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1. Introduction

The depletion of fossil fuel reserves and the increasing rate of greenhouse gas emissions as a result of the current coal and oil-based chemical processes motivate the search for green and sustainable chemical technologies. The use of biomass, the only source of renewable carbon at this moment, opens up new opportunities for sustainable production of fuels and chemicals. Carbohydrates, the constituent monomers of the most abundant (hemi)cellulose biopolymers, contain much more oxygen than fossil feedstock. A major challenge involved in catalytic upgrading of biomass is, therefore, the cleavage of C–O bonds originating from hydroxide and ether bonds in the lignocellulosic feedstock.^{1–3}

Liquid phase reforming of water-soluble organic compounds obtained from woody biomass feedstock is an attractive process for obtaining a gas mixture of hydrogen and carbon dioxide. The product mixture can also be steered to obtain alkanes and monofunctional alcohols.⁴ Hydrogen is a

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Aqueous phase reforming of glycerol over Re-promoted Pt and Rh catalysts†

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The potential of Re promotion for carbon-supported Pt and Rh nanoparticles was investigated for aqueous phase reforming (APR) of glycerol as a model compound for biobased feedstock. Upon alloying with Re, the overall conversion rate of glycerol was substantially increased for both metal catalysts. Whereas Pt/C is more active than Rh/C in glycerol APR, the RhRe/C catalyst outperforms PtRe/C. The overall APR catalytic performance strongly correlates with the activity trend for the gas-phase water-gas shift (WGS) reaction. RhRe/C exhibited the highest activity in APR and WGS reactions. A very strong synergy between Rh and Re and Pt and Re is observed in the model WGS reaction. The role of Re in the bimetallic catalysts is to facilitate water dissociation, effectively increasing the WGS activity. During APR, this results in lower steady-state CO coverage and increased glycerol conversion rates. In terms of selectivity, the yield of renewable hydrogen is increased. The use of Re as a promoter also results in significant changes in the product selectivities during glycerol APR. Although gas-phase acetaldehyde decomposition measurements evidenced that alloying with Re increased C-C bond cleavage activities of Pt/C and Rh/C, the increased acidity due to acidic hydroxyl groups bound to Re resulted in a more substantial increase of dehydration reactions. Whereas Rh/C is more selective for formation of products involving C-C bond cleavage than Pt/C, the product mixtures of their alloys with Re reflect a much increased ratio of C-O vs. C-C bond cleavage reaction rates.

> key reactant in many refinery processes for producing liquid fuels and biofuels and may also become an important energy vector in the future.⁵ Glycerol serves as a model compound for the aqueous phase reforming (APR) process, as it contains C– O, C–C, C–H and O–H bonds in its structure, similar to complex biomass-derived carbohydrates.^{6–8} Glycerol can be obtained *via* hydrogenolysis of cellulose or C₆ sugars. At this moment, the dominant source of glycerol is as a by-product of biodiesel production. Utilization of this over-produced glycerol as a novel feedstock for green chemicals production is essential for the applicability of the biodiesel production process.^{9,10}

> Generally, Pt group metals are preferred as catalysts for APR.^{8,11,12} Recently, experiments in reforming and hydrogenolysis of polyols show that the overall conversion and selectivity towards deoxygenated products increases when a highly reducible metal catalyst (such as Pt, Rh, Ru or Ir) is combined with Re.^{13–22} So far, significant efforts have been devoted to explaining the nature of the active sites of the PtRe system. Due to their enhanced activity in C–O cleavage, RhRe catalysts have also been explored in recent studies for selective hydrogenolysis of polyols.¹³ For instance, Koso *et al.* found Rh–ReO_x/SiO₂ to be much more active and selective in the hydrogenolysis of the C–O bond of tetrahydrofurfuryl alcohol to form 1,5-pentanediol compared with conventional Pt hydrogenolysis catalysts.²³ In another study, a similar catalyst with a Re/Rh molar ratio of

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0.5 was found to give the highest activity in the hydrogenolysis of glycerol to 1,3-propanediol in a comparison with Mo and W modified Rh/SiO₂ catalysts.¹⁷ The C-C bond cleavage activity of Rh/SiO₂ was significantly suppressed upon addition of Re resulting in an increase of the yield of propanediols. Recently, Chia et al. studied the hydrogenolysis of polyols and cyclic ethers over a bifunctional RhRe catalyst.¹⁴ The hydrogenolysis activity of RhRe was explained by a bifunctional mechanism in which acid-catalyzed ring-opening at the more substituted carbon center was followed by metal-catalyzed hydrogenation. Heeres and co-workers reported the transformation of 5hydroxymethylfurfural to caprolactone in a process which involves the conversion of 2,5-THF-dimethanol (THFDM) to 1,6-hexanediol over a RhRe/SiO₂ catalyst in the presence of various solid acid catalysts.²⁴ The main advantage of Re-modified catalysts over conventional ones was reported to be the cleavage of the C-O bond neighboring a -CH₂OH group.

