

Silanol nest-assisted Rh nanoparticles inducing homogeneous-like kinetics in heterogeneous hydroformylation

Haofeng Chen^{1,2}, Jiahao Wang², Yizhe Liu², Tianli Hui¹, Tao Zheng¹✉, Zhichang Liu¹, Chunming Xu¹, Haiyan Liu¹, and Haibo Jin²✉

¹State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, Beijing 102249, China

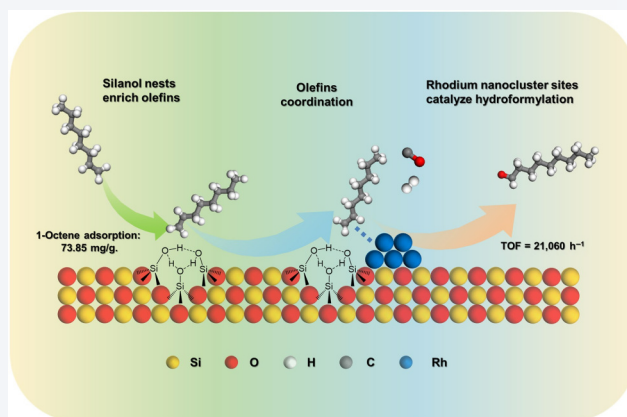
²Beijing Key Laboratory of Fuel Cleaning and Efficient Catalytic Emission Reduction Technology, Beijing Institute of Petrochemical Technology, Beijing 102617, China



Cite this article: Nano Research, 2026, 19, 94908341. <https://doi.org/10.26599/NR.2026.94908341>

ABSTRACT: Hydroformylation is a pivotal industrial process for high-value chemicals production. So far, compared with homogeneous systems, heterogeneous hydroformylation allows easier separation and recycling to simplify the operation procedure, however, the transformation efficiency toward targeted aldehyde of long-chain olefins remains unsatisfactory. To tackle this, we developed a Rh nanoparticle catalyst supported on BEA-OH zeolite with rich silanol nests, obtained via a simple dealumination treatment. The specific structure locally enriches long-chain olefins near the Rh active centers and enhances the coordination between olefins and metal sites, significantly improving catalytic performance. In 1-octene hydroformylation process, the optimized Rh catalyst reaches a turnover frequency (TOF) of 21,060 h⁻¹ and over 98% yield, exceeding most heterogeneous catalysts and outperforming the classic homogeneous Wilkinson catalyst (TOF ~ 10,000 h⁻¹). *In-situ* infrared (IR), density functional theory (DFT) calculations, and kinetic studies reveal that the silanol nests promote the enrichment of long-chain olefins near Rh sites (73.85 mg/g) and lower the olefin coordination energy (decreased by 34.4 kJ/mol), thereby inducing a nearly zero-order reaction kinetics with respect to the olefin—an effect previously observed mainly in homogeneous systems. This work offers a strategy to enhance heterogeneous hydroformylation by tuning the surface structure of zeolite-supported Rh nanoparticles.

KEYWORDS: long-chain olefins, syngas conversion, synergistic effect, hydroformylation, zeolite



1 Introduction

The hydroformylation of olefins to produce aldehydes is a critical industrial process, annually generating over 10 million tons of high-value chemicals [1–6]. Rhodium-based homogeneous catalysts are extensively utilized due to their excellent activity and selectivity in the hydroformylation process [7, 8]. However, homogeneous Rh catalysts face several operational challenges, including the recovery of the catalyst after the reaction, high energy demands for

separation, and loss of rhodium metal [9, 10]. In contrast, heterogeneous catalysts provide inherent advantages in terms of facile separation and catalyst recyclability, which are highly desirable for the development of greener and more sustainable catalytic processes.

In recent years, Rh nanoparticles [11, 12] stabilized through interactions with surface atoms or structures, have emerged as promising heterogeneous hydroformylation catalysts [13, 14]. Jing et al. [15] developed a K20 Rh@S-1 catalyst that achieved a turnover frequency (TOF) of ~ 2000 h⁻¹ with 67% linear selectivity for 1-hexene hydroformylation at 85 °C and 5 MPa by tailoring the steric environment to mimic a Rh-phosphine complex. Similarly, Sun et al. [12] reported a hollow zeolite-encapsulated Rh catalyst (Rh@H-S-1) exhibiting a TOF of 3471 h⁻¹ for 1-hexene hydroformylation at 100 °C and 5 MPa, attributed to the high Rh

Received: October 11, 2025; Revised: November 25, 2025

Accepted: December 14, 2025

✉Address correspondence to Haibo Jin, jinhaibo@bipt.edu.cn; Tao Zheng, zt@cup.edu.cn

dispersion and enhanced diffusion provided by the hollow “eggshell” structure. Despite these advances, heterogeneous Rh catalysts remain intrinsically less active, with TOFs still far below the $\sim 10,000 \text{ h}^{-1}$ benchmark of the Wilkinson catalyst, highlighting the challenge of bridging the performance gap with homogeneous systems [16–18].

The activity gap between homogeneous and heterogeneous systems arises partly from the differences of substrate accessibility and coordination. In homogeneous hydroformylation, olefins rapidly coordinate with Rh centers to establish a dynamic equilibrium (Scheme 1(a)). Aasif et al. [19] showed that homogeneous catalysts such as $\text{Rh}(\text{CO})_2(\text{acac})$, $\text{Rh}_4(\text{CO})_{12}$, and $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ exhibit zero-order kinetics in styrene hydroformylation, indicating that olefin concentration has little effect on activity. This suggests that rapid olefin adsorption at Rh sites sustains local concentration effects, contributing to the high efficiency of homogeneous systems. By contrast, in heterogeneous hydroformylation, reactants must diffuse to surface sites before activation, making substrate accessibility as a key rate-determining factor (Scheme 1(b)). For instance, Anders et al. [20] reported that rhodium supported ionic liquid-phase (Rh-SILP) catalysts exhibited a TOF of 501 h^{-1} for propylene hydroformylation at 130°C and 1 MPa, following first-order kinetics with respect to olefin concentration. Yu et al. [21] reported that zeolite-based catalysts ($\text{Rh}_1/\text{silicalite-1}$) exhibit approximately first-order kinetics with respect to 1-hexene during hydroformylation at 80°C and 4 MPa, indicating a pronounced influence of olefin concentration on catalytic activity. Furthermore, Liu et al. [22] show that silanol nests on the support surface effectively promote the enrichment of styrene near, further enhancing olefin availability. Based on these previous studies, it is rationally speculated that promoting enrichment and coordination of long-chain olefins in the Rh sites holds great promise to enhance the efficiency of heterogeneous hydroformylation reactions [23, 24].

In this study, we report silanol-nest-functionalized BEA zeolites that enable efficient hydroformylation of long-chain olefins by enriching substrates near the surface and stabilizing highly

dispersed Rh nanoparticle (Scheme 1(c)). Comprehensive characterization of the catalysts is conducted using infrared spectroscopy, ^1H NMR, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The catalytic performance for the hydroformylation of long-chain olefins is systematically investigated, and its effectiveness under solvent-free conditions for green and sustainable processes is evaluated. Additionally, mechanistic insights obtained from *in-situ* infrared spectroscopy and density functional theory (DFT) calculations confirm that the silanol nests enhance olefin adsorption and lower the energy of Rh-olefin coordination intermediates, thereby facilitating faster reaction rates. Kinetic studies further demonstrate that the catalyst exhibits a zero-order reaction order with respect to olefin concentration, consistent with homogeneous hydroformylation behavior. These findings highlight zeolite surface modification as an effective strategy to bridge the performance gap between heterogeneous and homogeneous hydroformylation, providing a feasible pathway for developing highly active, easily recoverable, and sustainable catalytic systems.

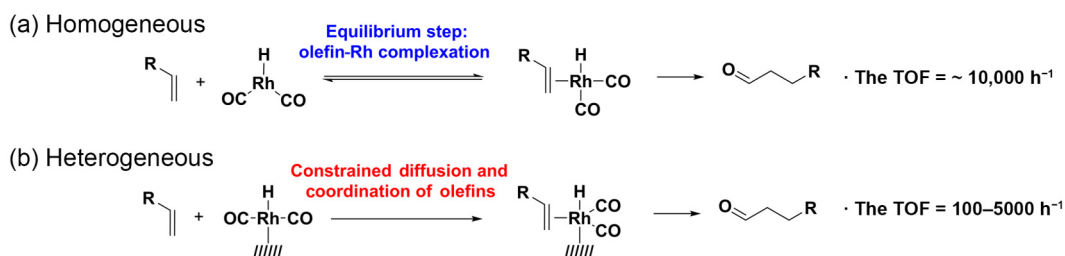
2 Experimental and computational section

2.1 Catalyst preparation

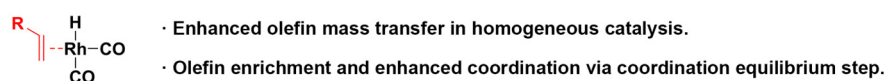
2.1.1 Materials

Nitric acid (68.0%) and toluene (99.8%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Rhodium(III) chloride trihydrate (Rh, 42.5%) was obtained from Shanghai Meryer Biochemical Technology Co., Ltd. H-BEA-25, H-BEA-30, and H-BEA-40 were supplied by Tianjin Nankai Catalyst Co., Ltd. 1-Octene (99%) was purchased from Beijing Innocem Technology Co., Ltd. A CO/H_2 gas mixture (1:1) was supplied by Beijing Huatuo Jingke Gas & Chemical Co., Ltd. Tris(triphenylphosphine) rhodium(I) chloride (98%) was obtained from Adamas Reagent Co., Ltd. All chemical reagents were used as received without further purification.

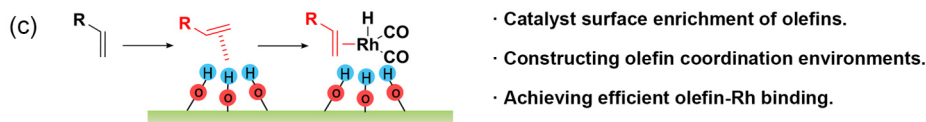
Previous work: Hydroformation of long-chain olefins



Reasons for high hydroformylation activity



Strategy: Olefin enrichment and enhanced coordination



Scheme 1 (a) and (b) Previous work for hydroformylation of long-chain olefins. (c) Strategy for olefin enrichment and enhanced coordination.

