spectroscopic investigations unravel the presence of both single atoms and clusters and detected at first propanal and then methanol. We find that the formation of methanol is associated with CO hydrogenation over Rh clusters which was further confirmed under CO hydrogenation conditions at elevated pressure. The activity of catalysts synthesized *via* a precipitation (PP) method over various supports towards the hydroformylation reaction follows the order: Rh/ZrO_2 > Rh/CeO_2 > Rh/MgO. Comparing Rh/CeO_2 catalysts synthesized *via* different methods, catalysts prepared by flame spray pyrolysis (FSP) showed catalytic activity for the hydroformylation reaction at lower temperatures (413 K), whereas catalysts prepared by wet impregnation (WI) showed the highest stability. These results not only provide fundamental insights into the atomistic level of industrially relevant reactions but also pave the way for a rational design of new catalysts in the future.

Introduction

The hydroformylation (HF) reaction, an industrially demanding reaction for producing aldehydes *via* the reaction of olefin and synthesis gas, is predominantly catalyzed by Rh molecular catalysts.[1,2] On the other hand, higher alcohol synthesis (HAS)[3–5] proceeds only in the presence of synthesis gas and is largely catalyzed by Rh solid catalysts.[5–7] Both reactions follow rather similar pathways *via* C–CO coupling reactions and yet the products are different. Recent studies show that Rh single-atom catalysts (SACs)[8–10] can be promising alternatives for heterogeneously catalyzed hydroformylation reactions[11,12] where the C–CO coupling reaction occurs like in conventional homogeneous Rh-phosphine complexes. Therefore, SACs are considered analogous to molecular catalysts.[13,14] The tunable local environment around the supported single atom makes it particularly attractive to investigate how the C–CO coupling reaction takes place. A recent example shows that Rh-WO_x pair site catalysts can boost the activity for gas phase hydroformylation reactions.[15] However, SACs are also prone to agglomeration due to their high surface energy particularly in a highly reductive environment.[16,17] Several reports claimed that Rh SACs stabilized by ionic liquids,[18] functionalized with an alkyl chain over a solid support,[19] synthesized by tuning surface deficiencies,[20] and even with strong metal–support cooperativity[21,22] show superior stability. Zhao *et al.* observed redispersion of Rh^0 clusters inside zeolite MFI to Rh single atoms and, ultimately, the formation of $Rh^+(CO)_2$ during hydroformylation of ethylene at 50 °C, which shows that the dynamic structural change plays a vital role under operating conditions.[23]

In the absence of an olefin, CO hydrogenation to higher alcohols (C_{2+}) over Rh catalysts[7,24,25] is a promising route since the synthesis gas mixture can be obtained from various

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d4sc02907k

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processes based on renewable resources such as biomass conversion,[26] CO_2 valorization,[27] dry-reforming of CO_2 with CH_4,[28] electrochemical conversion of CO_2,[29] photochemical conversion of CO_2,[30] conversion of plastic waste,[31] and many others.[32] However, until today, there has been no suitable catalyst that can achieve the desired activity and selectivity which are required for industrial scale production.[33] Therefore, it is extremely important to know the effect of Rh nuclearity,[24,34] support,[35] adsorbate–adsorbate interaction,[36] promoters,[32,33] morphology,[25] and particle size.[37] Cu-based catalysts are also promising alternatives for CO hydrogenation to higher alcohols; however, they compete with methanol synthesis and require promoters of alkali, transition, and rare-earth metals to produce higher alcohols as selective products.[38–40] The limitation of using other transition metals such as Co is that it catalyzes the competing Fischer–Tropsch process.[41]

A typical homogeneous HF reaction follows the classical Heck–Breslow mechanism[42,43] and usually proceeds *via* several steps such as (a) ligand dissociation from the complex, (b) olefin coordination, (c) alkyl formation *via* hydride insertion, (d) CO insertion, (e) H_2 oxidative addition and (f) reductive elimination. On the other hand, HAS involves (a) CO dissociation, (b) carbon–carbon bond formation, (c) CO insertion and (d) stepwise hydrogenation to the alcohol.[33,44] While in the HF reaction, all the steps can potentially occur over monometallic Rh, in HAS, synergetic effects between two neighbouring sites are likely required for C–C bond formation and CO insertion steps. For monometallic catalysts, the M^0 state is assumed to promote the C–C chain growth during HAS whereas $M^{\delta+}$ is responsible for CO insertion like in the classical HF reaction.[33,45]

This brings us to the question of whether Rh SACs can be active for both types of reactions as Rh exhibits a positive charge, and in a reductive environment, Rh^0 has been observed.[5] There have been many reports where the co-existence of SACs and small clusters was detected simultaneously under *in situ* conditions such as propane dehydrogenation,[46] dry-reforming of methane,[47,48] or CO_2 hydrogenation.[49,50] On the other hand, it is well known that Rh forms $Rh(CO)_2^+$-carbonyls in the presence of CO due to the strong interaction of CO with Rh.[51] In many of these catalytic processes, the presence of two species led to two different reaction pathways and hence two different products were observed. A recent study by Wu *et al.* claimed that the dynamic evolution of Rh single atoms to clusters over CeO_2 led to good activity for CO hydrogenation to ethanol, where the presence of Rh single atoms and clusters was found during the catalytic activity test.[34]

To understand these two reactions in detail, which can occur in parallel, we have synthesized Rh SACs and cluster catalysts over various supports (CeO_2, MgO, and ZrO_2) *via* precipitation,[16] atom trapping,[52,53] pyrolysis of molecular complexes[54] and flame spray pyrolysis (FSP).[55] These supports are chosen due to their variable acidity, reducibility, and, most importantly, variation in reactivity during the catalytic HF reaction as reported in the literature.[9] The as-synthesized catalysts were characterized *ex situ* by various state-of-the-art characterization methods and the dynamic behaviour[56] of Rh catalysts was tracked by *in situ* X-ray absorption spectroscopy (XAS)[57] and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS).[16] The products of the two reactions, (a) hydroformylation of ethylene to propanal and (b) CO hydrogenation to methanol/ethanol were monitored using an online mass spectrometer (MS).