Unlike H2-assisted polyol hydrogenolysis reactions, hydrogen and carbon dioxide are among the major products in the APR of glycerol. Hydrogen can be used directly to produce work, for instance in hydrogen fuel cells, or as an external source of hydrogen required in biomass upgrading processes.²⁵ During APR of glycerol, the *in situ* produced hydrogen is consumed to hydrogenate the dehydrated reaction intermediates which are produced via C-O bond cleavage. Hydrogen formation derives from the dehydrogenation of terminal alcohols (e.g., glycerol) to aldehydes (e.g., glyceraldehyde), followed by decarbonylation to CO and subsequent water-gas shift (WGS) to CO2.8,26-28 The WGS activity of APR catalysts has been found to be important for their overall activity. Dumesic and co-workers have attributed the promotional effect of Re on Pt/C in aqueous phase glycerol conversion to increased WGS activity.²⁰ In a recent study by Guo et al. the basic properties of a set of catalysts were correlated to their WGS and APR activities.29

In this work, we aimed at comparing the promotional effect of Re on the catalytic performance of Rh and Pt catalysts in the water–gas shift reaction and aqueous phase reforming of glycerol. Activated carbon is chosen as a hydrophobic high surface area support for dispersing the metal oxide precursors. Bimetallic RhRe and PtRe catalysts and their monometallic counterparts were prepared at similar Rh(Pt)/Re molar ratios. These catalytic materials were evaluated in the WGS reaction, acetaldehyde decomposition and APR of glycerol and characterized using X-ray absorption spectroscopy and temperature programmed reduction.

2. Experimental methods

2.1 Catalyst synthesis

Rh-, Pt- and Re-containing catalysts were prepared by incipient wetness impregnation using appropriate solutions of $H_2PtCl_6\cdot 6H_2O$, $RhCl_3\cdot (H_2O)_x$ and $HReO_4$. As the support, activated carbon (Norit RX3-EXTRA, S.A. = 1190 m² g⁻¹, P.V. = 1 ml g⁻¹) was used. Prior to preparation, the carbon support was

dried overnight at 110 °C. Bimetallic RhRe/C and PtRe/C samples were prepared by sequential impregnation of dried Rh/C and Pt/C catalysts with a perrhenic acid solution of appropriate concentration followed by drying at 110 °C overnight. The molar Rh/Re and Pt/Re ratios were targeted at 2.

2.2 Catalyst characterization

The metal content of the catalysts was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis performed on a Goffin Meyvis Spectro Cirus^{ccd} apparatus. The samples were dissolved in a 3:1 HCl-HNO₃ solution.

Temperature programmed reduction (TPR) was carried out in a flow apparatus equipped with a fixed-bed reactor, a computer-controlled oven and a thermal conductivity detector. Typically, 25 mg catalyst was loaded in a tubular quartz reactor. The sample was reduced in 4 vol% H_2 in N_2 at a flow rate of 8 ml min⁻¹, whilst heating from room temperature up to 800 °C at a ramp rate of 10 °C min⁻¹. The H_2 signal was calibrated using a CuO/SiO₂ reference catalyst.

Transmission electron micrographs were acquired on a FEI Tecnai 20 transmission electron microscope at an acceleration voltage of 200 kV with a LaB₆ filament. Typically, an amount of the sample was ground and suspended in pure ethanol, sonicated and dispersed over a Cu grid with a holey carbon film. All samples were reduced in 10 vol% H₂ in He (total flow 100 ml min⁻¹) at 300 °C for 2 hours, followed by passivation in 1 vol% O₂ in He for 2 hours.

X-ray absorption spectroscopy (XAS) measurements were carried out at the Dutch-Belgian Beamline (Dubble) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France (storage ring 6.0 GeV, ring current 200 mA). Data were collected at the Rh K, Pt LIII and Re LIII edges in transmission mode. Energy selection was done by a double crystal Si(111) monochromator solid-state detector. Background removal was carried out by standard procedures. EXAFS analysis was then performed with EXCURVE931 on k^3 -weighted unfiltered raw data using the curved wave theory. Phase shifts were derived from ab initio calculations using Hedin-Lundqvist exchange potentials and Von Barth ground states. Energy calibration was carried out using Rh and Pt foils and Re powder. The amplitude reduction factors S₀² associated with central atom shakeup and shake-off effects were set at 0.90, 0.75 and 0.99 by calibration of the first shell Rh-Rh, Re-Re and Pt-Pt coordination numbers to 12, respectively, for the k^3 -weighted EXAFS fits of the Pt foil, Rh foil and Re powder. Spectra were recorded in a stainless-steel controlled atmosphere cell. The cell was heated with two fire rods controlled by a temperature controller. A thermocouple was placed close to the catalyst sample. Typically, a predetermined amount of finely grinded sample was pressed in a stainless steel holder and placed in the cell. Carbon foils were held between two high-purity carbon spacers. Gases (He and H_2) were delivered by thermal mass flow controllers (Bronkhorst). The catalyst sample was heated at a rate of 10 °C min⁻¹ up to a final temperature of 550 °C, whilst recording XANES spectra. EXAFS spectra were recorded

at room temperature after reduction of the sample at the desired temperature for 1 hour. A second set of XAS measurements were performed under *in situ* WGS reaction conditions. After recording the room temperature EXAFS of the catalysts reduced at 300 °C, the sample was heated to 150 °C under helium flow. At 150 °C, CO was mixed with He and fed through a Controlled Evaporator Mixer unit where steam was generated to obtain a H_2O : CO ratio of 3. The sample was heated at a ramp rate of 10 °C min⁻¹ and EXAFS spectra for each sample were recorded during WGS reaction at 300 °C.