2.1.2 Synthesis

The support materials, BEA-OH- X ($X = 25, 30, 40$), were prepared by dealuminating H-BEA zeolites with Si/Al ratios of 25, 30, and 40. The dealumination process was carried out by stirring the zeolites in 13 M nitric acid at 373 K for 20 h. The resulting suspension was then filtered, thoroughly washed with deionized water until a neutral pH ($\text{pH} = 7$) was achieved, and subsequently dried overnight at 393 K to obtain BEA zeolites enriched with silanol nests (denoted as BEA-OH- X). Rh was introduced into the BEA-OH- X supports via an incipient wetness impregnation method. Specifically, an appropriate amount of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in water and stirred for 30 min to prepare a RhCl_3 solution. The amount of Rh was determined based on a loading of 0.05 wt.%. The RhCl_3 solution was then added dropwise in an equivalent volume to the support (1 mL of RhCl_3 solution per gram of support) and ultrasonically mixed for 1 h to ensure uniform dispersion. The resulting mixture was ground at 343 K to remove moisture, followed by overnight drying at 373 K. The dried samples were subsequently calcined in air at 673 K for 2 h. Finally, the samples were reduced in a 10% H_2/Ar mixture (flow rate: 60 mL/min) at 673 K for 2 h to obtain metallic Rh species. The final catalysts were designated as Rh/BEA-OH- X ($X = 25, 30, 40$) and Rh/BEA-25 (BEA Si/Al ratio = 25), where X corresponds to the Si/Al ratio of BEA prior to dealumination.

2.2 Catalytic evaluation

The hydroformylation of 1-octene was conducted in a 10 mL $\times$ 7 parallel reaction autoclave equipped with magnetic stirring. In a typical procedure, a specified amount of catalyst (30 mg), 1-octene (2.5 mmol), and toluene (5 mL) were added to a 10 mL quartz reaction tube. The autoclave was purged three times with nitrogen to remove residual air, followed by three cycles of purging and pressurization with a CO/H_2 (1:1) gas mixture to a final pressure of 5 MPa. The system was then heated to 373 K, and stirring was

initiated. After 5 h of reaction, the autoclave was cooled to room temperature, and the gas was slowly vented in a well-ventilated hood. The reaction tube was then removed and allowed to settle, after which the supernatant was collected. The reaction mixture was analyzed using gas chromatography (GC) equipped with a flame ionization detector (FID) to determine the concentrations of the reactants and products, enabling the calculation of conversion and yield.

3 Results and discussion

3.1 Structure characterization of the catalysts

A dealumination-impregnation strategy was employed to introduce silanol nests into BEA. The resulting catalysts were designated as Rh/BEA-OH- X , where X denotes the initial Si/Al ratio. The catalyst structures were systematically characterized using powder X-ray diffraction (PXRD). As shown in Fig. 1(a), there are the two primary diffraction peaks at 7.5° and 22.5° corresponding to the (101) and (302) crystal planes of the BEA zeolite, respectively. After dealumination treatment, the BEA zeolite remains the BEA-OH structure. Following Rh loading, the absence of characteristic diffraction peaks for Rh nanoparticles in the PXRD patterns indicates that the Rh species are highly dispersed on the catalyst surface [25, 26]. Notably, a high-angle shift in the diffraction peak position of the (302) crystal plane was observed after dealumination. This shift is attributed to the removal of framework aluminum, which induces a contraction of the zeolite unit cell, thereby altering the interplanar spacing [27].

The specific surface area and porosity of the synthesized catalysts were characterized via argon adsorption-desorption analysis (Fig. 1(b) and Table S1 in the Electronic Supplementary Material (ESM)). Compared with the unmodified sample, the Rh/BEA-OH-25 catalyst exhibited a slight decrease in specific surface area (from 528.7 to 515.3 m^2/g) and micropore volume (from 0.1559 to

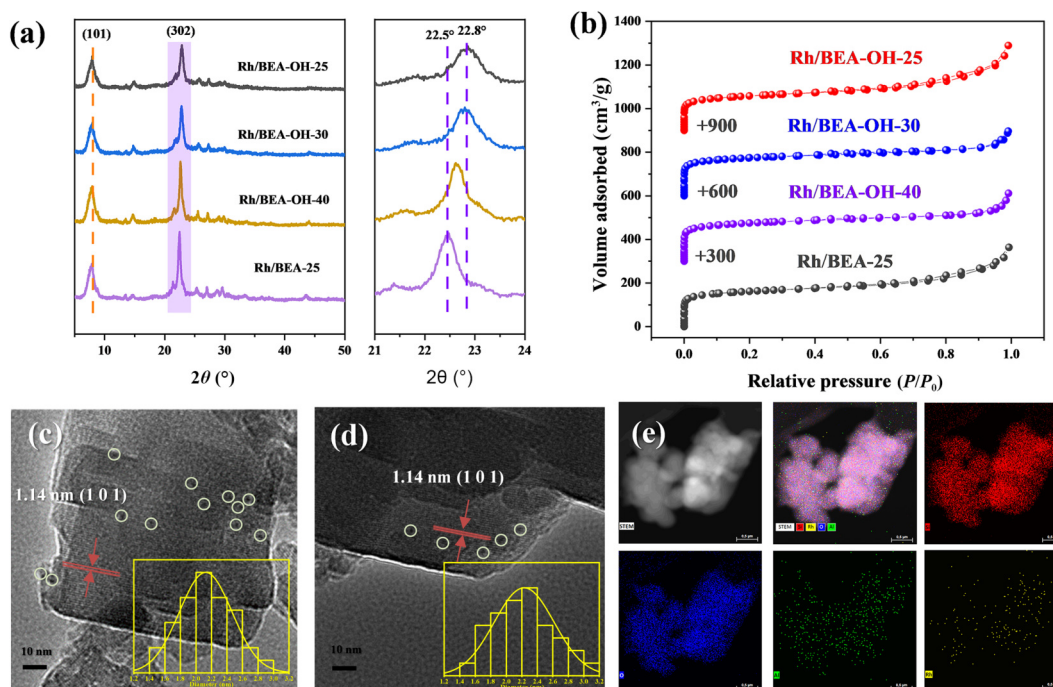


Figure 1 (a) XRD patterns and (b) Ar adsorption-desorption isotherms of Rh/BEA-25 and Rh/BEA-OH- X ($X = 25, 30, 40$). TEM images of (c) Rh/BEA-OH-25 and (d) Rh/BEA-25. (e) EDS elemental mapping images of Rh/BEA-OH-25.

0.1463 cm³/g), accompanied by a marginal increase in mesopore volume (from 0.2547 to 0.2947 cm³/g). This change is primarily attributed to the removal of framework metal species, leading to a partial collapse of the microporous structure.

Scanning electron microscope (SEM) images (Fig. S1 in the ESM) reveal that the Rh/BEA-OH-25 support primarily consists of nanoparticle (100–200 nm in size) forming a porous structure, with noticeable particle agglomeration. To further determine the dispersion and size distribution of Rh nanoparticles on the support surface, transmission electron microscopy (TEM) characterization was performed. TEM images of Rh/BEA-OH-25 (Fig. 1(c)) and Rh/BEA-25 (Fig. 1(d)) reveal lattice fringes with an interplanar spacing of 1.014 nm, corresponding to the (101) crystal plane of BEA zeolite [25]. Additionally, Rh nanoparticles were found to be uniformly dispersed on the external surface of the zeolite crystals. Energy-dispersive X-ray spectroscopy (EDS) mapping of Rh/BEA-OH-25 (Fig. 1(e)) further confirmed the homogeneous distribution of Rh across the catalyst surface, indicating uniform compositional dispersion. Statistical analysis based on TEM images showed that the Rh nanoparticles sizes on the Rh/BEA-OH-25 and Rh/BEA-25 surfaces, primarily ranged from 1.4 to 3.0 nm. The average Rh nanoparticle size was determined to be 2.1 ± 0.8 nm for Rh/BEA-OH-25 and 2.2 ± 0.8 nm for Rh/BEA-25. The dispersion of Rh is defined as the ratio of surface-accessible Rh sites to the total number of Rh atoms. Based on TEM measurements, the dispersion of Rh nanoparticles with an average size of approximately 2.1 nm is estimated to be about 48%. In contrast, CO pulse chemisorption analysis yields a dispersion of 43%. Considering the inevitable morphological irregularities of real nanoparticles, this slight

deviation falls within a reasonable range, indicating that the conclusion drawn from CO chemisorption is essentially consistent with the TEM observations [22].

In the infrared spectra of Rh/BEA-25, depicted in Fig. 2(a), characteristic absorption bands are observed at 3740 cm⁻¹. Upon dealumination, the relative intensity of band corresponding to terminal silanol groups exhibits a significant increase in intensity and shifts toward a lower wavenumber at 3730 cm⁻¹, indicating an increase in the number of terminal silanol groups. The bending vibration peak of hydroxyl groups, originally appearing sharply at 1650 cm⁻¹, becomes broader after dealumination, likely due to enhanced hydrogen bonding within the silanol nests [28]. Additionally, a broad and intense absorption band emerges at approximately 3500 cm⁻¹, spanning the range of 3300–3650 cm⁻¹ [29–31]. The red shift in peak position further supports the presence of hydrogen bonding among hydroxyl groups in the silanol nests. The spectral changes collectively indicate a significant formation of internal silanol groups and silanol nests within the zeolite framework after dealumination. Comparison of silanol nest structures formed in Rh/BEA-25 zeolites with different Si/Al ratios after dealumination reveals that the sample with an Si/Al ratio of 25 exhibits a relatively more intense absorption band at ~3500 cm⁻¹, indicative of a higher concentration of silanol nests, compared to samples with higher Si/Al ratios. This suggests that BEA zeolites with higher aluminum content tend to form more silanol nest structures during dealumination. Furthermore, the broad absorption band observed in the range of 800–1300 cm⁻¹ corresponds to the symmetric and asymmetric stretching vibrations of the T–O–T (T = Si, Al) framework of the BEA zeolite support [32].