Results and discussion

Synthesis and characterization of catalysts

The Rh catalysts synthesized *via* different routes have different metal contents in the range between 0.8 and 1.5 wt% as confirmed by the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. A plot of BET surface area as a function of metal content in the catalysts is shown in Fig. S1 of the ESI.† The surface area varies greatly depending on the support and synthesis procedure. For example, Rh/CeO_2 catalysts synthesized *via* FSP showed the highest specific surface area (133 $m^2\ g^{-1}$) in comparison to the one synthesized by wet impregnation (56 $m^2\ g^{-1}$) or precipitation methods (93 $m^2\ g^{-1}$). This is due to the fast quenching of the resulting solid synthesized by the FSP method which minimizes the particle growth, as explained elsewhere.[55] Among the catalysts prepared over different supports (CeO_2, ZrO_2 and MgO), ZrO_2 (synthesized by the precipitation method) showed the highest specific surface area of 201 $m^2\ g^{-1}$, which makes it attractive for application in catalysis.

The powder X-ray diffraction (XRD) patterns of the as-synthesized catalysts showed highly crystalline structures (Fig. S2–S7 in ESI†) in all cases. There is no Rh reflection (at $2\theta = 40°$) observed, confirming the high dispersion of Rh over different supports. Even when the content of Rh is increased from 0.6 wt% to 5 wt% over the CeO_2 support, we did not observe any reflection associated with Rh metal or RhO_x clusters as shown in Fig. S2.† The FSP method was also successful in preventing the formation of Rh nano-particles with long-range order (Fig. S3†), as also reported in the literature for other metals.[58–60] Aberration-corrected (C_s) high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) was used to visualize the nuclearity of Rh in the as-synthesized state of the catalysts over different supports. The images and the corresponding Energy Dispersive X-ray (EDX) maps are shown in Fig. 1 and in Fig. S8–S10.† The EDX maps confirm that Rh is uniformly distributed in all the catalysts except the Rh catalyst supported over CeO_2 synthesized by the pyrolysis method. In this case, RhP was formed, which showed nano-particle formation. The presence of some clusters (<2 nm) in the FSP synthesized catalyst cannot be entirely ignored, as observed in the EDX maps (Fig. S8†).

We further conducted X-ray absorption spectroscopy (XAS) to elucidate the local structure of the Rh catalysts as shown in Fig. 2. The extended X-ray absorption fine structure analysis (EXAFS) showed that Rh species over CeO_2, ZrO_2, and MgO are highly dispersed with Rh–O as the first coordination shell (without any Rh–Rh scattering) whereas the RhP/CeO_2 catalyst exhibits predominantly the Rh–Rh shell as shown in Fig. 2(a). The X-ray absorption near edge structure (XANES) spectra at the Rh K-edge showed that Rh is in an oxidation state of +3 over CeO_2, ZrO_2 and MgO and in a partially reduced state in the RhP/

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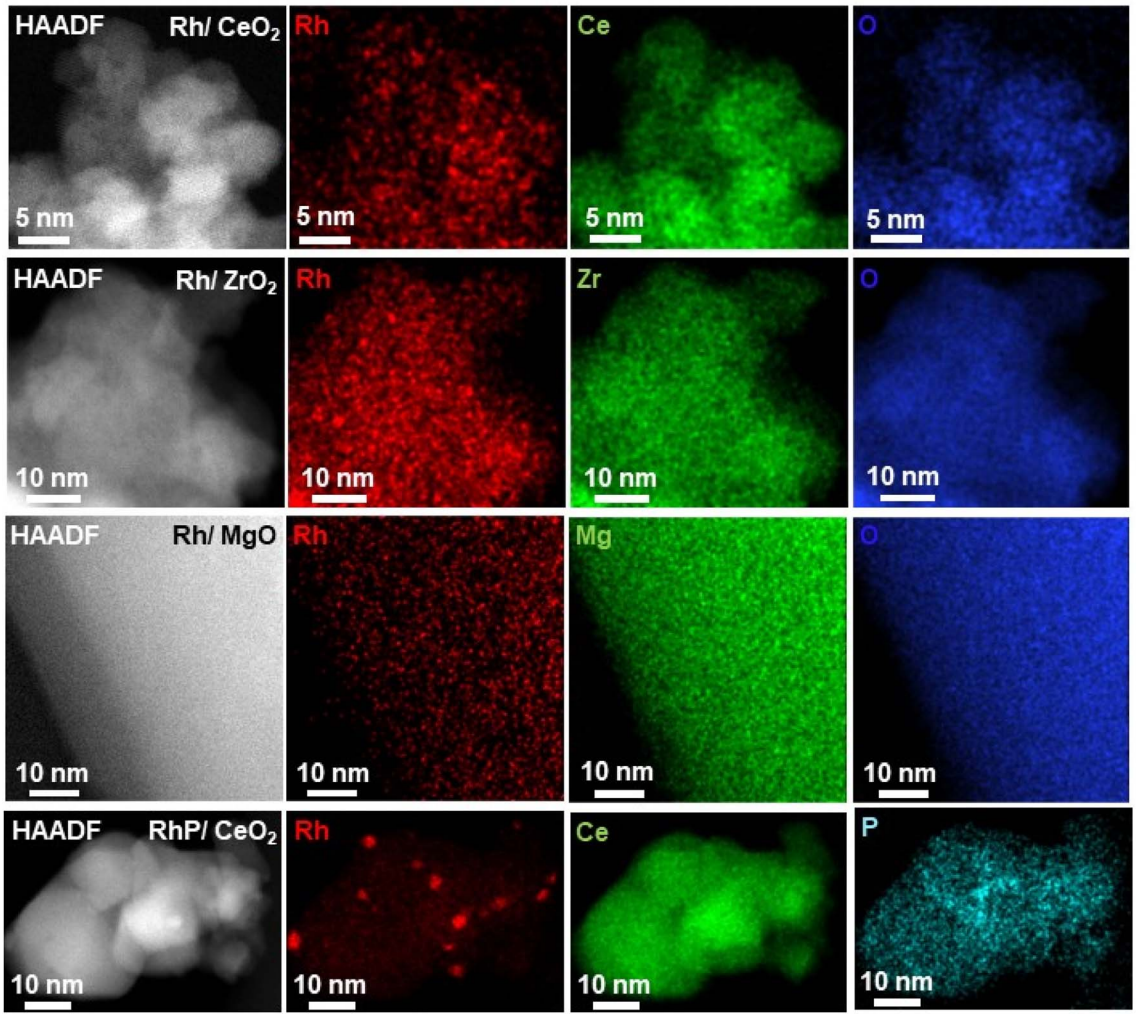