2.3 Catalytic activity measurements

Water-gas shift reaction. The water-gas shift (WGS) reaction was performed in a parallel ten-flow microreactor system.³⁰ Steam was supplied by evaporation of deionized water in a Controlled Evaporator Mixer unit (Bronkhorst) in combination with a liquid-flow controller and gas flows were controlled by mass flow controllers (Brooks and Bronkhorst). All tubings were kept above 100 °C after the point of steam introduction to avoid condensation. The dry product gas mixture was analyzed using an online gas chromatograph (Interscience CompactGC) equipped with Porapak Q (TCD) and Molecular sieve 5A (TCD) columns. Experiments were carried out in a mixture of 2.5 vol% CO and 7.5 vol% H₂O balanced by He at a dry GHSV of $\sim 1.5 \times 10^5$ h⁻¹ in the temperature range 130-400 °C. Typically, the catalyst was diluted with SiC of the same sieve fraction. The material was contained between two quartz wool plugs in a quartz reactor. Prior to catalytic activity measurements, the catalyst was reduced in a flow of 20 vol% H_2 in He at a ramp rate of 5 °C min⁻¹ to 300 or 500 °C followed by an isothermal period of 0.5 h. The reactor was cooled in He to the reaction temperature. The catalyst was exposed to the reaction mixture for 10 min prior to the start of recording the product gas mixture. At each reaction temperature, the product gas mixture was recorded for 1.5 h.

Acetaldehyde decomposition. Acetaldehyde decomposition experiments were performed in a continuous flow reactor setup. Hydrogen and acetaldehyde were fed in equimolar amounts as the feed components. Acetaldehyde was fed by bubbling helium through a saturator kept at a suitable temperature to obtain an acetaldehyde concentration of 3 vol%. Catalyst samples were first reduced at 300 °C. The reaction was carried out at 225 °C at a GHSV of 7200 ml_{acetaldehyde} g_{cat}⁻¹ h⁻¹. The reactor effluent was analyzed by online gas chromatography (Interscience GC-8000 Top). CO, CH₄ and H₂ were analyzed on a Shincarbon ST80/100 packed column connected to a TCD. Acetaldehyde and ethanol were analyzed on a RT-Q bond column connected to a FID.

APR of glycerol. APR reactions were carried out at 225 °C under 25 bar initial N_2 pressure using 60 g of 10 wt% aqueous glycerol solution in a 120 ml autoclave. An amount of 75 mg of reduced catalyst was loaded in the autoclave together with an appropriate amount of deaerated water in a N_2 -flushed glovebag. The autoclave was purged five times with 10 bars of N_2 in order to remove residual air from the autoclave. A 50/50 w/w mixture of glycerol and water was charged into the reactor

from an external holding vessel after the autoclave containing water and the catalyst reached the desired reaction temperature. The stirring speed was 600 rpm. Liquid samples were withdrawn by a ROLSI injector and analyzed using a Trace GC equipped with a Stabilwax column and a FID detector. Gas samples were collected online and analyzed using a Focus GC equipped with a TCD detector and CP-Porabond Q and RT-MolSieve-5A columns. The carbon product selectivities were calculated using:

$$S_i(\%) = \frac{\text{mol of product}_i \text{ formed } \times \text{ number of C atoms}}{\text{mol of glycerol in the feed } \times \text{ conversion } \times 3} \times 100$$

3. Results and discussion

3.1. Catalyst characterization

The metal contents of the catalysts are collected in Table 1. The Rh loading in Rh/C and RhRe/C is \sim 2 wt% and the Pt loading in Pt/C and PtRe/C is \sim 2.5 wt%. The molar ratios of Rh and Pt to Re in the bimetallic catalysts were determined to be \sim 1.5.

The TPR traces of the catalysts are plotted in Fig. 1. The trace of Re/C shows a hydrogen consumption peak at 378 °C and the reduction is complete at 410 °C. Reduction of Rh/C and Pt/C takes place at much lower temperature. The trace of Rh/C shows two maxima at 157 and 206 °C. H₂ consumption below 250 °C is typically attributed to the reduction of rhodium oxide.^{31,32} The reduction of Rh/C in two steps is in line with the literature.¹⁴ Similar to Rh/C, the TPR profile of the Re-promoted Rh catalyst (Fig. 1f) shows a low temperature peak at 162 °C accompanied by a broad peak centered at around 200 °C. The intensity of this second broad peak is higher than that observed for Rh/C, which suggests that the reduction of Re oxide precursor (Re₂O₇) takes place in this temperature regime. The easier reduction of Re in the presence of an easily reducible metal is attributed to hydrogen spillover from metallic Rh or Pt to neighboring Re-oxides.33-37 Reduction of RhRe/C commences around 75 °C, whereas reduction of PtRe/C starts at around 155 °C. Easier reduction of Rh than Pt is in agreement with results reported by Samoila et al.³⁸ The broad features observed at temperatures higher than 400 °C are attributed to reduction of oxygen-

Table 1	Metal loading	as determined	by ICP analysis
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	Metal loadi	ng (wt%)	
Catalyst	Rh (Pt)	Re	Rh(Pt)/Re atomic ratio
Rh/C	2.08	_	_
RhRe/C	2.04	2.41	1.54
Pt/C	2.44	—	
PtRe/C	2.48	1.53	1.54
Re/C	_	2.78	_



Fig. 1 TPR traces of (a) the bare carbon support, (b) Re/C, (c) Pt/C, (d) PtRe/C, (e) Rh/C and (f) RhRe/C.

functionalized groups on the surface of the activated carbon support.