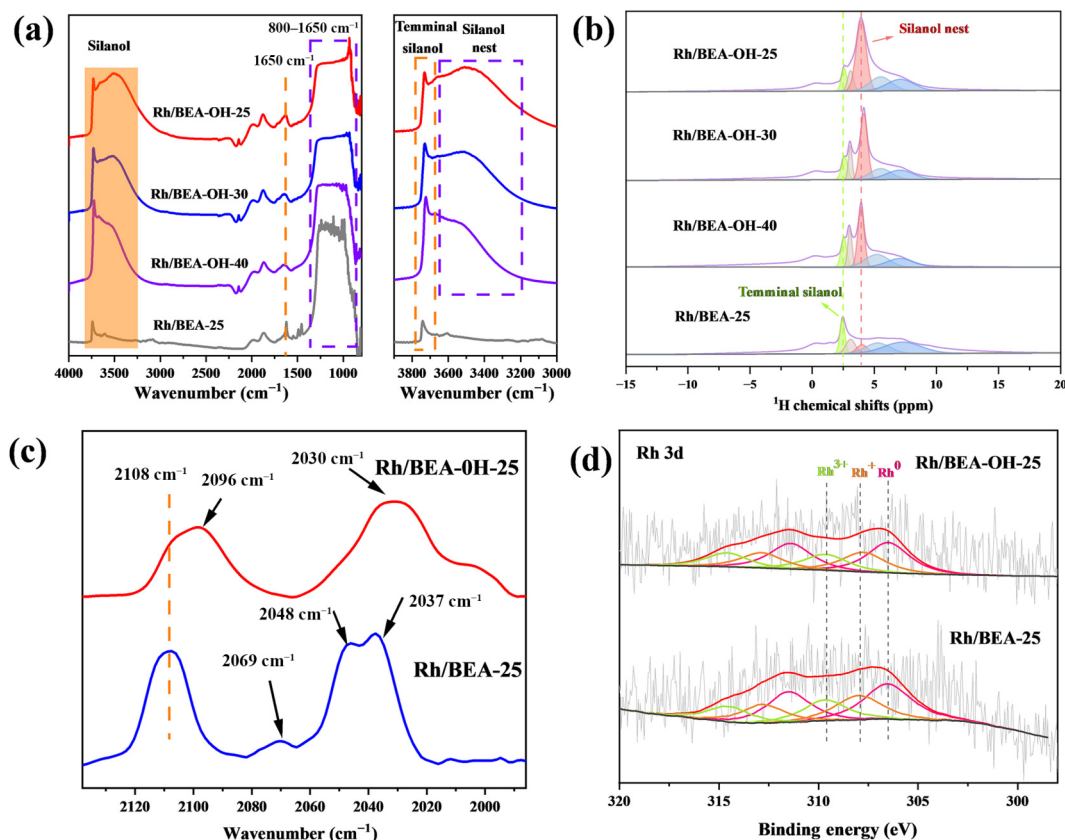


Figure 2 (a) FT-IR spectra and (b) ¹H MAS NMR spectra of Rh/BEA-25 and Rh/BEA-OH-X (X = 25, 30, 40). (c) CO-IR spectra of Rh/BEA-OH-25 and Rh/BEA-25. (d) XPS spectra of Rh 3d.

As shown in Fig. 2(b), the ^1H MAS NMR spectrum of Rh/BEA-25 exhibits a resonance at approximately 2.5 ppm, which can be assigned to terminal silanol groups predominantly located on the external surface of the BEA zeolite crystals. In contrast, the modified Rh/BEA-OH-25, Rh/BEA-OH-30, and Rh/BEA-OH-40 samples display an additional, well-resolved signal at around 4.0 ppm. This new resonance is attributed to hydroxyl groups engaged in hydrogen-bonding interactions within silanol nests, which leads to a downfield shift of the corresponding ^1H signal [31, 33, 34]. On this basis, the spectra were deconvoluted and the integral area of the terminal silanol signal was used as a reference to quantitatively compare the relative concentration of silanol nests in different samples. The relative integrated areas of the silanol-nest-related signals for Rh/BEA-25, Rh/BEA-OH-25, Rh/BEA-OH-30, and Rh/BEA-OH-40 are approximately 0.57:2.37:3.43:5.86. These results indicate that the lower the initial Si/Al ratio of the BEA zeolite (i.e., the higher the aluminum content before dealumination), the higher the concentration of silanol nests generated under identical dealumination conditions. This trend is consistent with the infrared spectroscopic characterization and further corroborates the enrichment and enhanced formation of silanol nests in the modified samples.

To investigate the dispersion of Rh nanoparticles on the support surface, CO adsorption infrared spectroscopy (CO-IR) analysis was performed at 293 K, drawing upon previous reports on CO-IR studies of Rh-based catalysts. As illustrated in Fig. 2(c), the CO-IR spectra of Rh/BEA-OH-25 and Rh/BEA-25 exhibit distinct features. For Rh/BEA-25, a characteristic peak at 2069 cm^{-1} is observed, corresponding to linearly adsorbed Rh monocarbonyl species, indicating the presence of Rh clusters. Additionally, spectral features centered at 2048 and 2037 cm^{-1} , along with bands at 2113 cm^{-1} , are attributed to the symmetric and asymmetric stretching vibrations of Rh dicarbonyl species. These peaks suggest the presence of small Rh clusters interacting with CO [35, 36]. In contrast, for Rh/BEA-OH-25, the characteristic peak of linearly adsorbed Rh monocarbonyl species at 2069 cm^{-1} is absent, suggesting that the silanol nest structure in the modified BEA support promotes the dispersion of Rh atoms and prevents their aggregation into large Rh clusters. Notably, the spectral bands at 2030 and 2096 cm^{-1} , assigned to the symmetric and asymmetric stretching vibrations of Rh dicarbonyl species, exhibit a red shift compared to those in Rh/BEA-25. This shift may be attributed to an increased CO coverage on Rh nanoparticles, influenced by the silanol nest environment on the Rh/BEA-OH-25 surface [37]. The CO-IR results indicate that the silanol nest structures on the BEA zeolite surface facilitate the dispersion of Rh species, thereby preventing their aggregation into larger clusters.

To investigate the chemical state of Rh atoms on the BEA zeolite surface, XPS analysis was performed on both Rh/BEA-OH-25 and Rh/BEA-25. The Rh 3d XPS spectra, illustrated in Fig. 2(d), were deconvoluted, and the analysis identified peaks at 306.6 and 311.4 eV , corresponding to the Rh $3d_{5/2}$ and Rh $3d_{3/2}$ states for both Rh/BEA-OH-25 and Rh/BEA-25 [38, 39]. These results indicate that Rh predominantly exists in the metallic Rh^0 state on the nanoparticle surface. Minor signals corresponding to Rh^+ (307.6 eV) and Rh^{3+} (309.5 eV) are also observed. However, their low intensities suggest that these features most likely originate from Rh–O–Si coordination of the Rh nanoparticles [37]. In the Al 2p XPS spectra (Fig. S2 in the ESM), the peak at 74.6 eV , attributed to trivalent framework Al, shows a significant decrease in Rh/BEA-OH-25 compared to Rh/BEA-25 [40].

3.2 Catalytic response for long-chain olefin hydroformylation

To further investigate the influence of silanol nest structures in BEA zeolites on the hydroformylation of olefins, a series of BEA zeolite supports with varying silanol nest concentrations were designed and tested for hydroformylation activity (Fig. 3(a)). Zeolites with different aluminum contents were dealuminated to prepare supports with controlled silanol nest densities (Fig. 1(a)); the silanol nest concentration increased with the aluminum content of the parent zeolites. Figure 3(b) shows the hydroformylation performance of the Rh-supported BEA zeolites. Under identical conditions, nonanal yields decreased in the order: Rh/BEA-OH-25 (98.5%) > Rh/BEA-OH-30 (90.3%) > Rh/BEA-OH-40 (87.0%) > Rh/BEA-25 (48.3%). This trend indicates a clear correlation between the silanol nest concentration and catalytic activity, with higher silanol nest densities promoting greater hydroformylation efficiency for long-chain olefins. Notably, although Rh/BEA-OH-40 has a lower silanol nest concentration than Rh/BEA-OH-25 and Rh/BEA-OH-30, it still outperforms the unmodified Rh/BEA-25 catalyst by a wide margin, highlighting the crucial role of silanol nests in enhancing catalytic performance.

The intrinsic activity of the catalysts was evaluated by measuring the TOF in the hydroformylation of 1-octene, which serves as a reliable indicator of their catalytic efficiency. Rh/BEA-OH-25 exhibited an average TOF of 9056 h^{-1} (conversion < 20%) based on total Rh loading, which estimated to be approximately $21,060\text{ h}^{-1}$ when Rh dispersion ($\sim 43\%$, determined by CO pulse adsorption) was taken into account. In contrast, under the same conditions, Rh/BEA-25 showed a much lower TOF ($\sim 2790\text{ h}^{-1}$, Rh dispersion $\sim 40\%$, determined by CO pulse adsorption), while the commercial Wilkinson catalyst $\text{RhCl}(\text{PPh}_3)_3$ gave only $\sim 8500\text{ h}^{-1}$, both significantly lower than that of Rh/BEA-OH-25 (Fig. 3(c)). Furthermore, according to the Ref. [41], rhodium on covalent triazine framework (Rh@CTF) has been reported as an efficient Rh-based heterogeneous catalyst for 1-octene hydroformylation, achieving a TOF of 4690 h^{-1} at 80°C and 8 MPa (Fig. 3(d)). These results clearly show that Rh/BEA-OH-25 exhibits much higher hydroformylation activity than most reported heterogeneous Rh catalysts and even some classical homogeneous systems (Table S2 in the ESM), highlighting its potential as a promising alternative to traditional homogeneous catalysts.

