Sulfur Poisoning on Rh Nanoparticles but Sulfur Promotion on Its Single-Site Catalyst for Carbonylation

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Abstract

Sulfur poisoning is a challenge for most nanoparticle metal catalysts. A trace amount of sulfur contaminants could result in dramatic catalytic activity reduction or even irreversible deactivation¹⁻⁵. Therefore, new approaches to enhance the catalyst sulfur-resistance have continuously attracted attention from academia and industry. Herein, a role reversal of sulfur from poison to promotor is presented for an Rh-based heterogeneous catalyst from supported Rh nanoparticles (NPs) to its single-site catalysts (Rh1/AC, AC: activated carbon) in methanol carbonylation, ethylene and acetylene hydrocarboxylic reaction with a feed containing 1000 ppm H₂S (S-feed). In situ free-electron laser/time of flight mass spectrometry (In situ FEL/TOF MS) indicated that H₂S could be quickly transformed into catalyst-friendly CH₃SCH₃ and/or CH₃SH on the Rh1/AC, which coordinated with the Rh ions and promoted its methanol carbonylation reaction, possessing a lower energy barrier based on DFT calculations. On the contrary, strong adsorption of H₂S on the surface of Rh NPs inhibited the reaction of reactants.

Main Text

As is well-known, sulfur species bring about great challenges for almost all metal catalysts. Even ppm or ppb levels of sulfur species in a raw stock-feed can result in dramatic activity reduction of NP metal catalysts, often leading to irreversible deactivation. For example, it has been shown that 13 ppb of H₂S could deactivate Ni/Al₂O₃ NPs catalysts in the methanation reaction⁶ and 7 ppm H₂S was reported to lead to 90% activity loss for Ni-Rh alloy NPs⁷ during methane reforming. The strong adsorption of sulfur on metal NPs was deemed to block the active sites and lead to deactivation^{1-5,8}. Accordingly, large efforts have been paid every year to the desulfurization of the raw stock-feeds in order to ensure the long-term activity of the metal catalyst. Therefore, removing sulfur species from the raw feed through expensive and energy intensive technologies or developing a high sulfur tolerance catalyst has been a significant research topic for industry.

Sulfur is not only detrimental to catalytic reactions, sometimes it can also act as a promoter. Recently, thiophene promoted Au⁹, sulfur promoted Pd¹⁰, thiol protected Au¹¹, as well as sulfur promoted Cu¹² have been reported. In addition, adjusting the metal NPs size could regulate the effect of sulfur poisoning or S-bonding^{13,14}. Small Pt NPs are easy to be poisoned by thiophene in ethylene hydrogenation due to the increased coordinatively saturated surfaces¹³. A strong damped oscillatory size dependence of the adsorption energy for sulfur on facets of Cu nanoclusters from 3 up to sizes of ~300 atoms is also demonstrated¹⁴. The limit of NP dispersion is single metal site catalyst, which has drawn much attention due to versatile coordinative ability and efficient catalytic activity¹⁵⁻²⁰. Herein, impacts of H₂S on Rh NPs and its single-site catalysts during methanol carbonylation will be addressed, respectively. And the process of non-toxic transformation of H₂S into CH₃SCH₃ and/or CH₃SH species will be disclosed on the single-Rh-site catalysts.