Representative TEM images of the reduced samples are shown in Fig. 2. The average particle size of all catalysts is close to 1 nm. Due to the small size of the particles, it is not straightforward to accurately determine the metal dispersion of the catalysts. The contrast is better for the Pt catalysts. The Rh-based catalysts appear to be somewhat smaller than the Ptones. The average size of the nanoparticles in Rh/C and RhRe/ C is around 1.0 and 0.8 nm, respectively. The Pt-based catalysts



Fig. 2 TEM images and average particle sizes determined for (a) Rh/C, (b) RhRe/C, (c) Pt/C and (d) PtRe/C.



Fig. 3 Rh K-edge (left) and Re L_{III}-edge (right) XANES spectra of RhRe/C during *in situ* reduction (b, k) at 100 °C, (c, l) 200 °C, (d, m) 250 °C, (e, n) 300 °C, (f, o) 400 °C, (g, p) 500 °C and (h, r) 550 °C. Re L_{III}-edge XANES spectrum of the as-prepared sample at room temperature is shown as trace (j). XANES spectra of Rh₂O₃ (a), Rh foil (i) and Re powder (s) are also included for comparison.

contain slightly larger nanoparticles, *i.e.* 1.2 nm for Pt/C and 1.0 nm for PtRe/C.

XANES spectra at the Rh–K and Re L_{III} -edge of RhRe/C as a function of temperature during reduction under H_2 flow are shown in Fig. 3. There is a clear shift to lower values of the Rh K and Re L_{III} -edge energies with increasing reduction temperature. In line with this, the intensities of the whiteline features, which originate from the density of the unoccupied d-states, decrease with increasing reduction temperature. Whereas at 100 °C the Rh XANES spectrum resembles that of the Rh₂O₃ reference (Fig. 3a), it is very similar to that of the Rh foil after reduction at 200 °C (Fig. 3i). This shows that reduction takes place between 100 and 200 °C. The most significant changes in the XANES spectra of RhRe/C at the Re L_{III} edge also occur in the same temperature regime. These findings are in line with the TPR results.

Fig. 4 shows the experimentally obtained FT EXAFS spectra and their fits at the Rh K, Re $L_{\rm III}$ and Pt $L_{\rm III}$ edges of the reduced catalysts. The fit parameters are collected in Table 2. Rh/C reduced at 300 °C contains a Rh-Rh shell with a coordination number (CN) of 6.9 and a bond distance (R) of 2.681 Å (Table 2). The CN of the Pt-Pt shell in reduced Pt/C is 8.3. The difference points to higher dispersion of Rh/C, although also less ordering of the atoms in nanoparticles can be the cause of lower metal-metal coordination numbers. For the bimetallic RhRe catalyst Rh-Re and Rh-Rh shells can be distinguished. The bond distance of the Re-Rh shell in the bimetallic catalyst is 2.656 Å (Table 2). In view of the metal bonding radii of 0.134 and 0.137 nm for Rh and Re, respectively,³⁵ this bond distance represents a direct Rh-Re interaction. A Re-O shell with a CN of 0.5 needed to be included during fitting, which implies that a small fraction of the Re species remains in the (partially) oxidic state in line with the XANES results. At the Rh K edge, no Rh-O shell was observed, which points to the presence of

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Fig. 4 FT EXAFS functions obtained from the k^3 -weighted Pt L_{III} edge EXAFS oscillations (left) of Pt/C (a) and PtRe/C (b) reduced at 300 °C; FT EXAFS functions obtained from the k^3 -weighted Rh K edge EXAFS oscillations (middle) of Rh/C (c) and RhRe/C (d) reduced at 300 °C; FT EXAFS functions obtained from the k^3 -weighted Re L_{III} edge EXAFS oscillations (right) of RhRe/C (e) and PtRe/C (f) reduced at 300 °C. Dotted lines represent the fitted spectra.

