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# Regioselective hydroformylation with subnanometre Rh clusters in MFI zeolite

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Achieving the regioselective hydroformylation of linear  $\alpha$ -olefins to linear aldehydes using solid catalysts with regioselectivities comparable to the corresponding homogeneous process is a great challenge in the chemical industry. Despite the tremendous efforts devoted to this research topic, most of the reported heterogeneous metal catalysts still give considerably lower regioselectivities than well-established homogeneous metal catalysts. Here we show the design of efficient Rh-zeolite catalysts, in which subnanometre Rh clusters are selectively confined in the sinusoidal ten-membered-ring channels of MFI zeolite, for the hydroformylation of long-chain linear  $\alpha$ -olefins (C<sub>6</sub>-C<sub>12</sub>) into linear aldehydes with very high linear-to-branched aldehyde ratios (up to 400). The exceptional catalytic performances result from the involvement of the MFI zeolite framework as a rigid solid ligand that accommodates subnanometre Rh clusters in the sinusoidal channels of the MFI zeolite.

Transition-metal-catalysed hydroformylation represents a premier route for the conversion of olefins into broadly applicable aldehydes and constitutes one of the largest homogeneous catalytic processes in the chemical industry (Fig. 1a)<sup>1-3</sup>. Tremendous efforts have been devoted to the development of catalysts with high linear-to-branched (l/b) ratios of aldehydes because linear aldehydes and the derived alcohols are more desirable than the branched isomers in downstream processes (Fig. 1b)<sup>4-7</sup>. Issues of unavoidable catalyst degradation, the necessary use of excessive/expensive ligands and catalyst separation/recycling impede further upgrading of the process and limit the adoption of olefins from different feedstock streams.

In comparison with their homogeneous counterparts, heterogeneous catalysts are advantageous in terms of their separation/ recycling and their feasibility for implementation in continuous processes. Enduring efforts have been made to develop heterogeneous hydroformylation catalysts through multiple approaches (Fig. 1c)<sup>8-15</sup>. However, none of these strategies can meet the high regioselectivity of the related homogeneous catalysts<sup>16-19</sup>. To overcome the abovementioned limitations, we sought to investigate subnanometre Rh clusters confined in zeolites as tunable catalysts for olefin hydroformylation reactions, as the crystalline microporous channels/cavities can not only accommodate the Rh sites with high structural uniformity but also provide a well-defined coordination environment for the Rh sites to constrain the transition states of the hydroformylation reaction for the selective production of linear aldehydes.

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**b** Previous studies: homogeneous hydroformylation catalysts



C Previous studies: heterogeneous hydroformylation catalysts

anchored in polymers



complexes



Metal complexes in a porous matrix The state of the s

Inorganic-supported metal catalysts

d This work: heterogeneous catalysts using the zeolite framework as the 'inorganic ligand' for Rh clusters



Fig. 1 | Catalytic conversion of linear α-olefins via the hydroformylation reaction. a, Role of hydroformylation processes in the chemical industry for the large-scale production of chemicals and materials. b, Homogeneous hydroformylation catalysts based on the use of organic ligands. c, Heterogeneous hydroformylation catalysts via the immobilization of metal complexes on inorganic solid carriers, metal complexes anchored in polymers Convenient catalyst separation/recycling
Moderate regioselectivity for linear aldehyde

- Noticeable Rh leaching/sintering
- Excellent regioselectivity for linear aldehyde
- Convenient catalyst separation/recycling
- Largely improved catalyst durability
- Facile catalyst preparation and scalability

or metal entities (from isolated metal atoms to clusters and nanoparticles) supported on solid carriers. **d**, Heterogeneous hydroformylation catalysts based on confining subnanometre Rh clusters in zeolite channels for the regioselective hydroformylation of long-chain linear  $\alpha$ -olefins. In **b**-**d**, the advantages of the catalysts are shown in bold.

Following this concept, here we report the development of Rh-zeolite catalysts, comprised of subnanometre Rh clusters specifically in the sinusoidal 10-membered-ring (10MR) channels of the MFI zeolite structure, which exhibit high structural uniformity and an appropriate surrounding coordination environment (Fig. 1d). We are particularly interested in the hydroformylation of linear  $\alpha$ -olefins (LAOs; C<sub>6</sub>-C<sub>12</sub>, supplied via the ethylene oligomerization or Fischer-Tropsch process) to complement the current industrial homogeneous routes, which were mainly established for the conversion of C<sub>3</sub>-C<sub>5</sub> olefins. The MFI-confined Rh catalyst shows very high regioselectivity (l/b ratios of up to 400) in the hydroformylation of LAOs. The exceptional catalytic performance of the Rh-zeolites is linked to the uniquely created chemical environment in which the MFI framework serves as an effective rigid solid ligand to accommodate the subnanometre Rh clusters in specific channels.

#### Results

#### Catalyst synthesis and characterization

The subnanometre Rh catalysts were generated using pure-silica MFI zeolite (Supplementary Fig. 1) via one-pot synthesis to confine the Rh species inside the rigid zeolite framework. This strategy is effective for stabilization of the subnanometre metal clusters during sintering, even after high-temperature oxidation-reduction treatments at >500 °C (refs. 20–24). The structural features of the Rh-MFI samples with various Rh loadings (between 0.007 and 0.619 wt%) were characterized via high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and integrated differential phase contrast STEM (iDPC-STEM) imaging, which enables the noble metal species in the zeolite structure to be imaged<sup>25</sup>. Taking the Rh-MFI-0.62 sample (which contains 0.619 wt% Rh) as an example, the Rh clusters are visualized in the HAADF images (Fig. 2a) and their locations are identified by correlating the paired HAADF and iDPC images (Supplementary



**Fig. 2** | **Structural characterization of Rh-MFI catalysts using the iDPC-STEM imaging technique. a**-**d**, HAADF-STEM images of the Rh-MFI-0.62 (**a**), Rh-MFI-0.35 (**b**), Rh-MFI-0.22 (**c**) and Rh-MFI-0.007 (**d**) samples. Rh clusters appear as small bright particles in **a**-**c**, whereas only a few bright dots ascribed to isolated Rh atoms are observed in **d**. **e**-**h**, Paired HAADF-STEM (**e**,**g**) and iDPC-STEM (**f**,**h**) images of the Rh-MFI-0.35 sample along the [010] (**e**,**f**) and tilted-[010] (**g**,**h**) orientations. **i**-**l**, Paired HAADF-STEM and iDPC-STEM images of the Rh-MFI-0.22 sample along the [010] (**i**,**j**) and tilted-[010] (**k**,**l**) orientations.