Mesoporous carbon, SiO₂ and AC supported Rh NPs catalysts (Rh/CMK-3, Rh/SiO₂ and Rh/AC) were separately prepared in the METHODS section. As indicated in **Table 1**, a severe deactivation from 80 and 100 to 0 mole_{acetyl}/(mole_{Rh}×h) was obtained for Rh NPs in the Rh/CMK-3 and Rh/SiO₂ catalysts for methanol carbonylation, respectively, when a normal feed was switched into S-feed. In addition, an initial activity of Rh NPs (Rh/AC) was reduced from 163 to 40 mole_{acetyl}/(mole_{Rh}×h) in an autoclave reactor and suppressed from 135 to 110 mole_{acetyl}/(mole_{Rh}×h) in a fixed-bed reactor, respectively. The activity of Rh/AC increased gradually with time on stream up to ca. 3100 mole_{acetyl}/(mole_{Rh}×h) in the normal feed due to the atomic dispersion of Rh NPs under the existence of CH₃I/CO only on AC^{21,22} (**Extended Figure 1**). The strategy was also used to prepare AC supported single-Rh-site catalysts (Rh₁/AC) with the molecular structure of Rh(CO)₂I₃(O=AC), where O=AC is the carboxyl oxygen groups on the surface of activated carbon²¹⁻²³ (METHODS). Furthermore, the characterization result of spent Rh/AC in S-feed indicated that H₂S could not inhibit the atomic dispersion of Rh NPs (**Extended Figure 1b-1h**). In contrast, the activity of Rh/AC in S-feed finally reach ca. 3800 mole_{acetyl}/(mole_{Rh}×h). Accordingly, it was expectable that the activity increased from 3192 to 3974 mole_{acetyl}/(mole_{Rh}×h) was consequentially observed on the Rh₁/AC catalyst in a continuous fixed-bed reactor after using S-feed (**Table 1** and **Extended Figure 2**). More interestingly, a sulfur-promoting activity increase from 2021 to 2353 mole_{acetyl}/(mole_{Rh}×h) and from 2016 to 2477 mole_{acetyl}/(mole_{Rh}×h) was observed, respectively, on both homogeneous single sites [Rh(CO)₂I₂]⁻ and heterogeneous Rh₁/AC catalyst after S-feed being introduced into the autoclave reactor. A similar effect of sulfur-poisoning on the Rh NPs and sulfur-promoting on the Rh₁/AC was also observed for ethylene and acetylene hydrocarboxylic reaction in the autoclave reactor (**Extended Data Table 1**).

The high-resolution transmission electron microscopy (HR-TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) showed only isolated Rh atoms on fresh and spent Rh₁/AC in both normal feed and S-feed (**Figure 1a**, **Extended Data Figure 3a, 3b** and **4**). *In-situ/ex-situ* extended X-Ray absorption fine structure (EXAFS) verified that no bond of Rh-Rh was detected on the Rh₁/AC before, during or even after the reaction. These indicated a real process of single-sites catalysis in both normal feed and S-feed (**Figure 1b-1c**, **Extended Data Figure 5-6** and **Table 2**). Due to the small scattering factors of C, S and O in comparison to that of I abundant in the micropores of AC, longer Rh-ligand distances, and a large structural disorder, the fitting data of *in-situ* EXAFS characterization cannot reliably identify Rh nearest ligands other than I (or Rh).

X-ray photoelectron spectroscopy (XPS) showed that Rh³⁺ and Rh⁴⁺ existed in spent Rh₁/AC in S-feed (Rh₁/AC-SR) (**Extended Data Figure 7** and **Table 3**), which exhibited little change comparing with that on spent Rh₁/AC in normal feed. Meanwhile, the S 2p_{3/2} peak ascribed to Rh-S(CH₃)₂ and Rh-SHCH₃ species emerged at 162.7 eV and 164.3 eV respectively in Rh₁/AC-SR, implying that H₂S was preferentially transformed into CH₃-S-CH₃ and CH₃-SH species²⁴. The formation of Rh-S bonds on Rh₁/AC-SR might be indirectly evidenced from the IR experiment (**Extended data Figure 8**). Except for CO (m/z=28) and I• (m/z=127), a species with m/z=62 (probably CH₃SCH₃ species), originated from Rh₁/AC-SR, was also

observed by desorption ionization-time of flight mass spectrometry (LDI-TOF MS) (**Extended Figure 9**). Based on these combined characterization results, we suggest that the active mononuclear complexes exit as $(\text{CH}_3\text{-S-R})\text{Rh}(\text{CO})\text{I}_2(\text{O=AC})$ ($\text{R}=\text{H}, \text{CH}_3$) during carbonylation process on the $\text{Rh}_1/\text{AC-SR}$. Meanwhile, TEM, EDS-mapping, and the XPS of spent $\text{Rh}/\text{CMK-3}$ reacted in S-feed suggested that the strong adsorption of H_2S on the surface of Rh NPs blocked the adsorption of other reactants via an isolated Rh-S layer NPs (**Figure 1d-f, Extended Figure 10-12**).