Fig. 1 HAADF-STEM images of Rh catalysts and the corresponding EDX maps. Rh/CeO_2, Rh/ZrO_2, Rh/MgO are synthesized *via* the precipitation method, and RhP/CeO_2 is synthesized *via* the pyrolysis route.

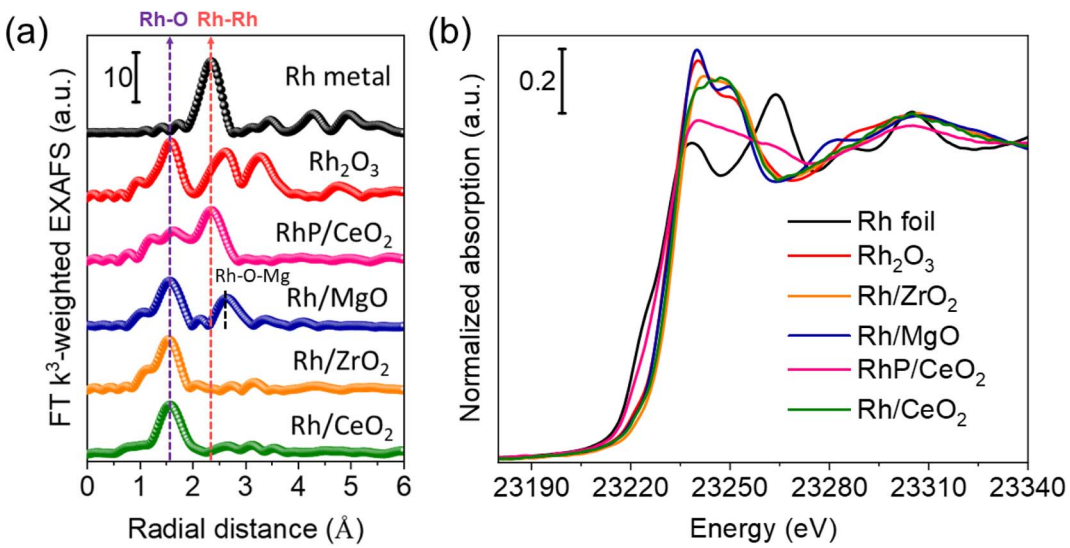

Fig. 2 (a) Fourier transform of the k^3-weighted EXAFS spectra and (b) XANES spectra at the Rh K-edge of the Rh catalysts supported over CeO_2, ZrO_2, and MgO. Rh_2O_3 and Rh foil are shown as references for comparison.