m-p, Paired HAADF-STEM and iDPC-STEM images of the Rh-MFI-0.007 sample along the [010] (m,n) and tilted-[010] (o,p) orientations. q-s, Schematic illustration of the structures of the Rh-MFI-0.62 (q), Rh-MFI-0.22 (r) and Rh-MFI-0.007 (s) catalysts, showing the representative Rh species and their locations in the MFI zeolite structure. To distinguish the subnanometre Rh species from the zeolite support in the high-resolution HAADF-STEM images (e, g, i, k, m and o), the Rh species (red to yellow) and zeolite support (blue to green) are shown in false colours.

Figs. 2 and 3). On careful analysis of the image simulation results, we can conclude that the Rh clusters are located mainly in the sinusoidal channels (Supplementary Fig. 4)<sup>26</sup>. For the Rh-MFI samples with lower Rh loadings (the Rh-MFI-0.22 and Rh-MFI-0.35 samples), the Rh clusters are located mainly in the 10MR sinusoidal channels (Fig. 2b,c and

Supplementary Figs. 5–8), indicating that varying the Rh loading in the range of 0.2–0.6 wt% can change the size distributions of the Rh species but does not modify the location of the Rh clusters, according to the paired HAADF and iDPC images in Fig. 2e–1. When the Rh loading is decreased to 0.06 wt%, only a few Rh clusters can be observed

#### Table 1 | Catalytic performance of supported Rh catalysts for the olefin hydroformylation reaction

	R +	H <sub>2</sub> + CO		R H Linear aldehyde	+ R H H H H H H	R <sup>1</sup> R <sup>2</sup> Isomerized olefins	+ R + R Other products (alkanes and alcohols)	∽∽он
Entry	Catalyst	Rh loading (%)	Mass of solid catalyst (mg)	Reaction time (h)	Olefin conversion (%)	Selectivity for aldehydes (%)	Linear-to-branched ratio in aldehyde products	Selectivity for isomerized olefins (%)
1 <sup>a</sup>	Rh-MFI-0.62	0.619	20	0.5	9.2	90.9	138.3	8.1
2ª	Rh-MFI-0.35	0.352	20	0.5	8.3	95.5	565.5	3.8
3ª	Rh-MFI-0.22	0.217	20	0.5	7.3	95.9	582.5	4.1
4 <sup>a</sup>	Rh-MFI-0.06	0.060	20	5	9.3	91.5	120.7	8.1
5ª	Rh-MFI-0.007	0.007	60	24	6.2	79.0	18.6	20.0
6ª	Rh/SiO <sub>2</sub>	0.137	20	5	6.0	48.3	2.7	50.2
7 <sup>a</sup>	Rh/MCM-41	0.128	20	5	3.6	46.7	2.7	54.2
8ª	Rh/MFI-imp <sup>d</sup>	0.134	20	5	3.7	78.0	27.9	21.1
9 <sup>a,c</sup>	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	-	1.2 (no support)	1	15.7	91.1	2.7	8.1
10 <sup>b</sup>	Rh-MFI-0.35	0.352	20	3	>98	95.8	385.0	2.8
11 <sup>b,c</sup>	HRh(CO)(PPh <sub>3</sub> ) <sub>3</sub>	_	1.2 (no support)	1	66.7	90.2	2.3	9.3

<sup>a</sup>Reaction conditions: 80°C, H<sub>2</sub> (2MPa), CO (2MPa), 1-decene (5mmol) as the substrate and toluene (4ml) as the solvent. <sup>b</sup>Reaction conditions: 80°C, H<sub>2</sub> (2MPa), CO (2MPa), 1-decene (1mmol) as the substrate and toluene (4ml) as the solvent. <sup>c</sup>The substrate-to-Rh molar ratio is similar to that of the Rh-MFI-0.62 sample. <sup>d</sup>The Rh/MFI-imp sample was prepared by conventional impregnation method.

(Supplementary Figs. 9 and 10), whereas in the case of the Rh-MFI-0.007 sample, the vast majority of the Rh species should be atomically dispersed due to the absence of Rh clusters/nanoparticles (Fig. 2d,m-p and Supplementary Fig. 11). The HAADF and iDPC images together with the simulated images (Supplementary Figs. 12–14) further suggest that the isolated Rh atoms are located in the sinusoidal 10MR channels.

#### Catalytic tests for the olefin hydroformylation reaction

Because of the different Rh loadings and particle size distributions in the Rh-MFI catalysts, the catalytic performances of the various supported Rh catalysts were compared at low conversion levels (<10%) to show the intrinsic activity of the Rh species. As shown in Table 1, taking the l/b ratio of the aldehvdes as the critical evaluation criterion, the Rh-zeolite catalysts, regardless of the Rh loading, show remarkably high l/b ratios (reaching >500) compared with the Rh catalysts prepared using conventional impregnation methods. Even at full conversion (Table 1, entry 10), an extremely high l/b ratio close to 400 can be obtained. The catalytic performances of the Rh-MFI catalysts clearly surpass a classic Wilkinson's catalyst (Table 1, entry 9) and other homogeneous and heterogeneous Rh catalysts reported in the literature so far (Supplementary Tables 1-4 and Supplementary Fig. 15). The heterogeneous nature of the olefin hydroformylation reaction is confirmed by the control experiment after separation of the solid catalyst from the reaction mixture (Supplementary Table 5).