Table 2 Fit parameters of k^3 -weighted EXAFS spectra at the Rh K, Re L_{III} and Pt L_{III}-edges of supported catalysts recorded at room temperature (catalyst reduced at 300 °C)

Catalyst	EXAFS ana	EXAFS analysis								
	Shell	<i>R</i> (Å)	CN	$\Delta\sigma^2$ (Å ²)	E_0 (eV)					
Rh/C	Rh–Rh	2.681	6.9	0.007	-2.5					
Pt/C	Pt–Pt	2.745	8.3	0.009	-9.8					
RhRe/C	Rh–Rh	2.678	2.5	0.006	-1.6					
	Rh–Re	2.657	0.4	0.002						
	Re-O	2.060	0.5	0.007	-11.3					
	Re-Re	2.840	1.2	0.012						
	Re-Rh	2.656	2.5	0.005						
PtRe/C	$Pt-M_{Pt}$	2.728	7.5	0.010	-8.9					
	Re-M _{Re}	2.658	7.2	0.007	-3.6					

well-reduced Rh metal particles. The smaller CN of the Rh-Re shell (0.4) compared to the Re-Rh shell (CN = 2.5) points to the isolated nature of the Re atoms in the bimetallic nanoparticles.35 The CN of the Rh-Rh shell for the Re-modified bimetallic catalyst is lower (2.5), even if the Rh-Re coordination is taken into account (total 2.9), than the Rh-Rh CN of the monometallic Rh/C catalyst (6.9). This points to higher dispersion of the bimetallic catalyst. The EXAFS results for the PtRe/C catalysts are less informative, as the Pt-Re and Pt-Pt as well as Re-Pt and Re-Re interactions cannot be separated due to the quite similar backscattering properties of Pt and Re. The effect of setting the backscatterer to Pt vs. Re was found to be negligible in the EXAFS analysis of Pt and Re L_{III}-edge data. The backscattering atom used in fitting was denoted as M with a subscript to indicate the atom type. The PtRe/C catalyst contains a Pt- M_{Pt} shell with a CN of 7.5. The CN of the ReM_{Re}

shell is 7.2. No Pt–O or Re–O coordination shells were observed. In summary, X-ray absorption spectroscopy points to higher dispersion of RhRe/C compared to PtRe/C. The decrease in the CN of the metal–metal shell for Pt upon alloying with Re is much lower than for Rh. All catalysts are well reduced, although a small Re–O contribution is observed for reduced RhRe/C.

3.2. Catalytic activity measurements

The WGS reaction is a key step in the APR reaction mechanism, because it removes adsorbed CO product from the catalyst surface and generates additional H₂ by reaction with water.⁴ Separate gas-phase WGS activity measurements were carried out to establish possible differences in the WGS rate for the carbon-supported catalysts. Fig. 5 shows Arrhenius plots for all of the catalysts. Among the monometallic catalysts, Re/C is more active than Pt/C and Rh/C, especially at higher temperatures. Rh/C and Pt/C have nearly similar catalytic activities. The bimetallic catalysts are significantly more active in WGS than the monometallic ones. The apparent activation energies are 70, 85, 106, 102 and 126 kJ mol⁻¹ for Pt/C, Rh/C, Re/C, PtRe/C and RhRe/C, respectively. The promotional effect of Re is substantially higher for Rh than for Pt. EXAFS recorded during the WGS reaction at 300 °C shows that the Rh and Pt nanoparticles in the monometallic catalysts remain metallic (Table 3, Fig. S1[†]). The metal-metal coordination numbers in Rh/C and Pt/C increase only slightly. For RhRe/C, the coordination numbers of the metal-metal shells increase significantly. These data suggest the growth of the initially small bimetallic RhRe nanoparticles during WGS operation. However, this is at odds with the finding that the WGS activity



Fig. 5 Arrhenius plot for WGS reaction over Pt/C (**I**), Rh/C (**O**), PtRe/C (**A**), RhRe/C (**V**) and Re/C (**•**). All catalysts were reduced at 300 °C, except for Re/C which was reduced at 500 °C (WGS conditions: 130–400 °C, H₂O : CO = 3, dry GHSV of ~1.5 × 10⁵ h⁻¹). Apparent activation energies in kJ mol⁻¹ are given in parentheses.

Table 3 Fit parameters of k^3 -weighted EXAFS spectra at the Rh K, Re L_{III} and Pt L_{III}-edges of supported catalysts recorded during the WGS reaction at 300 °C

Catalyst	EXAFS analysis								
	Shell	R (Å)	CN	$\Delta\sigma^2$ (Å ²)	E_0 (eV)				
Rh/C	Rh–Rh	2.675	7.1	0.010	-0.3				
Pt/C	Pt–Pt	2.744	9.8	0.014	-9.5				
RhRe/C	Rh–Rh	2.679	6.2	0.008	-1.6				
	Rh–Re	2.645	0.6	0.002					
	Re-O	2.001	0.5	0.003	-8.0				
	Re-Re	2.729	4.8	0.016					
	Re-Rh	2.670	3.5	0.009					
PtRe/C	Pt-M _{Pt}	2.734	7.8	0.013	-9.6				
	Re-M _{Re}	2.675	8.3	0.010	-4.6				

of RhRe/C was very similar during cooling from 400 °C as it was during the initial forward heating trend. An alternative interpretation of the EXAFS data is that the RhRe particles become better ordered during the WGS reaction. This would then also be in line with the nearly similar total Rh–(Rh + Re) coordination shells (~6.8) as compared to that of Rh/C during WGS (7.1). EXAFS data analysis does not show significant changes in the structure around Pt and Re for the PtRe catalyst during the WGS.