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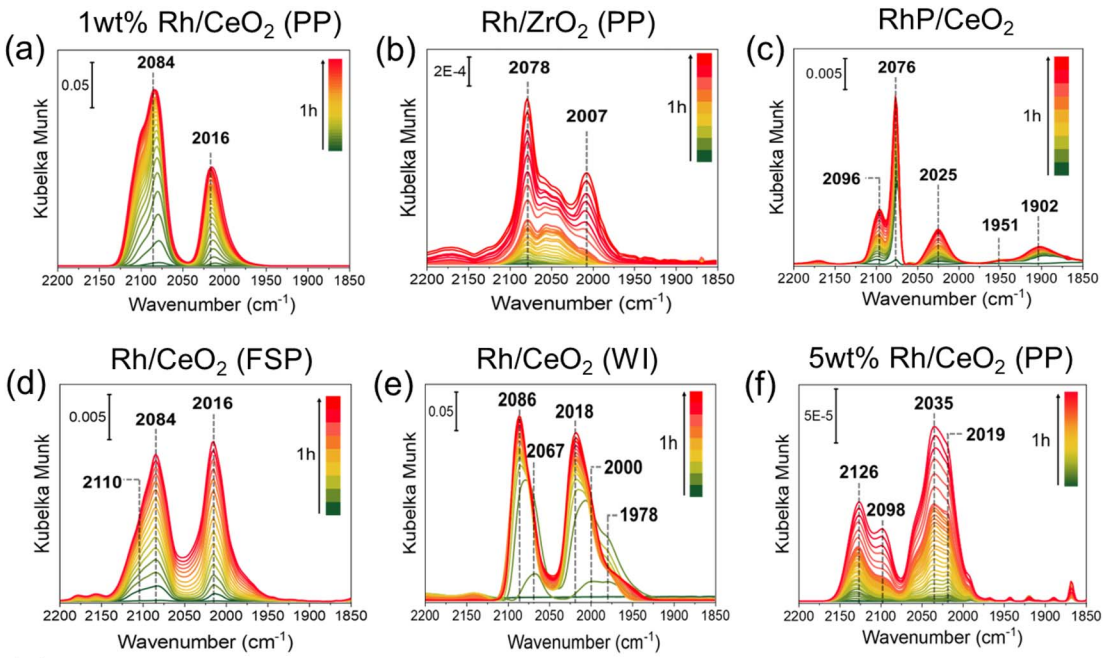
CeO_2 catalyst as shown in Fig. 2(b). The spectra of Rh catalysts synthesized over ceria with various methods are shown in ESI Fig. S11,† and the corresponding free parameters derived from the fit are shown in Table S2.† The X-ray photoelectron spectroscopy (XPS) investigation further supported the results obtained from XAS. All the catalysts except RhP/CeO_2 contain Rh^{III} as the predominant species on the surface as shown in Fig. S12 of the ESI.† The components present and their percentages are shown in Table S2.†

XAS[57] is an averaging technique over all species present and has certain limitations when used on heterogeneous samples. For example, over the oxide-supported catalyst, EXAFS cannot distinguish between single site and clusters of a few atoms as explained by Finzel *et al.*[61] Therefore, as a complementary technique, we carried out diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) investigations with CO as a probe molecule to elucidate the nuclearity of the Rh catalysts synthesized over different supports as shown in Fig. 3. CO adsorbed on Rh shows characteristic symmetric and anti-symmetric CO vibrational frequencies of single site $Rh^{I}(CO)_2$ in the range of 2070–2090 cm^{-1} and 2000–2020 cm^{-1} respectively.[16,49,62,63] Rh/CeO_2 synthesized *via* precipitation (PP), flame spray pyrolysis (FSP) and wet impregnation (WI) exhibit Rh single sites as the predominant species as shown in Fig. 3(a), (d) and (e) respectively. Similarly, Rh/ZrO_2 (PP) also showed the presence of symmetrical and asymmetrical CO vibrational frequencies at 2078 and 2007 cm^{-1} respectively.[64] On the other hand, the RhP/CeO_2 catalyst synthesized *via* the pyrolysis method showed the presence of CO adsorption over the Rh clusters in the lower frequency region (1850–1950 cm^{-1})[16] as shown in Fig. 3(c). The spectra are also shown on the logarithmic scale in Fig. S13.† These results are in agreement with the TEM observations (Fig. 1), which indicate the presence of Rh clusters as RhP/CeO_2. The DRIFT spectra of Rh/CeO_2 (5 wt%) with adsorbed CO showed various features (2126, 2035 cm^{-1}), which can be attributed to the weakly adsorbed CO over Rh^{3+} or Rh^{2+} species present in the form of RhO_x clusters.[23] Upon flowing Ar, two distinct CO absorption frequencies at 2023 and 2092 cm^{-1} were observed, as shown in Fig. S14,† which we believe arise from the fraction of Rh single atoms present in this high loading catalyst. Moreover, the presence of a broad CO adsorption peak between 1850 and 1900 cm^{-1} (Fig. S14†) infers the presence of Rh clusters in this catalyst. The Rh/MgO catalyst did not show any CO vibrational frequencies in the range 1800–2100 cm^{-1}, which indicates that Rh supported on MgO is coordinatively saturated as also found previously.[9,65] The CO



(g)

CO adsorption frequency (cm^{-1})	Assignments	CO adsorption frequency (cm^{-1})	Assignments
2084 (v_s), 2016 (v_{as})	$Rh(CO)_2/CeO_2$	2110	$Rh^{+}(CO)/CeO_2$
2078 (v_s), 2007 (v_{as})	$Rh(CO)_2/ZrO_2$	2046	$Rh_2(CO)/CeO_2$
2098 (v_s), 2035 (v_{as})	$Rh^{+}(CO)_2/CeO_2$	1902	$Rh_2(CO)/CeO_2$
2126	$Rh^{3+}(CO)/CeO_2$	2150-2180	Gas phase CO

Fig. 3 CO-DRIFTS spectra at room temperature over various Rh catalysts. (a) Rh/CeO_2 (PP), (b) Rh/ZrO_2 (PP), (c) RhP/CeO_2, (d) Rh/CeO_2 (FSP), (e) Rh/CeO_2 (WI), and (f) 5 wt% Rh/CeO_2 (PP). (g) Table of CO absorption frequency with assignments of Rh species. PP: precipitation, FSP: flame spray pyrolysis, and WI: wet impregnation. ν_s and ν_{as} stands for symmetric and anti-symmetric CO vibrational frequencies. The green to red color bar represents the experiment over 1 hour at room temperature.