To evaluate its performance with various olefins, Rh/BEA-OH-25 was tested under identical conditions (Fig. 3(e)). It gave a 98.6% aldehyde yield from 1-hexene, higher than Rh/BEA-25 (93.4%). For styrene, both catalysts showed similar yields ($\sim 98.6\%$ vs. 98.4%). For greater sterically hindered olefins diisobutylene, Rh/BEA-OH-25 achieved a much higher yield (44.1%) than Rh/BEA-25 (17.1%). Moreover, with increasing chain length of linear olefins, the yield gradually decreased from 91.3% (1-decene) to 54.2% (1-dodecene) and 46.0% (1-hexadecene), yet remained significantly higher than that of Rh/BEA-25 (30.8%, 24.1%, and 10.1%, respectively). These results demonstrate that Rh/BEA-OH-25 offers consistently high hydroformylation activity for long-chain and sterically hindered olefins.

In industrial hydroformylation, solvent-free systems can simplify downstream product separation and enhance process greenness. The long-term stability of Rh/BEA-OH-25 was investigated under neat 1-octene conditions (Fig. 3(f)). As the reaction progressed, the yields of nonanal and 2-methyloctanal steadily increased, and the l/b ratio stabilized at approximately 2.9 after 20 h, with no

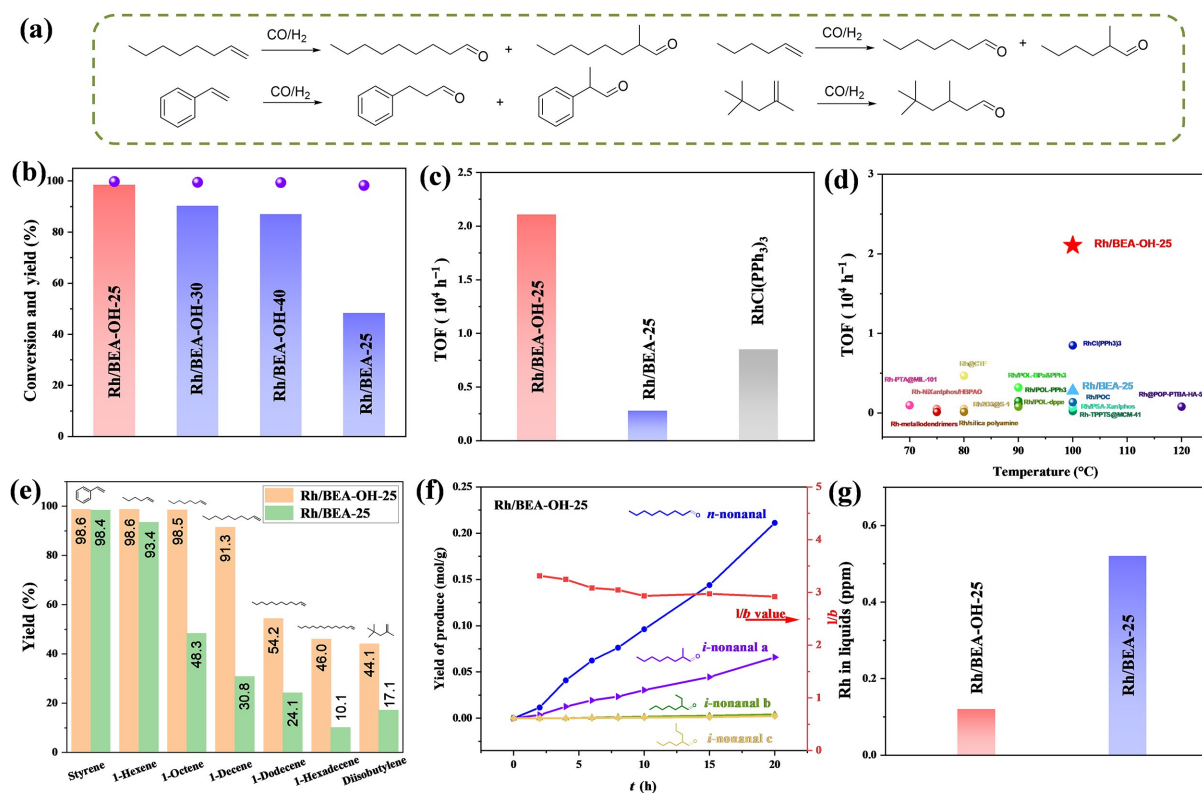


Figure 3 (a) Chemical formula for different olefins hydroformylation. (b) Rh/BEA-OH-25, Rh/BEA-OH-30, Rh/BEA-OH-40, and Rh/BEA-25 in the hydroformylation of 1-octene. (c) Comparison of TOF for the hydroformylation of 1-octene among Rh/BEA-OH-25, Rh/BEA-25, and RhCl(PPh₃)₃. (d) Comparison of TOF between Rh/BEA-OH-25, Rh/BEA-25 and Rh catalysts tested previously in the hydroformylation of 1-octene. (e) Comparison of hydroformylation activity of Rh/BEA-OH-25 and Rh/BEA-25 for different olefin substrates. (f) Yield-time profiles of hydroformylation of 1-octene over Rh/BEA-OH-25 under solvent-free condition. Reaction conditions: 1-octene (20 mL), catalyst (100 mg), 5 MPa, 100 °C. (g) Leaching amount of Rh from Rh/BEA-OH-25 and Rh/BEA-25 in the reaction solution after the reaction.

significant loss of catalytic activity, indicating excellent stability. The controlled reaction conditions effectively suppressed side reactions, and the amount of byproduct nonanoic acid and nonyl alcohol was negligible (< 0.1%). These results demonstrate the potential of Rh/BEA-OH-25 for efficient and sustainable hydroformylation under solvent-free conditions.

To further investigate the effect of Rh leaching on the catalytic performance of Rh/BEA-OH-25 during the reaction, a hot filtration experiment was conducted [42]. After 2 h of reaction, with 1-octene conversion reaching 55.8%, the catalyst was removed by filtering through an organic membrane, and the filtrate was allowed to react for another 3 h. The final 1-octene conversion was 56.4%, indicating that reaction effectively ceased upon catalyst removal. To evaluate Rh leaching, inductively coupled plasma optical emission spectrometer (ICP-OES) analysis is performed. As shown in Fig. 3(g), after 5 h, the Rh concentration in the solution is 0.12 ppm for Rh/BEA-OH-25, much lower than 0.5 ppm for Rh/BEA-25. These results show that the silanol nest-rich support effectively suppresses Rh leaching and enhances catalyst stability. In addition, recycling experiments were carried out to further assess the catalyst stability (Fig. S3(b) in the ESM). After five consecutive reaction cycles, both the 1-octene conversion and aldehyde selectivity over Rh/BEA-OH-25 remained above 90%, indicating excellent stability and reusability of the catalyst under the tested conditions.

Considering the significant influence of temperature and pressure on hydroformylation, systematic optimization is carried out to determine appropriate reaction conditions (Fig. S3 and Table S3 in the ESM). Using 30 mg of catalyst with 2.5 mmol of 1-octene

in 5 mL of toluene, the catalytic activity decreases markedly when the temperature is below 100 °C or the pressure is lower than 5 MPa. Further increases beyond these thresholds do not lead to additional improvements. Therefore, 100 °C and 5 MPa are selected as the standard reaction conditions for subsequent experiments. Under these conditions, the effect of Rh loading is also investigated. When the Rh loading is below 0.05 wt.%, increasing the Rh content improves the aldehyde yield, which exceeds 98% at 0.05 wt.%. Hence, a Rh loading of 0.05 wt.% is used in this study.

3.3 Mechanistic study

To elucidate the role of surface silanol nests in long-chain olefin adsorption and enrichment, 1-octene adsorption IR spectroscopy, adsorption energy calculations, and adsorption tests under reaction conditions were conducted. As shown in Fig. 4(a), the IR spectra of gas-phase 1-octene and its adsorbed states on Rh/BEA-OH-25 and Rh/BEA-25 were analyzed. The characteristic peaks of terminal alkenes include the C=H stretching vibration at 3080 cm⁻¹, the C=C stretching vibration at 1630 cm⁻¹, and strong absorption peaks corresponding to the stretching vibrations of methyl and methylene groups at 2958, 2930, 2873, and 2856 cm⁻¹. Additionally, bending vibrations of methyl and methylene groups in saturated bonds appear at 1460 and 1378 cm⁻¹ [43]. Comparing the IR spectra of gas-phase 1-octene with those of adsorbed 1-octene on Rh/BEA-OH-25 and Rh/BEA-25, a significant attenuation of the C=H and C=C stretching bands at 3080 and 1630 cm⁻¹, respectively, was observed after adsorption, indicating a strong interaction between 1-octene's C=C bond and the BEA zeolite-based catalysts [44, 45].