Acetaldehyde decomposition was used as a model reaction to probe catalytic activity in C–C bond cleavage. The feed mixture contained hydrogen to avoid excessive carbon laydown on the metal nanoparticles. The decomposition products CO and CH₄ were found in equimolar ratios. For PtRe/C, a small amount of ethanol was found due to acetaldehyde hydrogenation (selectivity ~10%). Fig. 6 shows the yield of CO as a function of time on stream for the various catalysts. Re/C was inactive under the reaction conditions, which is likely due to its high metal–carbon energy resulting in blocking of the active sites by carbonaceous deposits. The acetaldehyde





Fig. 6 Yield of acetaldehyde decomposition product CO as a function of time on stream for Rh/C (\bullet), Pt/C (\blacksquare), RhRe/C (\bigtriangledown), PtRe/C (\blacktriangle) and Re/C (\diamond).

decomposition activity of Rh/C is three times higher than that of Pt/C. This difference is consistent with the higher activity of Rh compared to Pt in ethane hydrogenolysis as reported by Sinfelt.³⁹ Whereas the rate determining step in ethane hydrogenolysis is the C-H bond cleavage step, the higher rate of Rh in ethane and acetaldehyde hydrogenolysis compared to Pt should be related to the higher metal-carbon bond energy for the former metal.⁴⁰ Addition of Re to the monometallic catalysts strongly increases the reaction rate. Although there might be an effect of the smaller particle size upon alloying with Re, the higher metal-carbon bond energy of Re is expected to be the dominant factor for the higher activity in decarbonylation. The presence of Pt or Rh in the alloy with Re ensures the removal of the CH3 surface intermediates following acetaldehyde decarbonylation, these metals being better hydrogenation catalysts than Re. Based on pseudo-first order kinetics with respect to acetaldehyde, the activity increased by a factor of ~2.2 for Pt/C and ~1.8 for Rh/C upon alloying with Re. In contrast to the other catalysts, RhRe/C deactivates slowly. The reason for this deactivation is not clear but might be related to the high rate of acetaldehyde decomposition and the low rate of hydrogenation resulting in carbon deposition on the catalytic surface.

The glycerol conversion in APR as a function of time on stream for the various catalysts is shown in Fig. 7. All catalysts were reduced at 300 °C, except for Re/C which was reduced at 500 °C to ensure complete reduction. The activity increases in the order Re/C < Rh/C < Pt/C < PtRe/C < RhRe/C. The low activity of Re/C is consistent with the literature on the reforming and hydrogenolysis of polyols.^{14,19,23,41} Pt/C exhibits higher APR activity than Rh/C, in line with the results reported by Dumesic *et al.* for APR of ethylene glycol.¹¹ As the atomic Pt(Rh)/Re ratios of the two bimetallic catalysts are very similar, the promoting effect of Re is higher for Rh/C than for Pt/C in glycerol APR.



Fig. 7 Glycerol conversion as a function of time on stream for Rh/C, Pt/C and RhRe/C, PtRe/C and Re/C (APR reaction conditions: 225 °C, 25 bar initial N₂ pressure, batch autoclave, 10% aqueous glycerol solution).

The reaction mechanism in APR involves two competing reaction pathways differing in the way oxygen is removed.¹⁸ In the first one, oxygen is removed by dehydration of an alcohol group followed by hydrogenation of the resulting olefinic bond (C-O bond cleavage) and, in the second one, by decarbonylation of aldehyde intermediates obtained after initial dehydrogenation (C-C bond cleavage). Dehydrogenation of glycerol to glyceraldehyde is the first step in the latter reaction pathway. Decarbonylation of glyceraldehyde via C-C cleavage leads to the formation of CO and ethylene glycol. Product CO is converted to CO2 via the water-gas shift reaction. Because of the low temperature and excess water, the gas phase will mainly contain CO₂ with only minor amounts of CO.⁴ Dehydration and subsequent hydrogenation removes oxygen as water. The intermediate product observed following glycerol dehydration is hydroxyacetone. Upon hydrogenation, 1,2-propanediol and a small amount of 1,3-propanediol are formed and they are converted to propanols and finally to propane by similar reactions.8 The hydrogenation reaction in the C-O bond cleavage pathway consumes the hydrogen produced in the dehydrogenation step of the C-C bond cleavage pathway. Thus, while the formation of propane requires exclusively dehydration and hydrogenation reactions (C-O bond cleavage), formation of ethane involves one decarbonylation step and two dehydration steps. Ethanol is formed via hydrogenolysis of ethylene glycol.^{14,42} Methane is the product of decarbonylation of acetaldehyde obtained from ethanol. Note that blank reactions in APR and also in the WGS reaction did not show any formation of methane, so that we can exclude undesired reforming of the carbon support.