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absorption frequencies of Rh catalysts over various supports and their assignments are shown in Fig. 3(g) as well as in Table S4 of the ESI.†

In situ XAS investigations

In order to understand the electronic state of Rh under operating conditions, we further carried out *in situ* XAS studies at the Rh K-edge for hydroformylation of ethylene (experimental setup is shown in S15 of the ESI†). The catalysts were exposed to a mixture of a 1 : 1 : 1 ratio of ethylene : CO : H_2 while heating from room temperature to 573 K (2 K min^{-1} and 30 min dwell time) at atmospheric pressure with a total flow of 40 mL min^{-1}. The gas mixture at the outlet was monitored with an online mass spectrometer. The temperature-dependent *in situ* XANES spectra were collected continuously at the Rh K-edge from room temperature to 573 K in the presence of the reaction mixture as shown in Fig. 4(a)–(d). All Rh catalysts were reduced under HF conditions with a change in the oxidation state of Rh from Rh^{3+} to Rh^0. Linear combination analysis (LCA) was used to derive the oxidized and reduced components during the reaction as shown in Fig. 4 (e)–(h). The trend of the reduction temperature from the highest to the lowest follows the order of Rh/MgO > Rh/ZrO_2 > Rh/CeO_2 > RhP/CeO_2. However, the catalytic activity does not follow the same trend. Both in Rh/CeO_2 and Rh/ZrO_2, we observed propanal at around a temperature of 500 K, which is the product formed *via* the HF reaction as shown in Fig. 4(i) and (j). At this stage, almost 80–90% of the Rh species are already reduced which indicates the possible involvement of clusters during catalysis. Interestingly, when all the Rh is reduced, methanol is detected in the MS. This indicates that when Rh forms clusters, the pathway for CO hydrogenation is enhanced as also shown by Wu *et al.*[34] This is supported by our catalytic test over the RhP/CeO_2 catalyst which contains a significant fraction of Rh clusters, for which formation of methanol was detected almost parallel to the formation of propanal (Fig. 4(l)). Rh/MgO did not show any activity even in the presence of reduced rhodium, which indicates that the basic support does not promote HF or methanol formation. Among the Rh/CeO_2 catalysts, Rh synthesized by FSP showed catalytic activity at a lower temperature (*ca.* 410 K) compared to the catalysts synthesized by precipitation or wet impregnation methods, as shown in Fig. S16 of the ESI.† This might be due to better accessibility of the Rh atoms deposited on high surface area CeO_2 when synthesized *via* the FSP method.[55]

In order to find the origin of methanol formation, we further carried out the reaction in the absence of ethylene (CO : H_2 of 1 : 1) in a quartz capillary micro-reactor at 10 bar pressure in the temperature range of RT-573 K. The temperature dependent

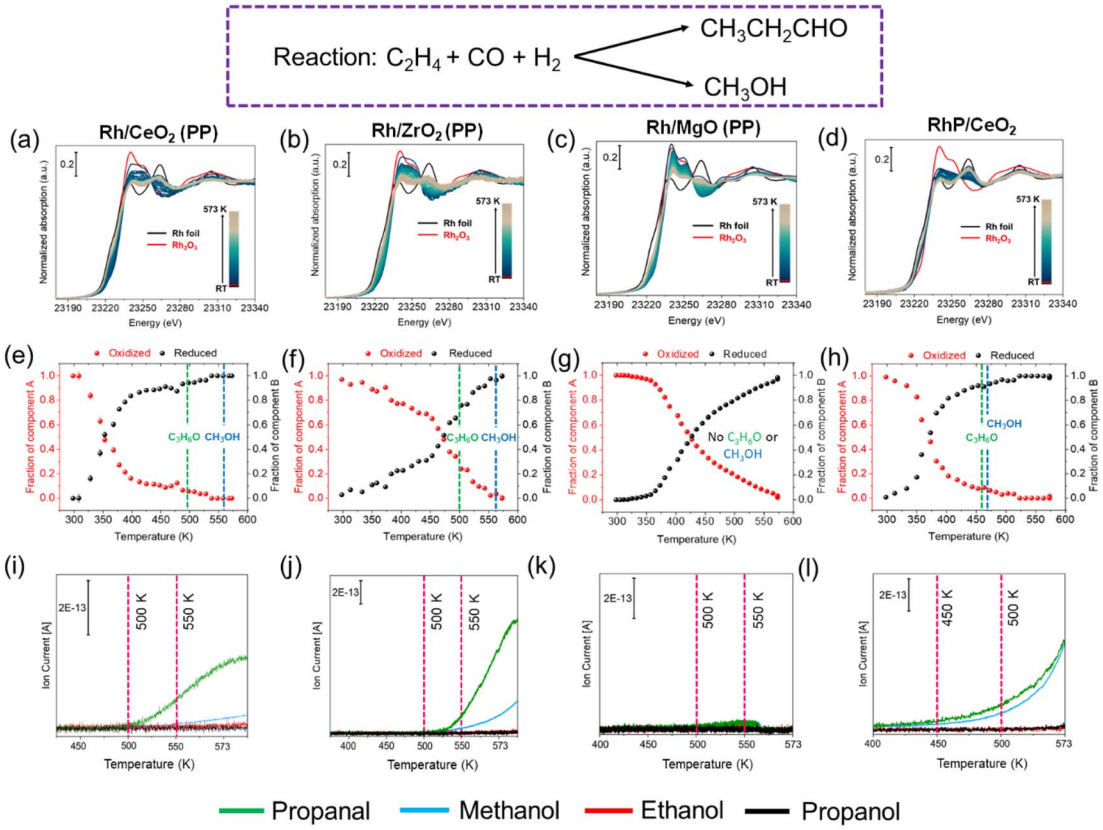

Fig. 4 *In situ* XANES spectra at the Rh K-edge of catalysts prepared over different supports ((a)–(d)), the fraction of components (oxidized and reduced) derived from linear combination fitting ((e)–(h)) during the hydroformylation reaction of ethylene, and selectivity of different products monitored using an online mass spectrometer (i)–(l). The dotted lines are a guide to the eye. PP stands for precipitation. Reaction conditions: 25 mg catalysts, 1 : 1 : 1 mixture of ethylene : CO : H_2, T = RT-573 K (ramp rate 2 K min^{-1}), P = 1 bar, flow rate: 40 mL min^{-1}.