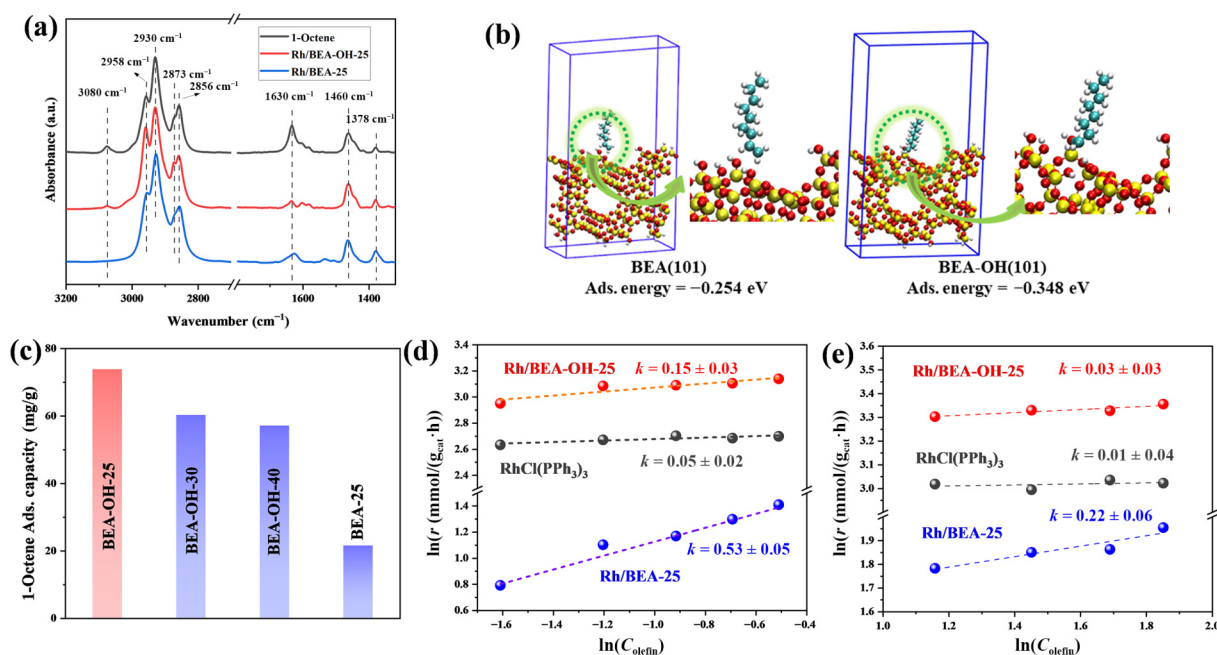


Figure 4 (a) Adsorption capacities of 1-octene on different zeolite supports under reaction conditions. (b) Structures and adsorption energies of 1-octene on BEA-OH and BEA. (c) IR spectra of adsorbed 1-octene and gaseous 1-octene on Rh/BEA-OH-25 and Rh/BEA-25. Kinetics of 1-octene hydroformylation over Rh/BEA-OH-25, Rh/BEA-25, and RhCl(PPh₃)₃ catalysts at (d) low and (e) high olefin concentrations.

Furthermore, a comparison of the C=C stretching vibration at 1630 cm⁻¹ between Rh/BEA-OH-25 and Rh/BEA-25 reveals a weaker relative peak intensity for Rh/BEA-OH-25, suggesting that the silanol nest-rich zeolite exhibits stronger hydrogen bonding interactions with 1-octene. This observation supports the role of silanol nests in enhancing the adsorption of 1-octene on the catalyst surface.

DFT calculations were employed to construct and optimize surface models of silanol nest-rich BEA-OH and BEA (Fig. 4(b)). The (101) crystal facet, identified from TEM images, was chosen to represent the catalyst surface. As illustrated in Fig. 1(c), the adsorption energies of 1-octene on different zeolite supports were further computed. The results indicate that the adsorption energy on the silanol nest-containing BEA was -0.348 eV, significantly higher than that on BEA without silanol nests (-0.254 eV). The increase in adsorption energy can be attributed to the hydrogen- π interactions between the silanol nests on the BEA-OH surface and 1-octene, thus enhancing the adsorption strength.

To further elucidate the effect of silanol nest concentration on the adsorption behavior of 1-octene, adsorption capacity measurements were conducted on the zeolite supports under reaction-relevant conditions. As shown in Fig. 4(c), the adsorption capacity of BEA-OH-25 for 1-octene reached 73.85 mg/g, while that of BEA-OH-30 and BEA-OH-40 slightly decreased to 60.33 and 57.13 mg/g, respectively. In contrast, the adsorption capacity of BEA was significantly lower at 21.61 mg/g, highlighting that a higher silanol nest concentration greatly enhances the adsorption for long-chain olefins.

To confirm that the observed rates reflect intrinsic catalytic activity rather than diffusion limitations, kinetic tests were performed under various stirring rates and catalyst particle sizes (Fig. S4 in the ESM). The reaction rate was independent of stirring speed and catalyst particle size, indicating negligible external and internal diffusion effects.

Kinetic studies of olefin hydroformylation provide an effective

means to evaluate substrate adsorption behavior during the catalytic process. Kinetic investigations of the hydroformylation of 1-octene reveal that the reaction order with respect to 1-octene over Rh/BEA-OH-25 is approximately 0.15, which is close to that of the homogeneous catalyst triphenylphosphine rhodium chloride (0.05) (Fig. 4(d)). In contrast, the reaction order over Rh/BEA-25 is about 0.53, significantly higher than that of Rh/BEA-OH-25. The near-zero-order dependence of the reaction rate on 1-octene concentration indicates that variations in substrate concentration have minimal influence on the reaction rate when catalyzed by Rh/BEA-OH-25 [19]. This phenomenon can be attributed to the abundant silanol nests on the catalyst surface, which effectively enrich olefins and mimic the localized concentration modulation observed in homogeneous catalysis. This facilitates the surface enrichment of 1-octene, thereby promoting efficient hydroformylation [23, 24]. In addition, the reaction orders under near solvent-free hydroformylation conditions were investigated (Fig. 4(e)). At high olefin concentrations, both Rh/BEA-OH-25 and RhCl(PPh₃)₃ maintain a zero-order dependence, whereas the reaction order for Rh/BEA-25 decreases from 0.53 at low concentrations to 0.22. This indicates that at high olefin concentrations, Rh/BEA-25 also exhibits nearly saturated olefin coverage; however, even under near-saturation, its catalytic activity remains significantly lower than that of Rh/BEA-OH-25. The observed change in reaction order suggests that the effect of silanol nests on hydroformylation extends beyond enhancing olefin adsorption and enrichment, and may also provide additional contributions to subsequent reaction steps.

To further elucidate the role of silanol nests in the hydroformylation process and to probe the configuration of reactive species during the reaction, *in-situ* infrared spectroscopy was conducted on Rh/BEA-OH-25 and Rh/BEA-25 under syngas atmosphere. As shown in Figs. 5(a) and 5(b), the characteristic absorption peaks of 1-octene were observed at 2958, 2928, 2873, and 2856 cm⁻¹, corresponding to the stretching vibrations of methyl

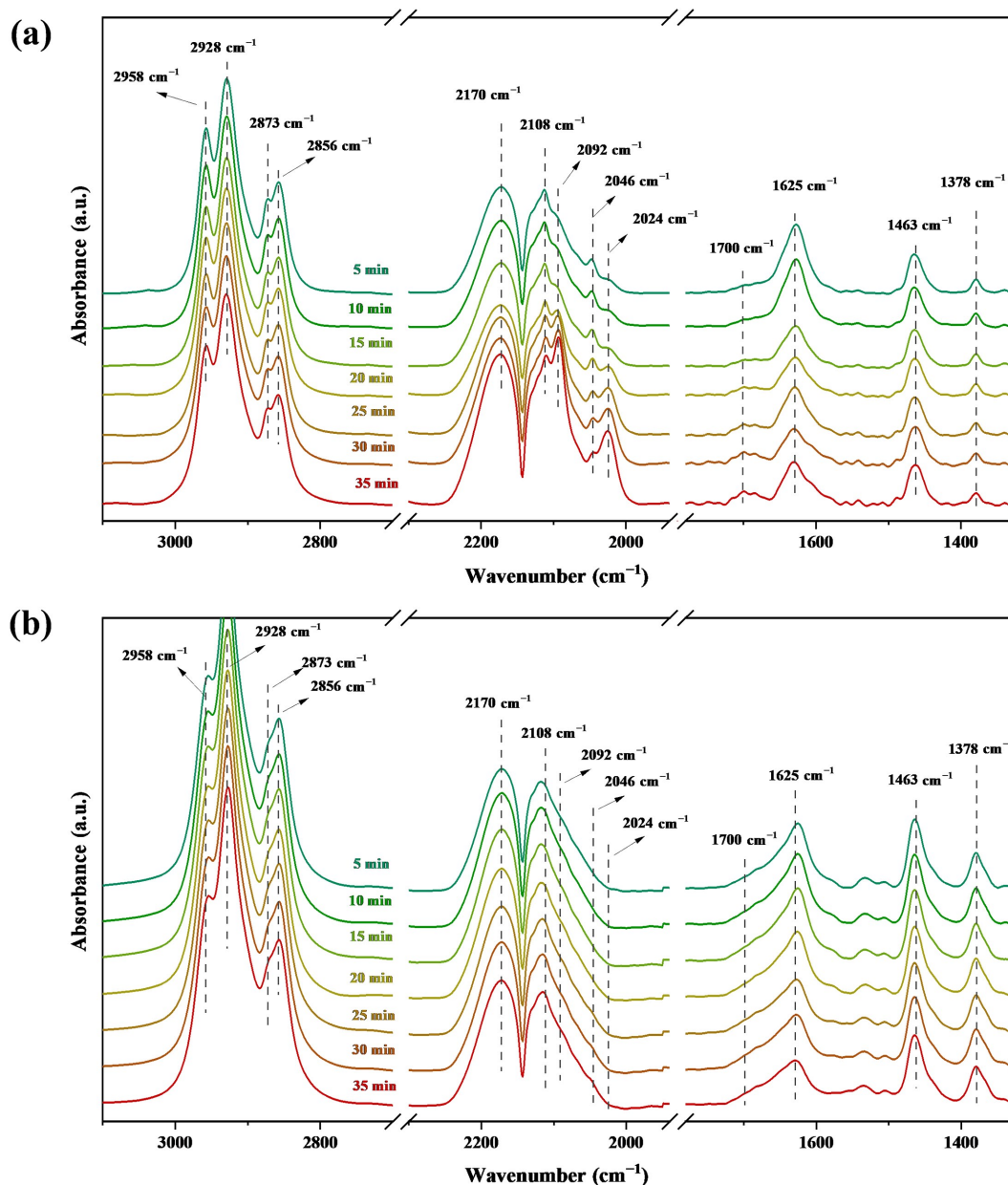


Figure 5 *In-situ* IR spectra of the hydroformylation of 1-octene over (a) Rh/BEA-OH-25 and (b) Rh/BEA-25.

and methylene groups in saturated bonds. The C=C stretching vibration of 1-octene appeared at 1625 cm^{-1} , and the bending vibrations of methyl and methylene groups were located at 1463 and 1378 cm^{-1} . Broad peaks around 2170 and 2110 cm^{-1} were attributed to the stretching vibrations of CO. Additionally, sharp bands at 2108 and 2046 cm^{-1} corresponded to the symmetric and asymmetric stretching vibrations of rhodium dicarbonyl species [16]. As the reaction progressed, new CO stretching bands appeared at 2092 and 2024 cm^{-1} , corresponding to symmetric and asymmetric modes. These shifts are likely caused by changes in Rh coordination with hydrogen and olefins during the reaction, indicating the formation and accumulation of hydroformylation reaction intermediates [46, 47]. In comparison with Rh/BEA-25, Rh/BEA-OH-25 exhibited a greater accumulation of reaction intermediates, suggesting that the silanol nest support facilitates olefin coordination and the generation of other reactive intermediates. Moreover, a new characteristic band appeared at

1700 cm^{-1} and gradually intensified, which was attributed to the C=O stretching vibration of Rh-adsorbed acyl species, suggesting the formation and accumulation of nonanoyl ($\text{C}_8\text{H}_{16}\text{CO}^*$) intermediates [16, 43]. The presence of Rh-acyl complexes has been previously reported, typically exhibiting C=O stretching vibrations around 1700 cm^{-1} . Meanwhile, Rh/BEA-OH-25 also exhibited a higher accumulation of nonanoyl species compared to Rh/BEA-25.