On the basis of the electron microscopy characterization results (Fig. 2), we attempted to correlate the catalytic performances of the Rh-zeolite catalysts with their structural features. The initial reaction rates normalized to the total amount of Rh species in the whole solid catalyst are displayed in Fig. 3a. First, the very low activities of the supported Rh catalysts prepared via impregnation (Supplementary Figs. 16–18) indicate the minor contribution of Rh nanoparticles (with sizes larger than 1.5 nm) for the hydroformylation reaction (Table 1, entries 6–8). Furthermore, we can correlate the histograms of the size distributions of Rh species in three representative Rh-MFI samples (Fig. 3b and Supplementary Fig. 19) with their catalytic performance to figure out the most active Rh species. The Rh-MFI-0.22 sample presents

a higher contribution of Rh clusters of 0.3–0.6 nm compared comparison with the Rh-MFI-0.62 sample. A good match between the percentage of Rh clusters of 0.3–0.6 nm size and the normalized initial reaction rates is established, indicating that small Rh clusters are the most active species for the hydroformylation of LAOs, whereas large Rh clusters, nanoparticles and isolated Rh atoms are less efficient.

After the hydroformylation tests, the subnanometre Rh clusters confined in the MFI zeolite channels remain stable, as observed with the spent Rh-MFI-0.22 and Rh-MFI-0.35 samples (Supplementary Figs. 20–22). Furthermore, the Rh-MFI-0.22 sample was further tested for eight cycles of reaction–regeneration, and remarkably high regiose-lectivities were obtained in these tests (Supplementary Table 6). The size and location of the subnanometre Rh clusters remain unchanged in the recycled catalyst (Supplementary Figs. 23 and 24), showing the critical role of the MFI zeolite structure for generation and stabilization of the active Rh clusters.

#### Characterization of electronic features

We carried out in situ infrared spectroscopy study to elucidate the actual state of the working catalysts under the conditions applied during hydroformylation. The Rh-MFI catalysts were treated with a reaction atmosphere of syngas (CO (2 MPa) plus H<sub>2</sub> (2 MPa)) at 80 °C, and the infrared spectra were collected after different treatment times. As shown in Supplementary Figs. 25–27, three sets of infrared bands were observed in the reaction atmosphere: the band centred at -2,039 cm<sup>-1</sup> is associated with CO linearly adsorbed on Rh clusters; the paired bands centred at -2,086 and -2,013 cm<sup>-1</sup> are well recognized as the symmetric and asymmetric vibrations of *gem*-dicarbonyl on a same Rh atom; and the broad bands across the 2,000–1,850 cm<sup>-1</sup> region are characteristic of CO adsorbed on metallic Rh clusters in a bridge configuration (Supplementary Note 1)<sup>27-29</sup>.

The chemical states and coordination environment of Rh species under the working conditions were further studied via in situ X-ray absorption spectroscopy (XAS). The XANES (X-ray absorption near-edge structure) spectra show the reduction of the initial Rh-MFI-0.35 sample after exposure to a high-pressure syngas



Fig. 3 | Catalytic performance of the supported Rh catalysts. a, The normalized initial reaction rates for the production of aldehydes and iso-olefins on various Rh catalysts at conversion levels below 15%. b, The percentage of different types of Rh species in three representative Rh-MFI catalysts: Rh-MFI-0.62, Rh-MFI-0.22 and Rh-MFI-0.007.

atmosphere at 80 °C, as indicated by the decrease in the white-line intensity compared with that of the initial sample (Supplementary Fig. 28a), which is also confirmed by the X-ray photoelectron spectroscopy (XPS) results (Supplementary Fig. 29). The reduction of the Rh species in the syngas atmosphere is further revealed by the Fourier transform extended X-ray absorption fine-structure (FT-EXAFS) data (Supplementary Fig. 28b,c). The FT-EXAFS spectrum of the initial Rh-MFI-0.35 sample is dominated by the Rh-O scattering, whereas considerable Rh-Rh scattering is observed in the sample treated with syngas. Moreover, the presence of the short-range contribution at 2.0-2.1 Å can be associated with Rh-CO bonding from the adsorption of CO on Rh clusters and Rh-O bonding from the interaction between the Rh clusters and the MFI zeolite framework. The fitting results of the EXAFS spectra (Supplementary Table 7) suggest the formation of  $Rh_n$  clusters (n < 10) in the Rh-MFI-0.35 sample, which is in line with the CO results via infrared and XPS (Supplementary Table 8) as well as the observation of subnanometre Rh clusters in the HAADF-STEM images<sup>30</sup>.

#### Theoretical calculations

To gain further insight into the size-dependent catalytic behaviour of the Rh catalysts, we carried out theoretical studies (using density functional theory (DFT)) to examine various Rh models for the hydroformylation of 1-decene (Fig. 4a, Supplementary Note 2 and Supplementary Figs. 30-33). According to iDPC-STEM images, isolated Rh atoms and Rh<sub>7</sub> clusters in the sinusoidal 10MR channels of MFI zeolite are models for the respective Rh-MFI-0.007 and Rh-MFI-0.22 samples. In the model comprising a single Rh atom located at a defect site of the MFI framework ( $Rh_1$ @framework), the Rh atom is highly coordinated by surrounding O atoms, which results in substantially obstructed reactivity for the hydroformylation reaction due to the absence of sufficient space for the binding of reactants (Supplementary Fig. 34a). However, the isomerization of 1-decene to 2-decene is feasible with the Rh<sub>1</sub>@framework model, which explains the higher selectivity observed with the Rh-MFI-0.007 sample towards isomerized olefins (20% for Rh-MFI-0.007 versus <10% for other Rh-MFI catalysts that include Rh clusters). The hydroformylation activity of the Rh-MFI-0.007 catalyst can be attributed to the reactivity of the molecular Rh complex formed under the reaction conditions (the Rh<sub>1</sub>@channel model in Supplementary Fig. 34b). The calculation results show that isolated Rh atoms confined in the MFI zeolite structure can show minor reactivity for olefin hydroformylation reaction, but the side reaction (olefin isomerization) will compromise the regioselectivity towards the desired linear aldehydes.