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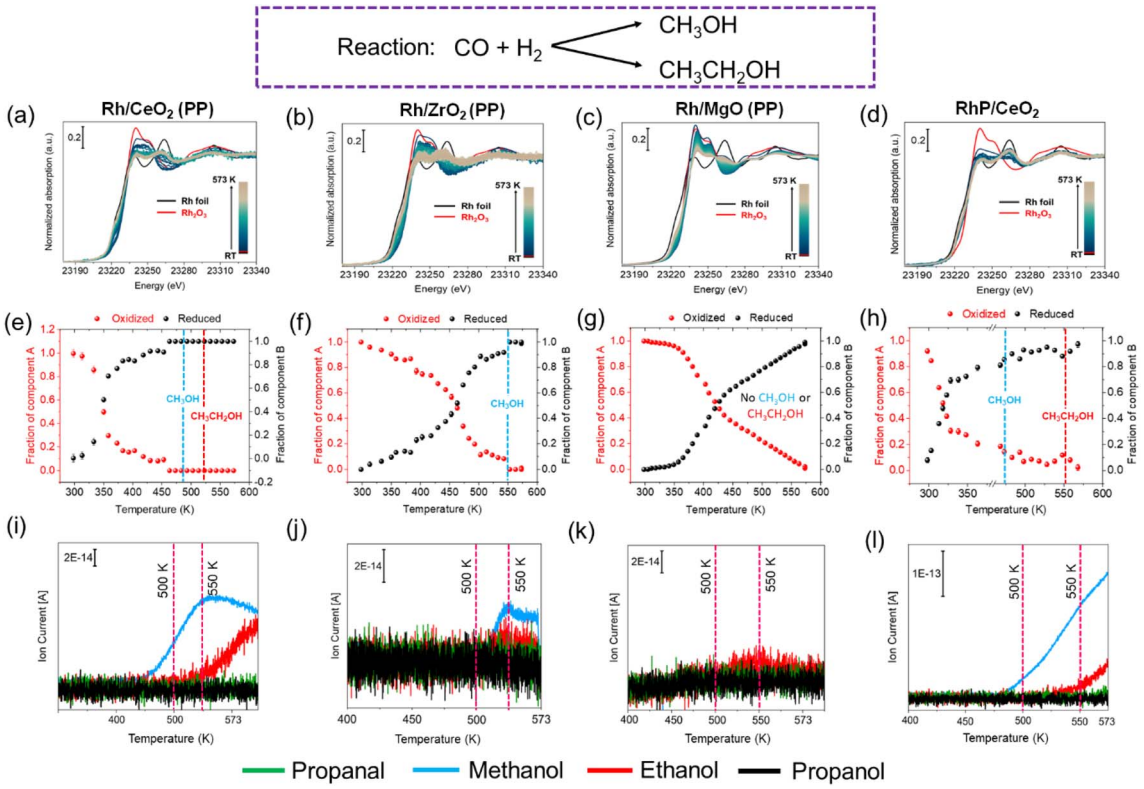

Fig. 5 *In situ* XANES spectra at the Rh K-edge of catalysts prepared over different supports ((a)–(d)), the fraction of components (oxidized and reduced) derived from linear combination fitting ((e)–(h)) during CO hydrogenation, and selectivity of different products monitored using an online mass spectrometer (i)–(l). The dotted lines are a guide to the eye. PP stands for precipitation. Reaction conditions: 25 mg catalysts, 1 : 1 mixture of CO : H_2, T = RT-573 K (ramp rate 2 K min^{-1}), P = 10 bar, flow rate: 40 mL min^{-1}.

XANES spectra and the linear combination analysis of the oxidized and reduced components during the reaction are shown in Fig. 5. The mass spectrometer (MS) detected both methanol and ethanol over Rh/CeO_2 synthesized *via* the precipitation method (Fig. 5(i)). This further indicates that the nuclearity of Rh plays a crucial role in obtaining methanol and ethanol products as previously reported.[24,34] The Rh/ZrO_2 catalyst showed only methanol in the product stream and no ethanol was observed. Rh/MgO did not show any activity as was also the case for the HF reaction. RhP/CeO_2 showed initially only methanol, and ethanol was only observed at higher temperatures (550 K) when a significant portion of Rh^0 formed. The Fourier transformed k^3-weighted EXAFS spectra after the HF reaction and CO hydrogenation reaction are shown in Fig. S17 of the ESI.† The predominant presence of the Rh–Rh shell indicates that most of the catalysts were reduced completely at the end of the reaction except Rh/MgO and Rh/ZrO_2, which showed a significant proportion of the oxidic species (presence of the Rh–O shell). We further carried out fitting of the Rh–Rh shell to calculate the coordination number of Rh in the spent catalysts. The fits and the free parameters are shown in ESI Fig. S18 and in Table S5.† The coordination numbers obtained from the fits are in the range between 1 and 6. Nevertheless, such low coordination values indicate that the size of the reduced Rh species is extremely small.[66,67] To further confirm whether the concentration of Rh plays a significant role during the reaction, we have conducted the CO hydrogenation reaction over Rh/CeO_2 with three different Rh loadings (1.1, 2.2 and 4.5 wt%). The results are shown in Fig. S19 of the ESI.† The catalytic results indicate that upon increasing Rh content over the CeO_2 support, the formation of methanol and ethanol is enhanced. 4.5 wt% Rh/CeO_2 showed the formation of methanol and ethanol simultaneously like the RhP/CeO_2 catalyst, which indicates that for a highly loaded sample, Rh easily forms nanoparticles which can promote the C–CO coupling reaction. These results further signify the role of clusters during HF and CO hydrogenation reactions.