Regarding the reaction mechanism of hydroformylation, the homogeneous catalytic pathway proposed by Heck and Breslow has been widely recognized and accepted [48, 49]. For Rh-based catalysts that lack phosphine ligands and incorporate support effects, the reaction pathway for 1-octene hydroformylation is depicted in Fig. 6. This pathway has been adaptively modified to account for the influence of different supports, especially regarding the number and spatial arrangement of carbonyl ligands involved in the catalytic cycle. It provides detailed annotations and illustrates the two distinct reaction routes leading to the formation of linear

and branched aldehyde products. The hydroformylation reaction proceeds through the following fundamental steps: (1→2) dissociation of the carbonyl ligand on the Rh-based catalyst; (2→3) Olefin coordination; (3→4) olefin hydrogenation to form alkyl; (4→5) carbon monoxide coordination; (5→6) carbonyl insertion to form acyl; (6→8) hydrogen addition; (8→2) hydride transfer from acyl to form aldehyde and elimination [50]. Both experimental and theoretical studies have demonstrated that the surface structure of the catalyst plays a crucial role in determining the efficiency and selectivity of the hydroformylation reaction.

To further clarify the role of silanol nests in the reaction mechanism, DFT calculations were performed to compare 1-octene hydroformylation over Rh/BEA(101) and Rh/BEA-OH(101), with key intermediates identified through stability analysis. The analysis focuses on the linear hydroformylation pathway, which represents the predominant reaction route under the studied conditions. Figure 7(a) presents the free energy profiles of the Rh/BEA(101) and Rh/BEA-OH(101) systems, comparing the energy evolution of intermediates for both catalysts. The energy profiles of Rh/BEA-OH(101) and Rh/BEA(101) indicate similar reaction barriers. In both systems, the highest energy barrier in both cases associated with the transition state TS-2, at 67 and 69 kJ/mol, respectively,

indicating that the rate-determining step of the reaction is carbonyl insertion. This trend in the rate-determining energy barrier is consistent with the results of thermodynamic experiments, where the apparent activation energies of the two different supports are similarly close (as shown in Fig. 7(b)). Notably, depending on the substrate, catalyst, and reaction conditions, olefin insertion, carbonyl insertion, or hydrogenolysis may serve as the rate-determining step [29]. The comparable activation barriers for the rate-determining step suggest that the difference in catalytic activity between the two supports does not originate from variations in this energy barrier. Instead, a notable distinction lies in the relative energy of intermediate 3 (Table S4 in the ESM), which is 34 kJ/mol lower in the Rh/BEA-OH (101) system than in Rh/BEA (101). This indicates that the olefin-coordinated intermediate in Rh/BEA-OH (101) possesses higher thermodynamic stability, likely due to the interaction between the olefin and the silanol nests on the support. As this intermediate corresponds to the olefin-rhodium complex, its enhanced stability implies that the active precursor forms more readily, promoting the initiation of the hydroformylation cycle. This finding is in good agreement with the *in-situ* IR observations, which revealed that Rh/BEA-OH-25 exhibited more pronounced olefin coordination and a greater accumulation of acyl intermediates,

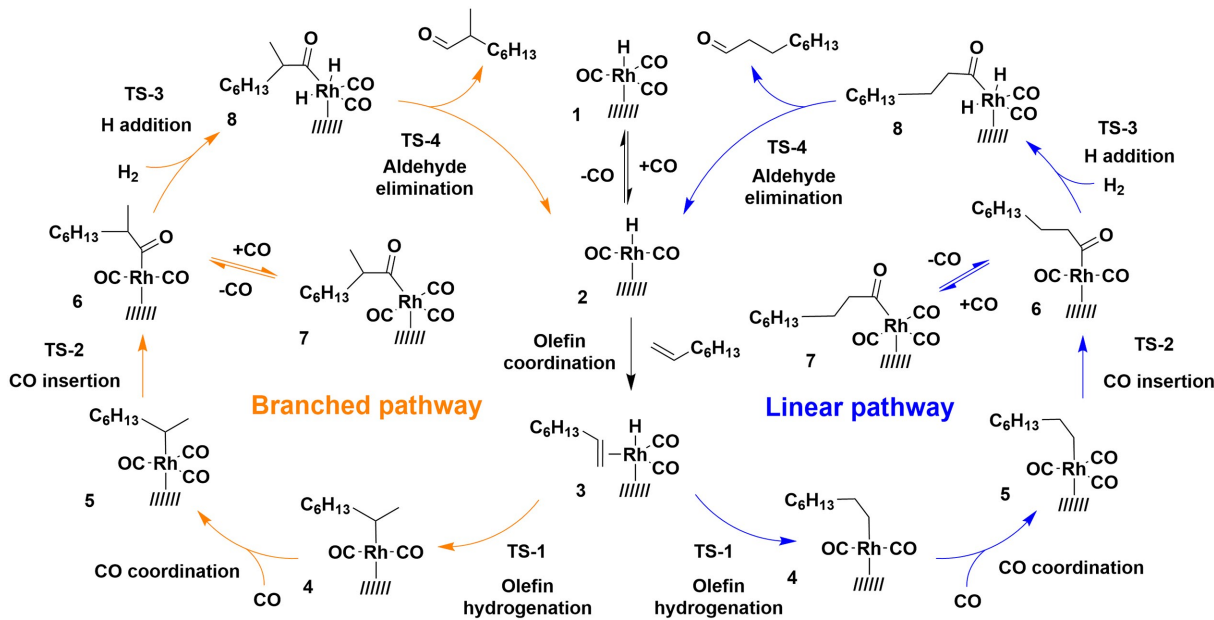


Figure 6 Mechanism of hydroformylation applicable to Rh-based heterogeneous catalysts.

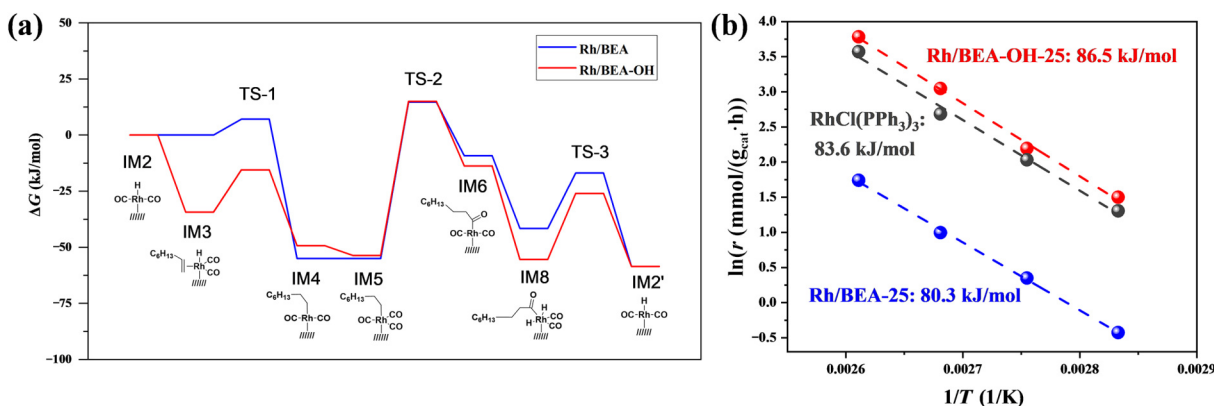


Figure 7 (a) Energies of intermediates and transition states in the hydroformylation of 1-octene over Rh/BEA-OH and Rh/BEA predicted using DFT calculation. (b) Thermodynamics of the hydroformylation of 1-octene over Rh/BEA-OH-25, Rh/BEA-25, and RhCl(PPh₃)₃ catalysts.

further corroborating the enhanced stabilization of reactive species on the silanol-rich support.

Based on the catalytic performance, structural characterizations and theoretical calculations, a silanol nest-synergistic hydroformylation pathway is proposed, as shown in Fig. 8. In homogeneous hydroformylation, an equilibrium step involving the formation of olefin-Rh complexes facilitates olefin diffusion and leads to a zero-order kinetic dependence on the olefin. In contrast, such coordination is generally absent in heterogeneous hydroformylation, often resulting in limited olefin transport and coordination efficiency. In this work, mechanistic studies reveal that silanol nests on the catalyst surface play a pivotal role in enabling effective olefin coordination. The hydrogen- π interaction between silanol nests and the olefin markedly enhances the adsorption energy of 1-octene on the support [51, 52], lowering the adsorption energy from -0.254 to -0.348 eV. Consequently, the amount of olefin adsorbed on the catalyst surface increases from 21.61 to 73.85 mg/g_{cat}, indicating substantial olefin enrichment in the vicinity of the active Rh sites. This enrichment ensures high olefin accessibility, creating a coordination environment analogous to that in homogeneous catalysis. Furthermore, DFT calculations reveal that the presence of silanol nests reduces the olefin coordination energy, with the olefin-Rh complex intermediate in the Rh/BEA-OH system exhibiting a relative energy that is 34 kJ/mol lower than that in the Rh/BEA system. This indicates that the olefin-coordinated intermediate forms more readily, thereby facilitating the initiation of the hydroformylation catalytic cycle. Collectively, these enhancements in olefin adsorption and coordination account for the near-zero apparent reaction order with respect to olefin, leading to catalytic behavior analogous to homogeneous hydroformylation.