The enhanced adsorption of 1-decene at under-coordinated sites of the Rh<sub>7</sub> cluster, and the notably lowered H addition energy barrier

at the C2 position of 1-decene, are mainly responsible for the superior activity of the hydroformylation reaction and excellent regioselectivity towards the linear aldehyde product. Results shown in Fig. 4c,d and Supplementary Fig. 35 suggest a considerably higher energy barrier for the formation of the branched aldehyde (pathway depicted in blue) than that for producing the linear aldehyde (pathway depicted in pink). The favoured formation of linear aldehydes could be related to the small pore dimension of the 10MR channels of the MFI zeolite, which imposes steric constraints on the reaction intermediates towards the production of linear aldehydes rather than branched aldehydes. Moreover, a very high energy barrier for hydroformylation and a minor difference between the two reaction pathways are found with the Rh(111) surface, consistent with the low activity and regioselectivity observed with supported Rh nanoparticles.

We also studied the influence of the electronic features of Rh clusters for the olefin isomerization and hydroformylation reactions. As shown in Supplementary Figs. 36–38, the addition of H to the C1 position, which leads to potential side reactions, proceeds more easily on oxidized Rh<sub>7</sub> clusters. Meanwhile the hydroformylation pathway to the linear aldehyde is markedly suppressed with oxidized Rh clusters. These results imply that metallic Rh clusters will be more efficient for the regioselective hydroformylation of olefins, whereas partially oxidized Rh clusters are less selective. These insights are confirmed by the experimental results with oxidized Rh clusters encapsulated in MFI zeolite crystallites, which give lower regioselectivity for the linear aldehyde (Supplementary Table 11). Therefore, we tentatively think that metallic Rh clusters confined in the sinusoidal channels of the MFI zeolite are the critical species for the regioselective hydroformylation reaction, due to their unique electronic and geometric features. At the current stage, operando spectroscopy characterization of the Rh-MFI catalysts under the hydroformylation reaction conditions is very challenging because of the low Rh loadings and interference of the solvent and/or high-pressure CO atmosphere (see the extended discussion in Supplementary Note 3). We anticipate that future progress in performing the structural characterization of active sites in Rh-MFI catalysts under working conditions will bring further insights regarding the nature of the active sites and thus guide the optimization of current catalysts.

#### **Scope studies**

As summarized in Fig. 5b, Supplementary Table 12 and Supplementary Fig. 39, the catalytic performance of the Rh-MFI-0.35 catalyst for LAOs with chain lengths spanning from  $C_6$  to  $C_{12}$  is observed to be chain-length-dependent. For most LAO substrates (1-hexene, 1-nonene, 1-decene, 1-undecene and 1-dodecene), excellent regioselectivities for



Fig. 4 | Theoretical studies of various solid Rh catalysts. a, DFT-calculated Gibbs free energy profiles of olefin isomerization (dotted line), and hydroformylation for the production of linear aldehyde ( $l-C_{II}$  aldehyde; solid line) and branched aldehyde ( $b-C_{II}$  aldehyde; dashed line) via Rh<sub>1</sub>@framework, Rh<sub>7</sub> and Rh(111) models. Detailed discussions on the reaction mechanism, DFT-optimized intermediates and structures of transition states can be found in Supplementary Note 2. b, DFT-calculated Gibbs free energy profiles of hydroformylation for the production of linear aldehyde (solid line) and branched aldehyde (dashed line) via Rh<sub>7</sub>-MEL, Rh<sub>7</sub>-MFI and Rh<sub>7</sub>\*BEA models. c, Activation energies of the first H addition at the C1 position (Si1  $\rightarrow$  Si2 in a; H@C1 (blue)) and the C2 position (Sa1  $\rightarrow$  Sa2 in a; H@C2 (pink)) of 1-decene for the Rh<sub>7</sub>-MFI

and Rh(111) models. **d**, Activation energies of subsequent CO insertion at the C2 position (Sb3  $\rightarrow$  Sb4 in **a**; CO@C2 (blue)) and the C1 position (Sa3  $\rightarrow$  Sa4 in **a**; CO@C1 (pink)) of the intermediate Rh–alkyl species for the Rh<sub>7</sub>-MFI and Rh(111) models. **e**, Activation energies of the first H addition at the C1 position (Si1  $\rightarrow$  Si2; H@C1 (blue)) and the C2 position (Sa1  $\rightarrow$  Sa2; H@C2 (pink)) of 1-decene for the Rh<sub>7</sub>-MFI, Rh<sub>7</sub>-MEL and Rh<sub>7</sub>\*BEA models. **f**, Activation energies of subsequent CO insertion at the C2 position (Sb3  $\rightarrow$  Sb4; CO@C2 (blue)) and the C1 position (Sa3  $\rightarrow$  Sa4; CO@C1 (pink)) of the intermediate Rh–alkyl species for the Rh<sub>7</sub>-MFI, Rh<sub>7</sub>-MEL and Rh<sub>7</sub>-\*BEA models. The Gibbs free energies of the transition states formed for the various models are listed in Supplementary Tables 9 and 21.



Fig. 5 | Scope study of Rh-zeolite catalysts for the hydroformylation of LAOs. a, Illustration of various zeolite supports for hosting Rh catalysts. b–i, Catalytic performances of Rh-zeolite catalysts and a homogeneous Rh catalyst: Rh-MFI (b), Rh-MEL (c), Rh-MWW (d), Rh\*BEA (e), Rh-TON (f), Rh-FER (g), Rh-MOR (h) and homogeneous HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (i). Reaction conditions: solid catalyst (20 mg), 80 °C, H<sub>2</sub> (2 MPa), CO (2 MPa), LAO (1 mmol) as substrate and toluene (4 ml)

as solvent. For the five catalysts giving an olefin conversion of >20% (Rh-MFI, Rh-MEL, Rh-MWW, Rh-\*BEA and HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>), the error bars of the l/b ratios (shown by the limits of the green shaded areas) and olefin conversions (red shaded areas) represent the standard deviation of three replicate experiments. For each set of repetitive tests, the average l/b ratios (filled circles) and olefin conversions (filled triangles) are marked.

the corresponding linear aldehydes are obtained with l/b ratios of >50 (l/b ratios of >100 are obtained with  $C_9-C_{12}$  LAOs), showing l/b ratios that are nearly one order of magnitude higher than those of reported heterogeneous Rh catalysts (Supplementary Tables 2–4 and Supplementary Fig. 15). In the case of 1-heptene and 1-octene, lower regiose-lectivities are seen than other LAO substrates, although they are still higher than most of the reported systems.