In-situ mass spectra, obtained by free-electron laser-time of flight mass spectrometry (FEL TOF-MS), showed new species at $m/z=33, 34, 47, 48$ and 62 from Rh_1/AC catalyst in S-feed (**Figure 2a-2b**), which could be assigned to $-\text{SH}$, H_2S , $-\text{SCH}_3$, CH_3SH , and CH_3SCH_3 species, respectively. Moreover, the obtained results through changing the wavelength of ionization radiation proved that the species of $m/z=62$ is CH_3SCH_3 (**Extended Data Figure 13**). Interestingly, the ion peak at $m/z=62$ emerged at 373 K and increased with temperature till 453 K , while that at $m/z=34$ rapidly decreased from 313 to 433 K (**Figure 2c**), implying quick transformation of H_2S to CH_3SCH_3 . Besides, the reaction of H_2S with CH_3OH or CH_3I could produce CH_3SCH_3 and CH_3SH on the Rh_1/AC (**Figure 2d and 2e**). Moreover, CH_3SCH_3 from the spontaneous reaction of CH_3I with H_2S was also observed (**Figure 2f**).

In-situ diffuse reflectance infrared Fourier transformation spectroscopy on Rh_1/AC catalyst in S-feed showed a peak at $\sim 1775\text{ cm}^{-1}$ ascribed to acetyl species, appearing after reaction for 20 min , earlier than that in the normal feed at 25 min (**Extended Data Figure 14a-b**), indicating that the existence of sulfur species accelerated the formation of acetyl. Meanwhile, signals of $\text{CH}_3\text{-}$ or $\text{CH}_2\text{-}$ groups at about 2967 and 2850 cm^{-1} were dramatically attenuated in S-feed, suggesting that a portion of $\text{CH}_3\text{-}$ species were probably quenched by H_2S to form CH_3SH or CH_3SCH_3 species (**Extended Data Figure 14c-d**)^{25,26}. Besides, the *in-situ* electron paramagnetic resonance spectrometry/electron spin resonance also confirmed that the free radicals species were dramatically quenched during methanol carbonylation on Rh_1/AC in S-feed (**Extended Data Figure 15**).

DFT calculations investigated the coordination effect of CH_3SCH_3 and CH_3SH on the Rh mononuclear complex. The minimum energy of $(\text{H}_2\text{S})\text{Rh}(\text{CO})\text{I}_3(\text{O=AC})$, $(\text{CH}_3\text{SH})\text{Rh}(\text{CO})\text{I}_3(\text{O=AC})$, and $(\text{CH}_3\text{SCH}_3)\text{Rh}(\text{CO})\text{I}_3(\text{O=AC})$ is $3.5, -9.2$ and -14.9 kcal/mol , respectively, when compared with $\text{Rh}(\text{CO})_2\text{I}_3(\text{O=AC})$ (**Extended Data Figure 16**), suggesting that the new formed CH_3SH and CH_3SCH_3 species from H_2S favored to coordinate with Rh mononuclear complex to obtain a more stable Rh mononuclear structure. Moreover, the bond length of $\text{CH}_3\text{-I}$ in the chemical adsorption structure of $[\text{I-CH}_3\text{-(SR)Rh}(\text{CO})\text{I}_2(\text{O=AC})]$ with H_2S , CH_3SH or CH_3SCH_3 species, is $2.15\text{ \AA}$, a little longer than that in $[\text{I-CH}_3\text{-Rh}(\text{CO})_2\text{I}_2(\text{O=AC})]^\#$ ($2.13\text{ \AA}$) (**Extended Data Figure 17**), implying that the coordination of H_2S , CH_3SH and $(\text{CH}_3)_2\text{S}$ could lower the chemical adsorption energy of CH_3I . More importantly, the transition state energy barrier of $[\text{I-CH}_3\text{-(SR)Rh}(\text{CO})\text{I}_2(\text{O=AC})]^\#$ is $10.0, 10.5$ and 16.5 kcal/mol for CH_3SCH_3 , CH_3SH and H_2S coordination, respectively, while that of $[\text{I-CH}_3\text{-Rh}(\text{CO})_2\text{I}_2(\text{O=AC})]^\#$ is 16.1 kcal/mol , demonstrating

that CH_3SCH_3 or CH_3SH coordination as a ligand is beneficial for the Rh mononuclear complex to lower the energy barrier of CH_3I oxidative addition step, accelerating the reaction rate of methanol carbonylation on the Rh_1/AC catalyst^{22,27-30} (**Figure 3** and **Extended Data Figure 18**).