4 Conclusions

In summary, this study successfully designs and synthesizes a Rh-based heterogeneous catalyst supported on BEA zeolite enriched with abundant silanol nests. The excellent catalytic performance in

the hydroformylation of long-chain olefins is obtained. The incorporation of silanol nests not only stabilizes the dispersion of Rh nanoparticles but also significantly enhances the enrichment of olefins at the catalyst surface, effectively emulating the localized concentration regulation observed in homogeneous catalysis through the formation of olefin-Rh complexes. As a result, the catalyst achieves a high turnover frequency of 21,060 h⁻¹ in the hydroformylation of 1-octene, surpassing the Wilkinson homogeneous catalyst and most other heterogeneous catalysts, with a yield exceeding 98% toward nonanal. Moreover, the catalyst exhibits remarkable stability with low Rh leaching (0.12 ppm). The study reveals that the silanol nests promote the enrichment and coordination of long-chain olefins, thereby enhancing hydroformylation activity. Importantly, surface modification of the zeolite to regulate local substrate concentration and substrate coordination further improves catalytic efficiency, offering new insights for the rational design of hydroformylation catalysts.

Electronic Supplementary Material: Supplementary material (catalyst characterization (SEM, XPS, and textural properties), DFT calculation conditions, reaction optimization studies (temperature, pressure, stirring speed, particle size), cycling performance, GC-MS analysis of hydroformylation products, and comparative evaluation of different Rh/BEA-OH catalysts) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908341>.

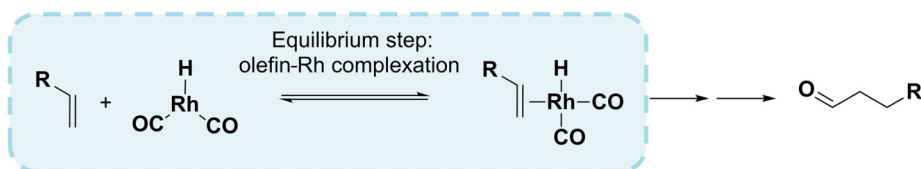
Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 22378026) and Beijing

Homogeneous hydroformylation:



Heterogeneous hydroformylation (Rh/BEA-OH-25):

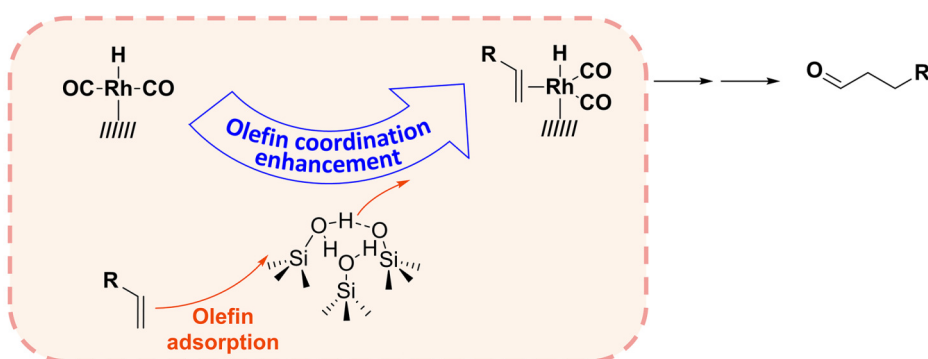


Figure 8 Proposed silanol nest-synergistic hydroformylation pathway over Rh/BEA-OH-25.

Municipal High-Level Talents Introduction and Cultivation Plan (No. IDHT20180508).

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

H. F. C.: Investigation, data curation, formal analysis, writing – original draft, Methodology, Software, Validation, Visualization. J. H. W.: Data curation, investigation. Y. Z. L.: Data curation, supervision, writing – review and editing. T. L. H.: Supervision, methodology. T. Z.: Supervision, investigation. Z. C. L.: Investigation, resources. C. M. X.: Resources, supervision. H. Y. L.: Resources, methodology, supervision, writing – review and editing. H. B. J.: Funding acquisition, methodology, project administration, resources, supervision, writing – review and editing.

Use of AI statement

None.

References

- [1] Zhang, X. J.; Yan, T.; Hou, H. M.; Yin, J. Q.; Wan, H. L.; Sun, X. D.; Zhang, Q.; Sun, F. F.; Wei, Y.; Dong, M. et al. Regioselective hydroformylation of propene catalysed by rhodium-zeolite. *Nature* **2024**, *629*, 597–602.
- [2] Ro, I.; Qi, J.; Lee, S.; Xu, M.; Yan, X.; Xie, Z.; Zakem, G.; Morales, A.; Chen, J. G.; Pan, X. et al. Bifunctional hydroformylation on heterogeneous Rh-WO₃ pair site catalysts. *Nature* **2022**, *609*, 287.
- [3] Shikhaliyev, K.; Onsree, T.; Jaeschke, A. H.; Ghoreishian, S. M.; Shariati, K.; Martinez, A.; Katz, A.; Hwang, S.; Gaffney, A.; Urban-Klaehn, J. M. et al. H-ZSM-5 Catalysts for the catalytic upcycling of polypropylene glycol. *Appl. Catal. B* **2023**, *337*, 122991.
- [4] Sun, Q.; Dai, Z.; Liu, X.; Sheng, N.; Deng, F.; Meng, X.; Xiao, F. S. Highly efficient heterogeneous hydroformylation over Rh-metalated porous organic polymers: Synergistic effect of high ligand concentration and flexible framework. *J. Am. Chem. Soc.* **2015**, *137*, 5204–5209.
- [5] Liu, B.; Wang, Y.; Huang, N.; Lan, X.; Xie, Z.; Chen, J. G.; Wang, T. Heterogeneous hydroformylation of alkenes by Rh-based catalysts. *Chem* **2022**, *8*, 2630–2658.
- [6] Wang, L. B.; Zhang, W. B.; Wang, S. P.; Gao, Z. H.; Luo, Z. H.; Wang, X.; Zeng, R.; Li, A. W.; Li, H. L.; Wang, M. L. et al. Atomic-level insights in optimizing reaction paths for hydroformylation reaction over Rh/CoO single-atom catalyst. *Nat. Commun.* **2016**, *7*, 14036.
- [7] Tewari, T.; Kumar, R.; Chandanshive, A. C.; Chikkali, S. H. Phosphorus ligands in hydroformylation and hydrogenation: A personal account. *Chem. Rec.* **2021**, *21*, 1182–1198.
- [8] Gonsalvi, L.; Guerriero, A.; Monflier, E.; Hapiot, F.; Peruzzini, M. The role of metals and ligands in organic hydroformylation. In *Hydroformylation for Organic Synthesis*. Taddei, M.; Mann, A., Eds.; Springer: Berlin, Heidelberg, 2013; pp 1–47.
- [9] Nenaseva, M. V.; Gorbunov, D. N. Recent progress and strategies on the design of zeolite-based catalysts for hydroformylation of olefins. *Catalysts* **2024**, *14*, 942.
- [10] Nurtila, S. S.; Linnebank, P. R.; Krachko, T.; Reek, J. N. H. Supramolecular approaches to control activity and selectivity in hydroformylation catalysis. *ACS Catal.* **2018**, *8*, 3469–3488.
- [11] Alsalahi, W.; Tylus, W.; Trzeciak, A. M. Green synthesis of rhodium nanoparticles that are catalytically active in benzene hydrogenation and 1-hexene hydroformylation. *ChemCatChem* **2018**, *10*, 2051–2058.
- [12] Sun, G. C.; Fan, S. B.; Lv, J. M.; Zhao, T. S. Effective hollow Rh@H-S-I catalyst for hydroformylation of 1-hexene. *J. Catal.* **2024**, *439*, 115770.
- [13] Hanf, S.; Alvarado Rupflin, L.; Gläser, R.; Schunk, S. A. Current state of the art of the solid Rh-based catalyzed hydroformylation of short-chain olefins. *Catalysts* **2020**, *10*, 510.
- [14] Shang, W. X.; Qin, B.; Gao, M. Y.; Qin, X. T.; Chai, Y. C.; Wu, G. J.; Guan, N. J.; Ma, D.; Li, L. D. Efficient heterogeneous hydroformylation over zeolite-encaged isolated rhodium ions. *CCS Chem.* **2023**, *5*, 1526–1539.
- [15] Zhang, J.; Sun, P.; Gao, G.; Wang, J.; Zhao, Z. L.; Muhammad, Y.; Li, F. W. Enhancing regioselectivity via tuning the microenvironment in heterogeneous hydroformylation of olefins. *J. Catal.* **2020**, *387*, 196–206.
- [16] Zhao, M. J.; Li, C. E.; Gómez, D.; Gonell, F.; Diaconescu, V. M.; Simonelli, L.; Haro, M. L.; Calvino, J. J.; Meira, D. M.; Concepción, P. et al. Low-temperature hydroformylation of ethylene by phosphorous stabilized Rh sites in a one-pot synthesized Rh-(O)-P-MFI zeolite. *Nat. Commun.* **2023**, *14*.
- [17] Lang, R.; Li, T. B.; Matsumura, D.; Miao, S.; Ren, Y. J.; Cui, Y. T.; Tan, Y.; Qiao, B. T.; Li, L.; Wang, A. Q. et al. Hydroformylation of olefins by a rhodium single-atom catalyst with activity comparable to RhCl(PPh₃)₃. *Angew. Chem., Int. Ed.* **2016**, *55*, 16054–16058.
- [18] Lee, H.; Shin, D.; Oh, D.; Jeong, B.; Kim, K. Y.; Hur, C.; Han, J. W.; An, K. Atomically dispersed Rh catalysts formed on defective CeO₂ surfaces with hydroformylation activity. *Chem. Eng. J.* **2024**, *496*, 153758.
- [19] Dabbawala, A. A.; Bajaj, H. C.; Jasra, R. V. Rhodium complex of monodentate phosphite as a catalyst for olefins hydroformylation. *J. Mol. Catal. A Chem.* **2009**, *302*, 97–106.
- [20] Riisager, A.; Fehrmann, R.; Haumann, M.; Gorle, B. S. K.; Wasserscheid, P. Stability and kinetic studies of supported ionic liquid phase catalysts for hydroformylation of propene. *Ind. Eng. Chem. Res.* **2005**, *44*, 9853–9859.
- [21] Yu, Z. N.; Zhang, S. X.; Zhang, L. L.; Liu, X. Y.; Jia, Z. H.; Li, L.; Ta, N.; Wang, A.; Liu, W.; Wang, A. Q. et al. Suppressing metal leaching and sintering in hydroformylation reaction by modulating the coordination of Rh single atoms with reactants. *J. Am. Chem. Soc.* **2024**, *146*, 11955–11967.
- [22] Liu, Y. F.; Liu, Z. Q.; Hui, Y.; Wang, L.; Zhang, J.; Yi, X. F.; Chen, W.; Wang, C. T.; Wang, H.; Qin, Y. C. et al. Rhodium nanoparticles supported on silanol-rich zeolites beyond the homogeneous Wilkinson's catalyst for hydroformylation of olefins. *Nat. Commun.* **2023**, *14*, 2531.
- [23] Fang, Y.; Zhao, H.; Guo, X. Y.; He, Y. L.; Yang, G. H.; Tsubaki, N. Silicalite-1 encapsulated rhodium nanoparticles for hydroformylation of 1-hexene. *Catal. Today* **2023**, *410*, 150–156.
- [24] Sudheesh, N.; Parmar, J. N.; Shukla, R. S. Hydroformylation of propene heterogeneously catalyzed by HRh(CO)(PPh₃)₃ encapsulated in to hexagonal mesoporous silica-Parametric variation and mass transfer study. *Appl. Catal. A Gen.* **2012**, *415–416*, 124–131.
- [25] Cui, Y. T.; Li, J. W.; Liu, Z. H.; Yu, H. J.; Ding, D. Q.; Wang, J. J. Alkali etching-free synthesis of hierarchical Zr-BEA zeolite as a robust catalyst for the efficient production of lactic acid from carbohydrates. *Microporous Mesoporous Mater.* **2023**, *360*, 112737.
- [26] Chandra Shekara, B. M.; Jai Prakash, B. S.; Bhat, Y. S. Dealumination of zeolite BEA under microwave irradiation. *ACS Catal.* **2011**, *1*, 193–199.
- [27] Oumi, Y.; Mizuno, R.; Azuma, K.; Nawata, S.; Fukushima, T.; Uozumi, T.; Sano, T. Reversibility of dealumination-redealumination process of BEA zeolite. *Microporous Mesoporous Mater.* **2001**, *49*, 103–109.
- [28] Yusuf, M. O. Bond characterization in cementitious material binders using fourier-transform infrared spectroscopy. *Appl. Sci.* **2023**, *13*, 3353.