The chain-length-dependent catalytic performances of alkanes and olefins are rarely observed with zeolite catalysts, but such behaviour has been observed with the diffusion and adsorption properties of linear hydrocarbon molecules in zeolites<sup>31,32</sup>. Considering the comparable kinetic diameter of the LAO molecules and the dimensions of the 10MR channel in the MFI zeolite, the diffusion of LAO molecules along the Rh-MFI catalyst may have a profound impact on the catalytic results. Moreover, according to previous theoretical studies, the geometric conformations of long-chain hydrocarbon molecules in the MFI zeolite structure are closely related to the carbon chain length<sup>33-35</sup>. Therefore, it is reasonable to assume that the chain-length-dependent regioselectivity may be associated with the chain-length-dependent diffusion properties and molecular conformations of the LAO molecules in the MFI zeolite (Supplementary Note 4).

We anticipate that the regioselectivity for the hydroformylation of LAOs will be modulated when the Rh clusters are located in the zeolite structures of other topologies beyond MFI. Following this hypothesis, we synthesized a series of Rh-zeolite catalysts by encapsulating Rh species in MEL-, \*BEA-, MWW-, MOR-, TON- and FER-type zeolites (Supplementary Figs. 40–49). The catalytic results summarized in Fig. 5 and Supplementary Tables 12–19 show that zeolites with three-dimensional pore structures (MFI, MEL and \*BEA) are effective supports for accommodating Rh species for the hydroformylation of LAOs, whereas the zeolites with two-dimensional (MWW and FER) or one-dimensional

(TON and MOR) pore structures exhibit relatively low activities. Regarding the regioselectivity with the catalysts that show an olefin conversion above 10%, the Rh-\*BEA catalyst shows a similar regioselectivity to the homogeneous Rh catalyst, whereas other Rh-zeolite catalysts (Rh-MFI, Rh-MWW, Rh-MEL and Rh-TON) show improved regioselectivities compared with the homogeneous counterpart. In particular, only the Rh-MFI catalyst show an exceptionally high l/b ratio (>380), whereas the other Rh-zeolite catalysts show much lower l/b ratios (<10) for the hydroformylation of 1-decene. By correlating the structural/compositional features of various Rh-zeolite catalysts with their catalytic properties, we tentatively ascribe the exceptionally high regioselectivity of the Rh-MFI catalyst to the unique framework structure of the MFI-type zeolite and the appropriate structural features of the subnanometre Rh clusters confined inside MFI zeolite (Supplementary Note 5).

We carried out theoretical calculations to understand the distinct regioselectivities of the Rh-zeolite catalysts Rh-MFI, Rh-MEL and Rh-\*BEA, which have three-dimensional pore systems and show high activities in the hydroformylation of LAOs. As shown in Fig. 4b,e,f, the Rh<sub>7</sub>-MFI model shows a large difference in the activation energies of comparative reaction pathways for the production of linear and branched aldehydes, whereas the gap is reduced markedly in the Rh<sub>7</sub>-MEL model and almost closed in the Rh<sub>7</sub>-\*BEA model (Supplementary Note 6). The calculation results are very consistent with the experimental data, in which the Rh-MEL and Rh-\*BEA catalysts have respective l/b ratios of 2.7 and 0.8 for the hydroformylation of 1-decene, far below that achieved for the Rh-MFI catalyst (>380).

The catalytic results obtained under challenging reaction conditions demonstrate the potential of the Rh-MFI catalysts for the industrial hydroformylation process, in particular for the conversion of LAO feedstocks produced via the Fischer–Tropsch process (Supplementary Tables 23–26 and Supplementary Note 7). Moreover, by adopting the suitable design of a large-scale reactor and optimizing the operation conditions, the efficiency of the whole catalytic process can be elevated further, which may lead to upgrading of the current industrial hydroformylation process using homogeneous metal catalysts.

# Conclusions

In this work we have shown the application of MFI-zeolite-confined subnanometre Rh clusters for catalysing the hydroformylation of LAOs, where the very high regioselectivity is associated with the unique coordination environment that surrounds the Rh clusters in the sinusoidal 10MR channels of the MFI zeolite. Considering the diversity of zeolite framework structures (>200 topologies), in principle, it should be possible to develop an optimum Rh-zeolite catalyst for a specific  $\alpha$ -olefin molecule when using the zeolite framework as a rigid inorganic ligand to accommodate the subnanometre Rh clusters and tuning the various properties of the LAO molecules in the microporous channels/cavities. Moreover, the strategy of utilizing crystalline porous materials for modifying the coordination environment of metal sites can be extended to the design of heterogeneous metal catalysts for reactions involving long-chain alkanes and olefins without the need for organic ligands.

# Methods

#### Materials for catalyst synthesis

Chemicals for synthesis of the Rh-zeolite catalysts: tetraethylammonium hydroxide (TEAOH; 35 wt%, Alfa Aesar (product no. N24G047)), tetrapropylammonium hydroxide (TPAOH; 20 wt%, Sigma-Aldrich (254533)), tetrabutylammonium hydroxide (TBAOH; 40 wt%, Sigma-Aldrich (178780, which contains K<sup>+</sup>)), hexamethyleneimine (98%, Alfa Aesar (10229055)), tetraethyl orthosilicate (TEOS; >99%, Alfa Aesar), rhodium(III) chloride hydrate (RhCl<sub>3</sub>·xH<sub>2</sub>O; Sigma-Aldrich, >99.9%, trace metals basis (520772)), 1,6-diaminohexane (99%, Adamas Reagent Co. (P2217758)), SiO<sub>2</sub> aqueous solution (30 wt% (Ludox AS-30) and 40 wt% (Ludox HS-40), Sigma-Aldrich), sodium metaaluminate (NaAlO<sub>2</sub>; AR, Shanghai Macklin Biochemical Co.), fumed SiO<sub>2</sub> (Aerosil 200, Degussa), MCM-41 (mesoporous silica, Sigma-Aldrich) N,N,Ntrimethyl-1-adamantanammonium hydroxide solution (25 wt%, Energy Chemical), ethylenediamine (99%, Aladdin Scientific (E112642)), aluminium sulfate octadecahydrate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O; AR, Sinopharm Chemical Reagent Co.), potassium hydroxide (KOH; AR, Sinopharm Chemical Reagent Co.), potassium chloride (AR, Sinopharm Chemical Reagent Co.), sodium hydroxide (NaOH: AR, Sinopharm Chemical Reagent Co.), sodium chloride (NaCl: AR, Sinopharm Chemical Reagent Co.) and distilled water (Shanghai Titan Scientific Co.).