In summary, a reversal sulfur poisoning effect from Rh NPs to its single-sites catalyst was reported. The supported Rh NPs was easily poisoned by H_2S , while the Rh_1/AC exhibited excellent sulfur-promoting activity for methanol carbonylation. Interestingly, H_2S cannot prevent atomic dispersion of Rh NPs on an AC in the presence of $\text{CH}_3\text{I}/\text{CO}$. Similar results were also obtained in ethylene and acetylene hydrocarboxylation. H_2S could be rapidly transformed into catalyst-friendly CH_3SCH_3 and CH_3SH ligands on the single-site, while strong adsorption of H_2S on Rh NPs formed an isolated Rh-S layer, blocking the adsorption of reactants. It is anticipated that the phenomenon reported here might also be extended to other single-metal-site catalysts in various reactions.

Methods

Catalyst preparation

Mesoporous carbon, AC and SiO_2 supported Rh NPs catalyst ($\text{Rh}/\text{CMK-3}$, Rh/AC and Rh/SiO_2) with 1% weight was synthesized by incipient wetness impregnation, followed by dry and calcination, and then reduced by H_2 at 573 K for 2 h. The Rh_1/AC catalyst (1 wt.%) was prepared through the atomic dispersion strategy of metal NPs. Typically, the coconut activated carbon (AC) was grinded to 40-60 mesh and washed with deionized water until the electrical conductivity of the washings is below $20\ \mu\text{S}/\text{cm}$, dried in static air at 393 K for 12 h. Subsequently, the AC support was impregnated by an aqueous $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ solution. After drying under static conditions at 393 K for 12 h, the catalysts were treated in a three-step procedure: 573 K for 2 h in N_2 (100 mL/min), 573 K for 2 h in H_2 (100 mL/min) (Rh/AC was obtained in this step) and 513 K for 2 h with a mixture of $\text{CO}/\text{CH}_3\text{I}$ (CO passed through a bottle filled with CH_3I at 30 mL/min), respectively. Finally, the samples were cooled to ambient temperature in a flow of CO . The obtained catalysts were denoted as Rh_1/AC .

Catalyst characterization

The high-resolution transmission electron microscope (**HR-TEM**) images of the samples were obtained with JEM-2100 equipped with an energy dispersive spectrometer (**EDS**). The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (**HAADF-STEM**) images were also recorded using a JEM-ARM200F STEM/TEM instrument with a CEOS probe corrector working at 200 kV to guarantee a resolution of 0.08 nm.

X-ray photoelectron spectroscopy (**XPS**) characterization was performed using a Thermo Fisher ESCALAB 250Xi, equipped with a monochromated Al Ka X-ray source ($h\nu = 1486.6\ \text{eV}$, 15 kV, 10.8 mA). During data collection, the vacuum and the working pressure were limited to $3 \times 10^{-8}\ \text{Pa}$ and $7.1 \times 10^{-5}\ \text{Pa}$, respectively.

In-situ electron paramagnetic resonance spectrometry/electron spin resonance (***In-situ* EPR/ESR**) (Bruker A200) was conducted to monitor the free electrons in samples to identify the effect of H₂S on the radicals produced in the reaction. 5 mg sample was placed in a specific in-situ reactor for in-situ methanol carbonylation reaction, and then cooled to -177 °C with liquid nitrogen. A magnetic field linear sweep was performed with a fixed frequency of microwave irradiation (concrete parameters: center field: 3300 G, sweep width: 6400 G, static field: 100 G, microwave bridge frequency: 9.5 GHz and the power is set as 10 mW). The EPR data was processed and outputted as a 1st derivative of the absorption spectrum. EPR absorption occurs when the irradiation frequency “matches” the energy level separation created by the magnetic field, Boltzmann distribution.

The spent Rh₁/AC catalyst in normal and S-feed was soaked in ethanol for 6 h at room temperature to dissolve metal carbonyl on the surface of AC. Ethanol and the scrubbing solution obtained was smeared to a thin slice of KBr. The infrared scanning and signal processing were carried out under normal conditions.