Product selectivities as a function of time on stream for Pt/C, Rh/C, PtRe/C and RhRe/C are shown in Fig. 8 (detailed product distribution in Tables S1–S6†). The main products for Re/C are hydroxyacetone and 1,2-propanediol with minor

amounts of CO₂ produced (see ESI[†]). This product distribution is consistent with the low acetaldehyde decarbonylation activity for Re/C. Note that initially no 1,2-propanediol is formed over Re/C (Table S1[†]). With increasing time on stream, only a minor part of hydroxyacetone is hydrogenated to 1,2propanediol, as Re/C alone is a poor hydrogenation catalyst.¹⁹ The product selectivities of Pt/C and Rh/C with time on stream are significantly different. At low conversion, hydroxyacetone is the dominant product for Pt/C (C-O bond cleavage), whereas Rh/C produces mainly CO2 and alkanes next to a much smaller amount of hydroxyacetone. The difference with Pt/C is due to the much higher decarbonylation activity of Rh/C consistent with the much higher rate of acetaldehyde decarbonylation. The ratio of 1,2-propanediol to hydroxyacetone is also much lower for Rh/C than for Pt/C, which points to a lower rate of hydrogenation. The most likely reason for the higher rate of decarbonylation of Rh/C is the higher metal-carbon bond energy for Rh compared to Pt. The overall differences in the product selectivities are also reflected in the data shown in Fig. 9. Fig. 9a shows the ratio of C–O and C–C bond cleavage reaction rates. The value determined for Pt/C (around 0.6) is in agreement with the results obtained by Zhang et al. in APR of glycerol over Pt/C in a fixed bed continuous flow reactor system.¹⁸ This ratio is initially lowest for Rh/C. Fig. 9b shows the H_2/CO_2 ratio, which is close to the theoretical value of 2.3 for complete reforming of glycerol to CO2 and H2. The reason is the low rate of hydrogenation over Rh/C throughout the experiment. Thus, it is concluded that the main reaction pathway for Rh/C involves dehydrogenation and decarbonylation of glycerol to alkanes and CO, which is rapidly converted to CO₂. With increasing time on stream more hydroxyacetone is formed. As the APR reaction proceeds, the dominance of C-C bond cleavage over Rh/C becomes less pronounced as intermediate products will also undergo C-O bond cleavage reactions. For Pt/C we observe a decreasing selectivity of hydroxyacetone with time on stream, which is related to its hydrogenation to 1,2-propanediol. Although Rh/C is slightly more active than Pt/C in the WGS reaction, Pt/C shows a higher glycerol conversion rate. The higher H₂ and CO₂ yields obtained for Pt/C when compared to Rh/C (Table 4) is also related to the higher overall conversion obtained using Pt/C. Alloying with Re leads to much higher overall reaction rates and significant changes in the product composition in the APR of glycerol. The ratio of C-O over C-C bond cleavage reactions is significantly increased (Fig. 9a). The acetaldehyde decomposition activity data show that addition of Re increases the decarbonylation activities of Pt/C and Rh/C. This is explained by the formation of an alloy of Pt and Rh with the more reactive Re metal. It is consistent with findings for PtRe alloys in naphtha reforming.⁴³ In classical reforming, Re sites are poisoned by H₂S to decrease the rate of undesired C-C bond cleavage reactions. In glycerol APR, the dominant effect of Re is to bring about a much higher rate of dehydration as is evident from the very different product distributions obtained upon alloying and the finding that the product distributions for PtRe/C and RhRe/C are similar. Fig. 9b shows that alloying



Fig. 8 Selectivities as a function of time on stream during APR of glycerol over (a) Pt/C, (b) PtRe/C, (c) Rh/C and (d) RhRe/C.



Fig. 9 C-O/C-C bond cleavage ratios (a) and H_2/CO_2 ratios (b) for Rh/C (\bullet), Pt/C (\blacksquare), RhRe/C (\bigtriangledown) and PtRe/C (\blacktriangle) during glycerol APR.

results in lower H_2/CO_2 ratios because of the use of product H_2 for hydrogenation of the intermediates obtained by dehydration. The initial values for Pt/C and PtRe/C of around 2.3 and 2.0 are in agreement with the results reported by Zhang *et al.* for similar catalysts in APR of glycerol.¹⁸ The shift to higher selectivity of ethane and propane at the expense of methane selectivity upon Re addition is also a consequence of the higher C–O over C–C bond cleavage reaction rates. In addition, the overall yields of H_2 and CO_2 are substantially increased upon alloying Rh and Pt with Re (Table 4). The increase in the H_2 (CO₂) yield is the highest for the RhRe/C catalyst.

The importance of Re to bring about Brønsted acidity during aqueous phase reactions has been well established by now.¹⁴ For instance, the formation of such acid sites upon steaming of PtRe/C at 225 °C has been followed by NH₃-TPD.¹⁸ The increased surface acidity of Rh/C upon addition of Re was also noted for non-steamed samples.¹⁴ Similar acidic properties were identified for Re-modified Ru/SiO₂ catalysts.⁴⁴ The work of Dumesic, Neurock and co-workers has shown that Re-OH surface species can catalyze dehydration reactions of alcohol groups.¹⁴ The stronger metal–oxygen bond energy results in more facile dissociation of water. Note that Re/C is apparently not very active for dehydration. This is most likely due to the propensity of Re to become oxidized when no other,