Based on our results, three summary points can be hypothesized for the reaction mechanism. (a) Rh single atom catalysts form the active center upon treatment with syngas and actively take part in the hydroformylation reaction, (b) when Rh clusters are formed, it mainly favors methanol synthesis, and (c) for ethanol formation, both atoms and clusters participate during the reaction as the CO insertion step requires $Rh^{\delta+}$ species for C–C chain propagation. These points are summarized in Fig. S20 of the ESI.†

In situ DRIFTS investigations

In order to investigate the change in the state of Rh, we carried out DRIFTS experiments under various conditions, as shown in

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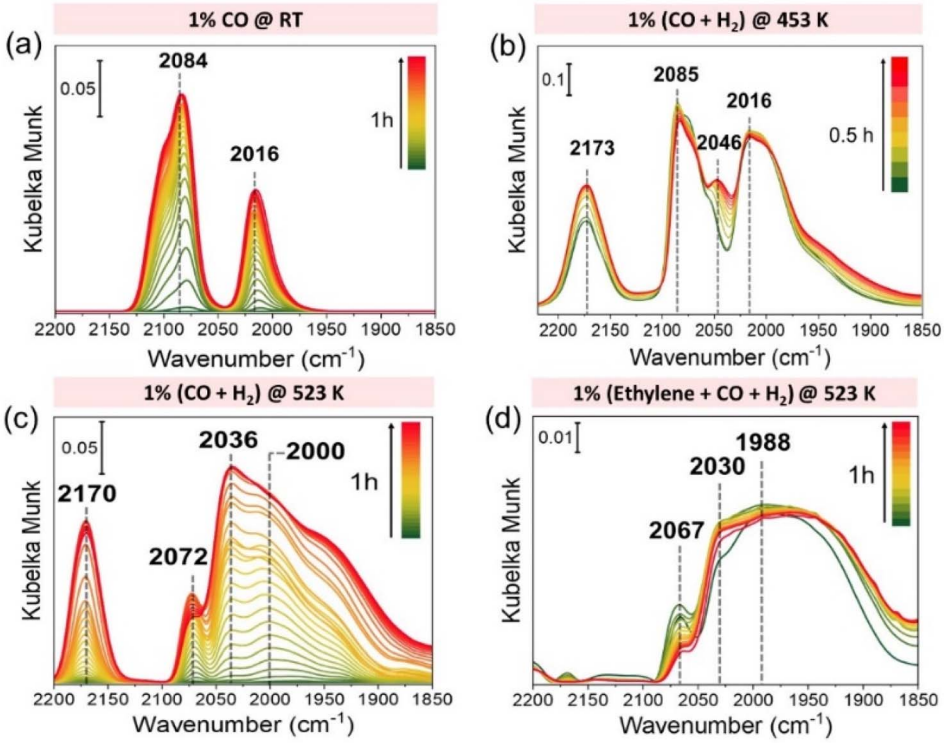

Fig. 6 *In situ* DRIFTS spectra collected for 1 hour under various conditions of the catalyst Rh/CeO_2 synthesized *via* precipitation method. (a) 1% CO at room temperature, (b) 1% ($CO + H_2$) at 453 K, (c) 1% ($CO + H_2$) at 523 K and (d) 1% (ethylene + CO + H_2) at 523 K.

Fig. 6. As discussed before, at room temperature Rh/CeO_2 showed CO vibrational frequencies at 2084 and 2016 cm^{-1} that correspond to symmetrical and anti-symmetrical vibrational modes of CO of $Rh^I(CO)_2$ species. The change in the state of Rh is already visible at 453 K under 1% ($CO + H_2$) as a new CO vibrational frequency appears at 2046 cm^{-1} (Fig. 6(b)), which corresponds to CO adsorbed on Rh clusters. Upon increasing the temperature to 523 K, clusters of Rh formed and an additional feature at 2036 cm^{-1} was observed (Fig. 6(c)), which we believe to occur due to the formation of Rh(CO)H species as reported in the literature.[37] This trend continued when ethylene was introduced to the reaction mixture. However, even under such a reductive atmosphere, there is still the presence of isolated Rh species (2030 cm^{-1}) as shown in Fig. 6(d). These results correlate with the *in situ* XAS studies and further hint that Rh atoms and clusters formed under reaction conditions play a crucial role during the HF reaction. Additionally, we carried out DRIFTS experiments on the Rh/CeO_2 catalyst synthesized *via* the wet impregnation method, which showed higher stability based on our *in situ* XAS studies (Fig. S16(c)†). The DRIFTS results showed no obvious formation of clusters, unlike for the catalyst synthesized *via* the precipitation method, as shown in Fig. S21 of the ESI.† A comparison of the H_2-temperature programmed reduction (TPR) profile and the DRIFT spectra collected at 453 K with the catalyst prepared over various supports (CeO_2, ZrO_2, and MgO) is shown in Fig. S23 of the ESI.† The results showed that based on the support, Rh exhibits different reduction temperatures, and it follows the order of $Rh/CeO_2 < Rh/ZrO_2 < Rh/MgO$. The DRIFT spectra recorded at 453 K under $CO + H_2$ indicated that Rh/ZrO_2 did not show any Rh cluster formation. On the other hand, Rh/MgO did not show any feature regarding CO adsorption, which infers that Rh is not easily available on the surface of MgO and may be located in the highly coordinated bulk environment.