Chemicals for hydroformylation tests: 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene and 1-dodecene (>95%, TCI), *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and *n*-undecane (>99%, Aladdin Scientific), toluene (AR, Sinopharm Chemical Reagent Co.) and carbonylhydridotris(triphenylphosphine)rhodium(I) (HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>; TCI (C1383)).

#### Synthesis of Rh-MFI samples

First, a solution of TPAOH was prepared by mixing TPAOH (16.24 g) and KOH (200 mg) with distilled water (12.0 g) at room temperature. Then, TEOS (8.24 g) was added to the TPAOH solution with stirring for 6 h at room temperature. RhCl<sub>3</sub> aqueous solution (0.48 mol l<sup>-1</sup>) and ethylenediamine (300  $\mu$ l) were added to the TEOS–TPAOH–water mixture and stirring was continued for 20 min. The resultant yellow solution was then transferred to Teflon-lined autoclave and heated using an electric oven to 100 °C for 24 h under static conditions. The amount of Rh in the final Rh-MFI material is between 0.007 and ~0.6 wt%, depending on the amount of RhCl<sub>3</sub> solution added. After the hydrothermal process, the solid product was isolated via centrifugation and washed with distilled water and ethanol, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C for 8 h before being reduced with H<sub>2</sub> (5% H<sub>2</sub> in argon) at 600 °C for 3 h. The Rh loadings in the final Rh-MFI

samples were determined via inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, as summarized in Table 1.

#### Synthesis of Rh-MEL sample

First, a solution of TBAOH was prepared by mixing TBAOH (13.65 g) and distilled water (7.0 g) at room temperature. Then, TEOS (15.0 g) was added to the TBAOH solution at room temperature with stirring for 16 h. The resultant solution was divided into three equal parts. To each portion of the solution, RhCl<sub>3</sub> aqueous solution (150  $\mu$ l; 0.48 mol  $\Gamma^{-1}$ ) and ethylenediamine (150  $\mu$ l) were added under stirring. The resultant yellow solution was then transferred to a Teflon-lined autoclave and heated using an electric oven at 135 °C for 48 h under static conditions. After the hydrothermal process, the solid product was isolated via centrifugation and washed with distilled water and ethanol, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C for 8 h before being reduced with H<sub>2</sub> (5% H<sub>2</sub> in argon) at 600 °C for 3 h. The amount of Rh in the final Rh-MEL sample was 0.327 wt%, determined via ICP-OES analysis.

#### Synthesis of Rh-TON sample

First, Ludox HS-40 (5.32 g) was diluted with distilled water (9.20 g). A solution containing  $Al_2(SO_4)_3 \cdot 18H_2O$  (0.245 g), KOH (0.58 g), 1,6-diaminohexane (1.24 g) and distilled water (13.10 g) was added to the Ludox solution under vigorous stirring. Then, RhCl<sub>3</sub> aqueous solution (150 µl; 0.48 mol l<sup>-1</sup>) and ethylenediamine (150 µl) were added under stirring. Finally, the gel was aged for 90 min at room temperature and transferred to a Teflon-lined autoclave and heated using an electric oven at 160 °C for 48 h under conditions of agitation (at 40 revolutions per min (r.p.m.)). After the hydrothermal process, the solid product was isolated via centrifugation and washed with distilled water and ethanol, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C for 8 h before being reduced with H<sub>2</sub> (5% H<sub>2</sub> in argon) at 600 °C for 3 h. The amount of Rh in the final Rh-TON sample was 0.244 wt%, determined via ICP-OES analysis.

#### Synthesis of Rh-FER sample

First, the aluminium source solution was prepared by mixing NaAlO<sub>2</sub> (0.33 g) and NaOH (70 mg) with distilled water (12.9 g), and the silica source solution was prepared by mixing the SiO<sub>2</sub> aqueous solution Ludox AS-30 (4.65 g) and ethylenediamine (1.83 g) at room temperature. Then, the aluminium source solution was added dropwise to the silica source solution with vigorous stirring to form a homogeneous suspension. Finally, aqueous RhCl<sub>3</sub> (150 µl; 0.48 mol l<sup>-1</sup>) and ethylenediamine (150 µl) were added under stirring. The resultant yellow solution was then transferred to a Teflon-lined autoclave and heated using an electric oven at 175 °C for 72 h under agitation (15 r.p.m.). After the hydrothermal process, the solid product was isolated via centrifugation and washed with distilled water and ethanol, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C for 8 h before being reduced with H<sub>2</sub> (5% H<sub>2</sub> in argon) at 600 °C for 3 h. The amount of Rh in the final Rh-FER sample was 0.244 wt%, determined via ICP-OES analysis.

#### Synthesis of Rh-MOR sample

First, an NaOH solution was prepared by mixing NaOH (0.34 g) and distilled water (0.7 g). Then, NaAlO<sub>2</sub> (0.26 g) was added to the NaOH solution with stirring until dissolved, followed by the addition of distilled water (11.5 g). Then, fumed SiO<sub>2</sub> (1.75 g) was added to the resultant solution under stirring. Finally, aqueous RhCl<sub>3</sub> (150  $\mu$ l; 0.48 mol l<sup>-1</sup>) and ethylenediamine (150  $\mu$ l) were added under stirring. The resultant yellow solution was then transferred to a Teflon-lined autoclave and heated using an electric oven at 170 °C for 24 h under static conditions. After the hydrothermal process, the solid product was isolated via centrifugation and washed with distilled water and ethanol, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C

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for 8 h and then reduced with  $H_2$  (5%  $H_2$  in argon) at 600 °C for 3 h. The amount of Rh in the final Rh-MOR sample was 0.330 wt%, determined via ICP-OES analysis.