Catalyst	Time (min)											
	20		80		140		200		260		320	
	$Y(H_2)$	$Y(CO_2)$	$Y(H_2)$	$Y(CO_2)$	$Y(H_2)$	$Y(CO_2)$	$Y(H_2)$	$Y(CO_2)$	$Y(H_2)$	$Y(CO_2)$	$Y(H_2)$	$Y(CO_2)$
Pt/C	_	0.1	4.2	1.7	10.2	5.4	15.3	9.3	18.2	12.0	17.2	12.9
PtRe/C	_	0.2	6.4	3.3	18.6	11.7	23.3	17.5	29.7	24.3	33.5	29.7
Rh/C	0.3	0.8	2.5	1.0	3.7	1.5	7.0	2.2	6.7	2.5	7.0	2.9
RhRe/C	—	0.2	6.8	3.6	23.3	13.6	32.3	20.7	38.6	28.1	40.7	31.8

more noble metal is present. The stability of the PtRe alloy appears to be in accord with the extensive alkane reforming literature for PtRe catalysts.^{45,46} DFT calculations suggest higher stability of RhRe alloys compared with PtRe alloys.⁴⁷ While we cannot draw firm conclusions on the stability of the RhRe bimetallic particles during APR of glycerol, the *in situ* EXAFS data show that RhRe is stable under gaseous WGS conditions.

The overall conversion of glycerol in APR for Rh/C increases more than an order of magnitude upon alloving with Re, whereas the PtRe catalyst is only twice as active as Pt/C. Although glycerol conversion after a reaction time of 320 min for Pt/C (9%) is similar to the value (7.4%) reported for a Pt/Ccatalyst with similar Re content in a recent study,¹⁸ glycerol conversion for PtRe/C (21%) is substantially lower than the one reported in the published work (68%). This difference most probably relates to the higher (double) Re content used during the synthesis of PtRe/C in the work of Zhang et al.¹⁸ A general feature of the APR reaction at relatively low temperatures is the poisoning of the metal surface by product CO.²⁰ A high rate of the WGS reaction will lower the steady-state CO coverage and, accordingly, increase the overall conversion during APR. The addition of Re has a strong positive effect on the WGS activity of the monometallic catalysts (Fig. 5). On the one hand, alloying with Re increases the WGS activity of Rh/C by almost 65 times at 225 °C. For Pt/C, on the other hand, the promotional effect of Re is less pronounced. At 225 °C, PtRe/C is nearly five times more active than Pt/C. These differences between the effect of Re on Pt/C and Rh/C in the WGS reaction are consistent with the trends for the overall conversion and yield of H₂ obtained in APR of glycerol. The main reason for the improved WGS performance of the bimetallic catalysts is argued to be the higher activity of metallic Re in the activation of water. Quantum-chemical calculations have shown that the main reaction path for the WGS reaction on Pt(111) involves COOH by reaction of CO with OH.48 As outlined before, the relatively weak metal-oxygen bond energy for Pt makes water dissociation to OH and O surface intermediates endothermic.⁴⁹ Comparatively, the stronger Rh–O bond energy makes O and OH surface intermediate formation nearly thermoneutral and slight exothermic, respectively. This trend is in line with the slightly higher WGS reaction rate for Rh. Accordingly, the strong Re-O bond energy can be argued to be at the origin of the higher WGS activity of Re/C. The nature of the strong synergy between Pt and Rh on the one hand and Re on the

other hand in the WGS reaction is the subject of our further studies. Summarizing, the strong increase in glycerol APR activity of carbon-supported Pt and Rh upon alloying can be related to the high WGS reaction rate for these bimetallic catalysts. This is confirmed by comparing Re promoter effects on Pt and Rh for intrinsic APR, WGS and acetaldehyde decomposition rates (Table S7,† note that the dispersion is close to 100% for all catalysts). Upon alloying Rh and Pt with Re, the product distributions for glycerol APR are very similar because of the dominance of C–O bond cleavage reactions on Re–OH sites. The role of Pt and Rh, besides bringing about strong synergy in the WGS reaction, is to retain the Re in bimetallic nanoparticles in its metallic state.

4. Conclusions

Carbon-supported Pt and Rh nanoparticles are active catalysts for wet reforming of glycerol for generating CO-free hydrogen and useful chemicals. Addition of Re to Pt and Rh increases the overall conversion rate of glycerol. Model reaction studies show how the promoter affects the elementary reaction steps. Addition of Re significantly enhances the gas-phase water-gas shift activity of Pt and Rh. The APR conversion rates trend well with these water-gas shift activities. The increased water-gas shift activity is argued to fastly remove product CO from the bimetallic nanoparticle surface as CO2, which would otherwise block the active sites. As a consequence, the yield of H₂ in APR of glycerol increases upon addition of Re to Rh and Pt catalysts. The increased water-gas shift activity is argued to be related to the stronger binding of OH on Re. The dominant effect of alloying Pt and Rh with Re on the product selectivities is increased formation of products derived from dehydration reactions involving Re-OH species. Besides, acetaldehyde decarbonylation activity measurements show that the alloys with Re are substantially more active in C-C bond cleavage reactions. The effect of acidity induced by the presence of Re on dehydration (C-O bond cleavage) reactions dominates over the increased C-C bond cleavage rate. As a consequence, the overall effect of alloying with Re is increased formation of products involving selective deoxygenation as well as an increase of the overall reforming to CO₂ and H₂.

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