Conclusions

In conclusion, we have found that highly dispersed Rh catalysts supported over CeO_2, ZrO_2, and MgO showed co-existence of supported single Rh atoms and clusters under conditions of HF of ethylene and CO hydrogenation reactions. The *in situ* XAS studies infer the formation of reduced Rh particles/clusters while both propanal and methanol were observed during the HF reaction. In addition, the *in situ* DRIFTS studies showed vibrational frequencies of CO adsorbed over Rh atoms and clusters under reaction conditions, which further supports that such unprecedented reactivity might have occurred due to the presence of both species. The formation of a significant amount of ethanol was observed during the CO hydrogenation reaction over the RhP/CeO_2 catalyst, which also showed the presence of nano-particles (>2 nm) already in the as-synthesized catalyst. Moreover, by increasing the concentration of Rh from 1.1 wt% to 4.5 wt% over the CeO_2 support, we observed the CO hydrogenation reaction at a relatively low temperature. This indicates that a certain size of Rh nano-particles is important to promote the C–C coupling reaction during higher alcohol synthesis.

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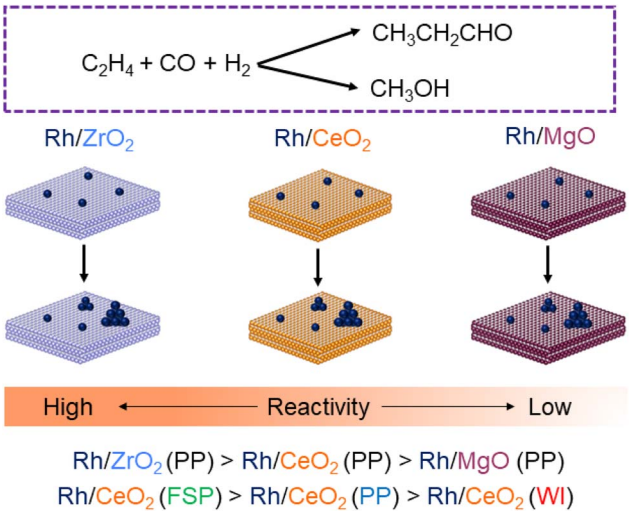

Fig. 7 Summary of reactivity towards the hydroformylation reaction of ethylene with supported Rh catalysts on CeO_2, ZrO_2, and MgO. PP, FSP, and WI stand for precipitation, flame spray pyrolysis, and wetness impregnation, respectively.

Comparisons of catalytic activity over various supports showed that acidic supports, such as ZrO_2, promote the hydroformylation reaction, whereas basic supports, such as MgO, result in negligible catalytic activity. The varying reactivity towards hydroformylation of ethylene is dependent on the preparation method and support, as summarized in Fig. 7. Among the catalysts synthesized over CeO_2 with various methods, catalysts prepared *via* flame spray pyrolysis showed activity at low temperatures which indicates that the method of preparation plays a vital role during the reaction. This study will pave the way for further development of catalysts for such an industrially relevant reaction. In the future, we plan to investigate the CO insertion mechanism of the two reactions in more detail by introducing promoters and extending the reactions over further industrially relevant supports.

Data availability

Data supporting the article (experimental protocols, XRD, XPS, BET, and TPR results) are available in the ESI.† The raw data can be provided upon request to the corresponding author.

Author contributions

BBS: conceptualization; investigation, data curation & formal analysis (catalyst preparation & catalytic testing, including *in situ* XAS and DRIFTS); formal analysis (XAS, DRIFT, and XRD); writing the original draft. DN: data curation (XAS and XPS) and formal analysis (XPS); writing-review and editing. DD: data curation and formal analysis (XAS); writing-review and editing. ALN: data curation and formal analysis (TEM); writing-review and editing. LB: data curation (XAS); writing-review and editing. BK: data curation and formal analysis (XPS); writing-review and editing. JDG: overall supervision, funding acquisition, resources, writing–discussion–review and editing.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors would like to thank Dr Eduardo Barbosa and Angela Deutsch for nitrogen physisorption measurements and Armin Lautenbach for ICP-OES analysis. Alisa Sinigalia is thanked for her assistance during the XPS measurements. Andrea De Giacinto and Dr Linda Klag are thanked for their assistance with the FSP synthesis. Michael Borchers is thanked for the H_2-TPR measurements. Dr Lu Chen (University of Cambridge, UK) and Prof. Philippe Serp (LCC, CNRS, France) are thanked for the fruitful discussion during the preparation of the manuscript. We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of beamtime, allocated to the proposals I-20200891 and I-20211473 and KIT light source (A2020-031-018713). We would like to thank Dr Edmund Welter (P65, DESY) and Dr Anna Zimina (CATACT, KIT Light Source and IKFT) for their assistance in setting up the beamline. HAADF-STEM imaging and EDX imaging were carried out with the support of the Karlsruhe Nano Micro Facility (KNMFi, **https://www.knmf.kit.edu**), a Helmholtz Research Infrastructure at the Karlsruhe Institute of Technology (KIT, **https://www.kit.edu**). Support from the Helmholtz Association and Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – SFB 1441 – Project-ID 426888090 is gratefully acknowledged. BBS would like to thank CNRS for startup funding.

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