#### Synthesis of Rh-\*BEA sample

First, a TEAOH solution was prepared by mixing TEAOH (5.12 g), potassium chloride (72 mg), NaCl (28 mg) and distilled water (2.33 g) at room temperature. Then, aqueous RhCl<sub>3</sub> (150  $\mu$ l; 0.48 mol l<sup>-1</sup>) and ethylenediamine (150  $\mu$ l) were added to the resultant TEAOH solution with stirring for 30 min. Fumed SiO<sub>2</sub> (-1.4 g) was then added to the resulting solution with stirring for 2 h. Finally, the aluminium source solution (250  $\mu$ l) mixed with NaOH (66 mg), NaAlO<sub>2</sub> (0.36 g) and distilled water (4.0 g) was added with stirring for 16 h. The resultant solution was then transferred to a Teflon-lined autoclave and heated using an electric oven at 150 °C for 48 h under agitation (30 r.p.m.). After the hydrothermal synthesis, the solid product was isolated by centrifugation and washed with distilled water and ethanol, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C for 8 h before being reduced with H<sub>2</sub> (5% H<sub>2</sub> in argon) at 600 °C for 3 h. The amount of Rh in the final Rh-\*BEA material was 0.783 wt%, determined via ICP-OES analysis.

#### Synthesis of Rh-MWW sample

NaCl (0.237 g) was dissolved in a mixture of *N*,*N*,*N*-trimethyl-1adamantanammonium hydroxide solution (9.68 g; 0.55 mol l<sup>-1</sup>) and distilled water (6.0 g). Then, hexamethyleneimine (0.655 g), RhCl<sub>3</sub>·3H<sub>2</sub>O (100 mg) and ethylenediamine (150  $\mu$ l) were added to this solution. The above solution was kept stirring at room temperature for 2 h. Then, fumed SiO<sub>2</sub> (1.2 g) was added under vigorous stirring. After 3 h, the resultant suspension was transferred to a Teflon-lined autoclave and then heated at 150 °C under agitation (60 r.p.m.) for 120 h. After the hydrothermal process, the solid product was isolated via centrifugation and washed with distilled water and acetone, and then dried at 60 °C. Then the solid sample was calcined in static air at 560 °C for 8 h before being reduced with H<sub>2</sub> (5% H<sub>2</sub> in argon) at 600 °C for 3 h. The amount of Rh in the final Rh-MWW material was 0.408 wt%, determined via ICP-OES analysis.

#### Synthesis of Rh/SiO<sub>2</sub>, Rh/MCM-41 and Rh/MFI-imp samples

The three supported Rh catalysts as reference samples were prepared via conventional wet impregnation. SiO<sub>2</sub> and MCM-41 were obtained from Sigma-Aldrich. The MFI zeolite support was prepared using the same procedure as for the Rh-MFI catalyst but without the addition of Rh. For the impregnation procedure, the solid carrier (-2.0 g) was first mixed with RhCl<sub>3</sub> solution (25 ml; -1.0 mmol l<sup>-1</sup>) and stirring was continued for -2 h. The excess water was removed by heating the mixture at 110 °C. The resultant solid powder was recovered and dried at 60 °C overnight. Finally, the solid sample was calcined in static air at 560 °C and then reduced with H<sub>2</sub> at 600 °C for 3 h. The final loading of Rh in each of the three samples was 0.13 wt% according to ICP-OES analysis.

#### Structural characterization of Rh-zeolite materials

Powder X-ray diffraction was performed using a Rigaku RU-200b X-ray powder diffractometer with Cu K $\alpha$  radiation.

The chemical compositions of the Rh-zeolite samples were determined via ICP-OES (Optima 2100DV, PerkinElmer).

Samples for electron microscopy studies were prepared by adding a suspension of the solid samples in  $CH_2Cl_2$  dropwise directly on to holey carbon-coated copper grids. Electron microscopy measurements were carried out using two types of microscope: a JEOL 2100F microscope operating at 200 kV was used to record the HAADF-STEM images at low resolution; an FEI Titan<sup>3</sup> Themis 60–300 microscope operating at 300 kV was used to record HAADF-STEM and iDPC-STEM images at high resolution. To reduce the electron beam damage to the sample, the images were recoded with a beam current of 10–30 pA and a 2.5  $\mu$ s dwell time. More details about the optimization of the measurement conditions for the Rh-zeolite materials can be obtained by referring to our previous work  $^{\rm 25,26}$  .

The high-resolution HAADF-STEM image simulations were carried out using the TEMSIM software<sup>36</sup>. To match the experimental imaging conditions, the final simulated images were convolved using a Gaussian blur filter implemented in MATLAB<sup>25</sup>. The complex structural models used as the input in these simulations were built using Rhodius software<sup>37</sup>. Supercells in the [010] zone axis and the [010] tilted-zone axis were constructed to evaluate the influence of channelling effects in the MFI zeolite structure.

X-ray absorption spectra were recorded at the Rh K edge (23.220 keV) at the CLÆSS beamline (BL22) of the ALBA synchrotron light source<sup>38</sup>. The beam was monochromatized using a (311) double-crystal monochromator, and harmonic rejection was obtained by setting a suitable angle on a Pt-coated silicon mirror. XAS spectra for the Rh-MFI catalyst were collected in fluorescence mode using a multi-channel silicon drift detector. The powder sample was hand-pressed into a self-supported porous pellet and mounted in a multipurpose gas-solid cell equipped with high-precision mass flow controllers. Experiments were performed at 0.5 MPa under dynamic flow conditions (0.25 MPa of CO and 0.25 MPa of H<sub>2</sub>). EXAFS spectra were collected at selected isotherms. X-ray absorption spectra of Rh foil and Rh<sub>2</sub>O<sub>3</sub> references were also collected to calibrate the energy scale and for comparison, respectively. Data treatment and fitting were performed using the Artemis software package<sup>39</sup>. The extracted EXAFS signals after background correction at the pre- and post-edge were subsequently  $k^2$ -weighted. A model with three shells (with Rh–O, Rh-C and Rh-Rh) was used to fit the data. The fits were performed on the first coordination shell (fit range in R space:  $\Delta R = 2.0-3.0$  Å) over FT of the  $k^1 \cdot k^2 \cdot k^3$ -weighted  $\chi(k)$  functions performed in the interval in *k* space  $\Delta k = 2.0-12.0 \text{ Å}^{-1}$  interval.