The *in situ* diffuse reflectance infrared Fourier transform spectroscopy (**DRIFTS**) measurements were conducted on a VERTEX 80v FTIR spectrometer with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen. Catalysts were loaded into a PIKE High Temperature Reaction chamber (ZnSe windows). Mass flow controllers were used to control the gas rates across the reactor bed. For each DRIFTS experiments, the catalyst was first calcined in He (40 mL/min) at 573 K for 30 min. Then, the temperature of the catalyst was reduced to 513 K followed by flowing reaction gas. CH₃OH, CH₃I or liquid CH₃I and CH₃OH mixture (30 wt% CH₃I) were bubbled by reaction gas (CO, CO/H₂, He) at 298 K. During the reaction, spectra were recorded between 800 cm⁻¹ to 4000 cm⁻¹ by averaging 64 scans at a resolution of 4 cm⁻¹ to improve the signal to noise ratio.

The *in situ* flow-tube free-electron laser time of flight mass spectrometry (***In situ* FEL/TOF MS**) were conducted at Dalian Coherent Light Source³¹⁻³⁴ to detect the intermediates and the radicals during methanol gas phase carbonylation reaction. Laser desorption ionization/time of flight mass spectrometry (LDI-TOF MS) was conducted to detect the dissociative fragment of spent Rh₁/AC catalyst in normal and S-feed and further identify its single complex structure. And the in-situ formed short-lived intermediate species were also detected with the same TOF-MS instrument. Experiments on a series of ultraviolet wavelengths, i.e., 112 nm, 115 nm, 118 nm, 125 nm, 140 nm, 150 nm, were performed according to the ionization energy of intermediate species. For the LDI-TOF MS experiments, 266 nm lasers were slightly focused on the sample. The skimmed He atom beam passed the sample surface with a distance of ~1mm to carry the dissociated and sputtering species to the detection chamber.

The *in situ* EXAFS (***In situ* EXAFS**) measurements were performed at the SuperXAS beamline at the Swiss Light Source³⁵⁻³⁸. The ring was operated in top-up mode with 400 mA of 2.4 GeV electrons, which emitted polychromatic radiation in a super bend magnet (2.9 T) with a critical energy of 11.9 keV. The beam was collimated by a Pt-coated mirror and then monochromatized using a channel-cut Si(311) crystal in the

QEXAFS monochromator. A rotation speed of 1 Hz was chosen, yielding one EXAFS spectrum each 500 ms. The samples were measured in transmission mode with a 15-cm ionization chamber filled with Ar in front of the sample and another 15-cm ionization chamber filled with Kr behind the powder sample. A third 30-cm ionization chamber filled with Ar was used to measure an Rh metal foil located between the second and a third chamber to obtain an absolute calibration value for the energy scale of each spectrum. This value was related to the relative position of the monochromator crystal, which was measured simultaneously to each data point with a fast optical angular encoder system, yielding an accurate energy scale for the time-resolved spectra. The ionization chambers were operated with a high voltage of 1.5 kV, and the signals were amplified with Keithley 428 current amplifiers and then measured with a national instrument DAC data acquisition board using a fast data acquisition software. The Rh₁/AC catalyst was held between 2 quartz wool plugs and placed in a stainless steel flow reactor with quartz flow reactor. The following gases: Ar (N₂), CO (50% in Ar), H₂ (50% in Ar), and 1000 ppm H₂S in Ar were supplied by digital mass-flow controllers. CH₃I and methanol vapor were prepared by bubbling CO through liquid CH₃I and methanol mixture (30 wt% CH₃I). The reaction was started by introducing the CO, CH₃I, CH₄OH, H₂, and H₂S mixture at 1 bar when the reactor temperature increased to 240 °C in vacuum conditions. We recorded data when the reactants mixture passed through the catalyst.