- [29] Qi, L.; Zhang, Y. F.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T. Ethanol conversion to butadiene over isolated zinc and yttrium sites grafted onto dealuminated beta zeolite. *J. Am. Chem. Soc.* **2020**, *142*, 14674–14687.
- [30] Paukshtis, E. A.; Yaranova, M. A.; Batueva, I. S.; Bal'zhinimaev, B. S. A FTIR study of silanol nests over mesoporous silicate materials. *Microporous Mesoporous Mater.* **2019**, *288*, 109582.
- [31] Fu, T. J.; Jia, L. H.; Li, C. Y.; Li, Z. Silanol nests-enriched silicalite-1 zeolite catalyst for efficient toluene alkylation with methanol to *para*-xylene. *Chem. Eng. J.* **2023**, *474*, 145768.
- [32] Ma, Y. K.; Rigolet, S.; Michelin, L.; Paillaud, J. L.; Mintova, S.; Khoerunnisa, F.; Daou, T. J.; Ng, E. P. Facile and fast determination of Si/Al ratio of zeolites using FTIR spectroscopy technique. *Microporous Mesoporous Mater.* **2021**, *311*, 110683.
- [33] Li, S. H.; Zhou, L.; Zheng, A. M.; Deng, F. Recent advances in solid state NMR characterization of zeolites. *Chin. J. Catal.* **2015**, *36*, 789–796.
- [34] Wang, W. Y.; Xu, J.; Deng, F. Recent advances in solid-state NMR of zeolite catalysts. *Natl. Sci. Rev.* **2022**, *9*, nwac155.
- [35] Qi, L.; Das, S.; Zhang, Y. F.; Nozik, D.; Gates, B. C.; Bell, A. T. Ethene hydroformylation catalyzed by rhodium dispersed with zinc or cobalt in silanol nests of dealuminated zeolite beta. *J. Am. Chem. Soc.* **2023**, *145*, 2911–2929.
- [36] Yang, Q.; Wang, P. F.; Li, C.; Wang, B. L.; Zheng, Y.; Feng, Y.; Miao, Z. D.; Li, M. S.; Wang, M. Y.; Huang, S. Y. et al. Unravelling structure sensitivity in heterogeneous hydroformylation of aldehyde over Rh. *Chem. Eng. J.* **2024**, *481*, 148529.
- [37] Yang, Q.; Zheng, Y.; Feng, Y.; Ding, J.; Li, M. S.; Huang, S. Y.; Wang, M. Y.; Ma, X. B. Balanced Rh⁺-Rh⁰ sites over Rh clusters enhance heterogeneous hydroformylation of aldehyde. *ChemCatChem* **2025**, *17*, e202401392.
- [38] Chen, M. D.; Gupta, G.; Ordonez, C. W.; Lamkins, A. R.; Ward, C. J.; Abolafia, C. A.; Zhang, B. Y.; Roling, L. T.; Huang, W. Y. Intermetallic nanocatalyst for highly active heterogeneous hydroformylation. *J. Am. Chem. Soc.* **2021**, *143*, 20907–20915.
- [39] Shan, J. J.; Li, M. W.; Allard, L. F.; Lee, S.; Flytzani-Stephanopoulos, M. Mild oxidation of methane to methanol or acetic acid on supported isolated rhodium catalysts. *Nature* **2017**, *551*, 605–608.
- [40] Tian, H.; Liu, S.; Han, Y. C.; Yang, K. M.; Xu, W. Y. Acid treatment to adjust zeolite hydrophobicity for olefin hydration reaction. *J. Porous Mater.* **2022**, *29*, 713–722.
- [41] Pilaski, M.; Artz, J.; Islam, H. U.; Beale, A. M.; Palkovits, R. N-containing covalent organic frameworks as supports for rhodium as transition-metal catalysts in hydroformylation reactions. *Microporous Mesoporous Mater.* **2016**, *227*, 219–227.
- [42] Wang, A.; Cao, H. C.; Zhang, L. L.; Wang, A. Q. Co/SiO₂ Catalyst for methoxycarbonylation of acetylene: On catalytic performance and active species. *Molecules* **2024**, *29*, 1987.
- [43] Kamer, P. C. J.; van Rooy, A.; Schoemaker, G. C.; van Leeuwen, P. W. N. M. *In situ* mechanistic studies in rhodium catalyzed hydroformylation of alkenes. *Coord. Chem. Rev.* **2004**, *248*, 2409–2424.
- [44] Wang, H. G.; Song, L. J.; Jiang, H.; Xu, J.; Jin, L. L.; Zhang, X. T.; Sun, Z. L. Effects of olefin on adsorptive desulfurization of gasoline over Ce(IV)Y zeolites. *Fuel Process. Technol.* **2009**, *90*, 835–838.
- [45] Wang, H. G.; Jiang, H.; Xu, J.; Sun, Z. L.; Zhang, X. T.; Zhu, H. L.; Song, L. J. Effects of benzene and 1-octene on desulfurization by selective adsorption with Ce(IV)Y. *Acta Phys. Chim. Sin.* **2008**, *24*, 1714–1718.
- [46] Leidecker, B. N.; Fuentes, D. P.; König, M.; Liu, J. L.; Baumann, W.; Sawall, M.; Neymeyr, K.; Jiao, H. J.; Franke, R.; Armin Börner, A. et al. *In situ* spectroscopic investigations on BiPhePhos modified rhodium complexes in alkene hydroformylation. *Catal. Sci. Technol.* **2024**, *14*, 3966–3983.
- [47] Chen, S. J.; Li, Y. Q.; Wang, Y. Y.; Zhao, X. L.; Liu, Y. Ionic Rh(I)-complexes containing π -accepting and hemilabile P,N-ligands as efficient catalysts for hydroformylation of 1-octene. *J. Mol. Catal. A Chem.* **2015**, *396*, 68–76.
- [48] Heck, R. F.; Breslow, D. S. The reaction of cobalt hydrotetracarbonyl with olefins. *J. Am. Chem. Soc.* **1961**, *83*, 4023–4027.
- [49] Sparta, M.; Børve, K. J.; Jensen, V. R. Activity of rhodium-catalyzed hydroformylation: Added insight and predictions from theory. *J. Am. Chem. Soc.* **2007**, *129*, 8487–8499.
- [50] Amsler, J.; Sarma, B. B.; Agostini, G.; Prieto, G.; Plessow, P. N.; Studt, F. Prospects of heterogeneous hydroformylation with supported single atom catalysts. *J. Am. Chem. Soc.* **2020**, *142*, 5087–5096.
- [51] Xiao, Y. H.; Wang, Y. J.; Wang, C. T.; Fang, W.; Liu, P.; Hui, Y.; Li, H. J.; Zhou, H.; Xiao, F. S. Tungsten species on beta zeolite with abundant silanol nests for efficient olefin metathesis. *Chem Bio Eng.* **2025**, *2*, 485–492.
- [52] Guo, L. W.; Shi, D.; Zhang, T. J.; Ma, Y. H.; Qi, G. D.; Xu, J.; Sun, Q. M. Unsaturated cobalt single-atoms stabilized by silanol nests of zeolites for efficient propane dehydrogenation. *Chin. J. Catal.* **2025**, *72*, 323–333.



This is an open access article under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0, <https://creativecommons.org/licenses/by/4.0/>).