Infrared spectra of CO adsorbed on the Rh-MFI zeolite samples were recorded at room temperature using a Bruker V80 FTIR spectrometer with a mercury cadmium telluride detector; the spectra were acquired at 4 cm<sup>-1</sup> resolution. For infrared studies, the Rh-MFI samples were pressed into self-supported thin pallets. A pre-reduction treatment was carried out at 80 °C with a 4 MPa syngas atmosphere (2 MPa CO and 2 MPa H<sub>2</sub>) for 1-3 h. To minimize the interference of gaseous CO, argon was gradually purged into the infrared cell after the treatment in syngas while the total pressure of the infrared cell was maintained at 4 MPa and the temperature was maintained at 80 °C. During the argon purging process, infrared spectra were collected. The infrared background was taken before pre-reduction treatment. To confirm the assignment of the infrared bands in the spectra recorded in the high-pressure atmosphere at 80 °C, we also recorded the infrared spectra of the Rh-MFI samples at room temperature after treatment with the 4 MPa syngas atmosphere (2 MPa CO and 2 MPa  $H_2$ ) at 80 °C for 3 h and subsequent cooling to room temperature in 0.1 MPa of argon flow. It should be noted that, owing to the large variance in the infrared extinction coefficients between the different types of carbonyl species bound to the Rh sites, the infrared spectra for CO can only provide useful information about the types of Rh species present in the working catalysts. However, quantifying of the abundance of Rh sites based on these CO infrared spectra is quite difficult.

XPS analysis was performed using a Thermal-Scientific XPS system (Model K-alpha) with a focused monochromatized Al K $\alpha$  source (1,486.6 eV). The diameter of the irradiated area was about 500  $\mu$ m. The binding energy was calibrated using the photoemission lines of the C 1s peak. Samples were pre-treated with a 0.1 MPa syngas atmosphere (0.05 MPa CO and 0.05 MPa H<sub>2</sub>) and a 4 MPa syngas atmosphere (2 MPa CO and 2 MPa H<sub>2</sub>) at 80 °C for 1–2 h, respectively, and these were were transferred to the XPS chamber without exposure to air. Argon-ion sputter etching was performed before XPS data acquisition to measure the Rh species encapsulated inside the zeolite crystallites.

# General procedure for the Rh-zeolite-catalysed hydroformylation of linear $\alpha$ -olefins (C<sub>6</sub>-C<sub>12</sub>)

In a representative procedure, a 12 ml screw-cap vial equipped with a magnetic stirring bar was charged with Rh-zeolite (20 mg), LAO (1 mmol) and toluene (4 ml). The vial was sealed with a phenolic cap and connected with a needle to the atmosphere. An alloy plate carrying one or multiple vials was then placed into an autoclave (250 ml), followed by three rounds of flushing with CO. Throughout the hydroformylation reaction, the pressure of both CO and H<sub>2</sub> was maintained at 2 MPa; likewise, a temperature of 80 °C (oil bath) and a stirring speed of 1,000 r.p.m. were applied steadily throughout the course. For the post-reaction treatment, the autoclave was allowed to cool to room temperature and the remaining pressure was released. Furthermore, 1-nonane (100 µl) was added as an internal standard to the product mixture, which was subsequently analysed via gas chromatography (Agilent 8890, equipped with an HP-5 column).

#### Theoretical studies

All DFT calculations were performed using the Vienna ab initio simulation package<sup>40,41</sup> with the atomic simulation environment<sup>42</sup>. Core electrons were described using the projector augmented-wave method<sup>43</sup>. The Kohn-Sham wavefunctions were expanded on a plane-wave basis with a kinetic energy cutoff of 300 eV to describe the valence electrons. The exchange-correlation term was described via the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional<sup>44</sup>. A softer version of the pseudopotential was used for  $O(O_s)$  and  $C(C_s)$ to balance the computational cost and chemical accuracy. Benchmark tests with respect to the regular potentials and an energy cutoff of 450 eV show that the error margin associated with soft potentials and a lower energy cutoff of 300 eV is <0.05 eV for adsorption energies and <0.02 eV for energy barriers, respectively. Long-range van der Waals interactions were corrected using the method of Tkatchenko and Scheffler, where the dispersion coefficients and damping function are derived from the charge density<sup>45</sup>. The Brillouin zone was sampled only on the Gamma point for geometry optimization. All geometries were considered to be optimized when the force on each atom was  $< 0.03 \text{ eV} \text{\AA}^{-1}$ . The structure and energy of the transition states were optimized using the climbing image nudged elastic band method<sup>46,47</sup> and refined using the dimer method if necessary<sup>48</sup>. Atomic charges were assigned based on the Bader charge partitioning method<sup>49</sup>.

# Data availability

The data that support the findings of this study are available within the Article and Supplementary Information or from the corresponding authors upon reasonable request. The optimized structures of all reaction intermediates and transition states derived from theoretical calculations are provided as Supplementary Data.

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# **Author contributions**

L.L. and Z.C. conceived the project. L.Z. designed the theoretical studies. X.D. carried out the materials synthesis and part of the structural characterization. T.Y. performed the hydroformylation reaction tests and data analyses. L.Q. performed the theoretical calculations. H.H. conducted the in situ infrared and XPS investigations and helped with analysis of the obtained XAS data. M.L.-H. characterized the Rh-MFI catalysts using the iDPC-STEM imaging technique and carried out the image simulations. L.L. analysed the iDPC-STEM images. C.M. and G.A. measured the Rh-zeolite materials via in situ XAS and analysed the data. D.M.M. contributed to the spectroscopic characterization of the Rh-zeolite materials via XAS. X.Z. participated in the catalytic studies and data analysis. L.L., Z.C. and L.Z. wrote the manuscript with input from all of the other authors.

# **Competing interests**

The authors declare no competing interests.

# **Additional information**

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