Ex-situ extended X-ray absorption fine structure (***Ex-situ* EXAFS**) data of Rh K-edge were collected at beamline BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF)^{39,40}. The sample was grinded into 400 meshes and pressed into a small slice with a size of 0.5 cm x 0.5 cm before mounted to the test site. The data were recorded in the fluorescence mode equipped with an Electro-Lytle detector, and the calibration energy is 22117 eV. The original EXAFS data were processed with Athena software and normalized with the energy of 23220 eV, and then analyzed by the Artemis software package. Fourier transformation was applied to process the k^3 -weighted raw data. The theoretical scattering amplitude and phase-shift functions of all the paths for fitting the EXAFS data were calculated with FEFF6 code. Paths of Rh-CO, Rh-I, Rh-Rh were based on the crystal structure of [C₄I₂O₄Rh₂] and Rh Fm-3m. The .cif files could be found in the database of crystallography open database (COD) with the number of 2202025, 2202025, 2100454, respectively. The Reffs of Rh-CO, Rh-I, Rh-Rh were calculated with single scattering at 1.854 Å, 2.621 Å and 2.539 Å, respectively, according to the .cif files mentioned above. Rh-O-AC was set with Reff of 2.2 Å according to the first quick shell path based on DFT calculated models.

Density function theory (DFT) calculation

The activate carbon (AC) model was constructed with carbonyl group based on the molecule geometry of Graphene-like structure. The all-molecular structures were optimized by the density function theory (DFT) calculation using Vienna ab initio simulation package (VASP)^{41–44}. The Perdew-Burke-Ernzerhof (PBE) was used as the exchange correlation function⁴⁵. The cut off kinetic energy was set to 420 eV. Brillouin zone integration was approximated using the Monkhorst-Pack k-points method⁴⁶ and set as 1 × 1 × 1. The height of vacuum slab was selected with 12 Å to eliminate the size error. Geometries were optimized until the energy was converged to 1.0 × 10^{−4} eV/atom and the force was converged to 0.05 eV/Å. Here, it

is need to note that the transition states were optimized using the Dimer method. To understand and account for dispersion effect in the entire reaction process, the energy corrections of van der Waals (vdW) were calculated using the semiempirical approach proposed by Grimme⁴⁷ (DFT-D2 method) in conjunction with the PBE functional. All the stable molecule geometries and the transition state structures of Rh₁/AC complexes were checked by the frequency calculations without imaginary frequency and with one imaginary frequency, respectively. In this study, the unit of molecule bond length or distance between atoms is angstrom.

Catalyst evaluation

The methanol carbonylation activity test of Rh/AC, [Rh(CO)₂I₂]⁻ and Rh₁/AC were conducted in high-pressure zirconium reactor (25 ml). The specific reaction conditions were noted below in Table 1. The 1wt% Rh/AC, Rh₁/AC, Rh/SiO₂ and Rh/CMK-3 were also tested in a fixed-bed reactor. 0.3 g catalyst was placed in the center of the Hastelloy C-276 reactor. The upper and lower space was filled with quartz sand. Upstream from the reactor, the liquid was vaporized and mixed with CO/H₂ or CO/H₂/H₂S in a Hastalloy tube wrapped with heat tape maintained at 513 K. The tailed gas was chilled at 278 K to collect the liquid product. Incondensable gas was analyzed using on-line gas chromatography Agilent 7890B equipped with TCD (chromatographic column: Plot Q), and the collected liquid product was off-line analyzed by FID (chromatographic column: HP-FFAP). The space-time-yield (STY) was calculated based on the total moles of CH₃COOH and CH₃COOCH₃ divided by total moles of Rh per hour.

Declarations

Extended Data

Extended data for this paper at XXXX. The data that support the findings in this study are in the published article and/or its extended data files. The data sources are deposited on the generalist repository of figshare, and the accession code is xxxxxxxx. The whole datasets are available from the corresponding author on reasonable request as well.

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Table 1

Table 1. Effect of H₂S on the catalytic activity of Rh NPs (Rh/AC, Rh/CMK-3 and Rh/SiO₂) and mononuclear complexes ([Rh(CO)₂I₂][−], Rh₁/AC) catalysts.

Reaction	CH ₃ OH	+	CO	Catalyst
	Catalysts		Reactor	Conditions		mol _{acetyl} /[(mol _{Rh} • h)
Rh NPs	Rh/AC	^a Autoclave	Normal feed	163 [*]		
			S-feed	40 [*] ↓		
	Rh/AC	^b Fixed-bed	Normal feed	135 [*]		
			S-feed	110 [*] ↓		
	Rh/CMK-3	^b Fixed-bed	Normal feed	80 ^{**}		
			S-feed	0 ^{**} ↓		
Mononuclear complexes			Normal feed	100 ^{**}		
			S-feed	0 ^{**} ↓		
	[Rh(CO) ₂ I ₂] ⁻	^c Autoclave	Normal feed	2021		
			S-feed	2353↑		
	Rh ₁ /AC	^a Autoclave	Normal feed	2016		
			S-feed	2477↑		
	Rh ₁ /AC	^b Fixed-bed	Normal feed	3015 ^{**}		
			S-feed	3974↑ ^{**}		

Reaction conditions: S-feed: S content 1000 ppm H₂S, Rh content was 1.0 wt.% for Rh/AC, Rh/CMK-3 and Rh/SiO₂ and Rh₁/AC. ^a 0.2g Rh/AC and 0.1g Rh₁/AC; 3.0 MPa CO, CH₃OH (218.75 mmol), CH₃I (20.98 mmol) for Rh₁/AC and 3.73mmol for Rh/AC, ultra-pure water (277.8 mmol), 433 K, 20 min in a zirconium autoclave reactor. ^b 0.3g catalysts, 513 K, 1.7 MPa, CO/CH₃OH=1.0 (mole ratio), CO/H₂=10 (mole ratio), CH₃I/CH₃OH =1/24 (mass ratio) for Rh/AC, CH₃I/CH₃OH =3/7(mass ratio) for Rh/CMK-3, Rh/SiO₂ and Rh₁/AC in Hastelloy fixed-bed reactor. ^c 0.1g RhI₃, 3.0 MPa CO, CH₃OH (81.25 mmol), CH₃I (7.82 mmol), ultra-pure water (277.8 mmol), 433 K, 20 min in a zirconium autoclave reactor. The dispersive rate of Rh NP on Rh/AC was in proportion to the concentration of CH₃I and CO.* Initial data obtained after 2 h on stream in methanol carbonylation. ** Data obtained after 40 h on stream in methanol carbonylation.

Figures

Figure 1

Effect of H₂S on the structure of Rh₁/AC and Rh/CMK-3 catalysts for methanol carbonylation reaction. (a) HAADF-STEM image of spent Rh₁/AC in S-feed. (b) The in-situ Rh k-edge EXAFS fitting of 1h average data of Rh₁/AC catalyst in S-feed or normal feed. (c) The ex-situ Rh k-edge EXAFS fitting of spent Rh₁/AC catalyst in S-feed or normal feed. (d) HAADF-STEM image of spent Rh/CMK-3 in S-feed, (e) EDS line scanning result of single Rh NPs in the spent Rh/CMK-3 in normal feed, (f) EDS line scanning result of single Rh NPs in the spent Rh/CMK-3 in S-feed.

Figure 2

The in-situ FEL/TOF-MS of Rh_1/AC for methanol carbonylation in normal feed, S-feed and the comparative experiments. The in-situ free-electron laser time of flight mass spectrum (FEL/TOF MS) of methanol carbonylation on Rh_1/AC catalyst in (a) normal feed and (b) S-feed at 513 K, 0.1 bar, FEL 112 nm and 40 $\mu\text{J}/\text{cm}^2$, H₂S 10000 ppm. (c) The normalized signal intensity of m/z 34 (H₂S) and m/z 62 (CH₃SCH₃) as a function of temperature at the condition of (b). (d) The comparative FEL/TOF MS experiment on Rh_1/AC catalyst with CH₃OH and H₂S. (e) The comparative FEL/TOF MS experiment on Rh_1/AC catalyst with CH₃I and H₂S. (f) The comparative FEL/TOF MS experiment only with CH₃I and H₂S.

Figure 3

The DFT calculations about the effect of H₂S, CH₃SH, CH₃SCH₃ on the energy barrier of CH₃I oxidative addition on single-site Rh1/AC catalyst, and the energy evolution during the heterogeneous methanol carbonylation. Gray ball represents Rh atom; red ball represents O atom; purple ball represents I atom; yellow ball represents S atom; green ball represents C atom; pink ball represents H atom.

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