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Article

MIL-53 (Al) derived single-atom Rh catalyst for the selective hydrogenation of *m*-chloronitrobenzene into *m*-chloroaniline

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ABSTRACT

The catalytic hydrogenation of halonitroarenes to haloanilines is a green and sustainable process for the production of key nitrogen-containing intermediates in fine chemical industry. Chemoselective hydrogenation poses a significant challenge, which requires the rational design of the catalysts with proper hydrogenation ability for nitro group and simultaneously preventing dehalogenation of halogen group. Herein, a highly effective Rh@Al₂O₃@C single-atom catalyst (SAC) was developed for the hydrogenation of *m*-chloronitrobenzene (*m*-CNB) to *m*-chloroaniline (*m*-CAN), through an in-situ grafting of metal during the assembly of MIL-53 (Al), followed by confined pyrolysis. Extensive characterizations reveal an exquisite structure of the Rh@Al₂O₃@C, containing atomically dispersed Rh sites onto Al₂O₃ confined by the amorphous carbon. The five-coordinated aluminum (Al^V) species are essential for achieving the atomic dispersion of Rh atoms, providing the unsaturated coordinative sites for metal. Compared to the benchmark Rh/γ-Al₂O₃ and Rh/C nanocatalysts, the Rh@Al₂O₃@C SAC affords an excellent turnover frequency of 2317 mol_{*m*-CNB}·mol_{Rh}⁻¹·h⁻¹, the highest value to date in heterogeneous catalyst systems for the hydrogenation of *m*-CNB at 313 K and 20 bar H₂, together with a sustained selectivity to *m*-CAN (~98%) during five consecutive runs. The superior catalytic performance of the Rh@Al₂O₃@C is attributed to a proper modulation of electronic structure of hydrogenation metal by forming SAC, together with an enhanced accessibility of acid function sites.

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1. Introduction

Haloanilines are important and valuable intermediates for the manufacture of many pharmaceuticals, polymers, dyes, and agrochemicals [1–3]. Commercial production of haloanilines generally applies metallic iron to reduce the related nitroarenes in acidic media, which is costly and environmentally unfriendly [4]. Recently, catalytic hydrogenation of halonitroarenes with heterogeneous metal catalysts has emerged as an effective, green and sustainable process for the production of haloanilines [5–8]. Still, the difficulty in selectively reducing the nitro group arises from the presence of the other reducible halogen groups, which often results in a decrease in selectivity at high conversions of halonitroarenes [9]. Attempts with adding a second substance (*i.e.* amines, thiophene, etc.) as inhibitors or modifying agents to reaction medium, were made for suppressing the side reactions, however, it brings new issues related to isolation and purification of the final products, resulting in such approach economically less viable [10–12]. Therefore, the rational design of heterogeneous catalysts for the selective hydrogenation of halonitroarenes into haloanilines, is still highly desirable but challenging.

Intensive research efforts have been devoted to the development of efficient heterogeneous catalysts [13–17]. Notably, Xiao et al. [18] successfully prepared a Pd@Beta via the fixation of Pd nanoparticles inside Beta zeolite crystals, which achieved a high selectivity of *m*-bromoaniline (>99%) by controlling the steric adsorption of nitro groups on Pd nanoparticles, for the chemoselective hydrogenation of the *m*-bromonitrobenzene at 383 K and 10 bar H₂. Cárdenas-Lizana and coworkers [19] reported a highly effective bimetallic Pd-Au/Al₂O₃ catalyst (>99% selectivity to *p*-chloroaniline) for the selective hydrogenation of *p*-chloronitrobenzene at 393 K and 10 bar H₂, by alloying Au with Pd to modulate the hydrogenation activity of metal sites. Recently, single-atom catalysts (SACs) approaches, owing to the increased uniformity and well-defined active sites, have emerged as a promising class of catalyst materials for the selective hydrogenation of halonitroarenes to haloanilines [20–23]. For example, a Pt/FeO_x SAC afforded a 97.4% selectivity to *o*-chloroaniline under mild conditions (*T* = 313 K, *P*_{H₂} = 3 bar) [24]. Another Pt/CeO₂ SAC could sustain 99.5% selectivity to *p*-chloroaniline at 313 K and 10 bar H₂ [25]. The great potential of SACs for such selective hydrogenation to haloaniline is possibly due to the nature of their positively charged chemical state, enabling a proper modulation of the hydrogenation ability to fulfill the optimization of the catalytic properties [20,26,27].

In this contribution, we have prepared a highly efficient Rh@Al₂O₃@C SAC, via an in-situ synthesis approach during the assembly of MIL-53 (Al), followed by confined pyrolysis. Combined characterizations of aberration corrected high angle annular dark field mode of scanning transmission electron microscopy (AC-HAADF-STEM) and infrared spectroscopy using CO as the probe molecule (IR-CO) reveal an exquisite structure of the Rh@Al₂O₃@C, containing atomically dispersed Rh sites

onto Al₂O₃ confined by the amorphous carbon. The presence of five-coordinated aluminum (Al^V) species, is demonstrated to be essential for achieving atomically dispersion of Rh sites in the Rh@Al₂O₃@C through ²⁷Al magic angle spinning nuclear magnetic resonance (²⁷Al MAS NMR) and DFT calculation. The obtained Rh@Al₂O₃@C SAC has been tested and compared with the benchmark Rh/C and Rh/γ-Al₂O₃ nanocatalysts for the hydrogenation of *m*-chloronitrobenzene (*m*-CNB) into *m*-chloroaniline (*m*-CAN). The Rh@Al₂O₃@C SAC affords an excellent activity (TOF = 2317 mol_{*m*-CNB}·mol_{Rh}⁻¹·h⁻¹) and a sustained *m*-CAN selectivity (~98% in five consecutive runs). Further characterization studies reveal that the superior catalytic performance of the SAC is attributed to a proper modulation of the electronic structure of hydrogenation metal, together with an enhanced accessibility of acid function sites. This work provides not only an effective strategy for the preparation of SACs via utilizing the metal-organic framework as scaffold, but also shows a prominent example on tuning the electronic structure of hydrogenation metal by forming SAC for an enhanced chemoselectivity in catalysis.

2. Experimental

2.1. Synthesis of materials

In a typical procedure, Al(NO₃)₃·9H₂O (5.2 g, 13.9 mmol, Tianjin Damao Chemical Reagent Factory, 99%), terephthalic acid (H₂BDC, 1.152 g, 6.9 mmol, J&K, 99%) and RhCl₃·3H₂O (8 mg, 0.03 mmol, Tianjin Sailboat Chemical Reagent Technology Co., Ltd., 99%) were dissolved in H₂O (20 mL) under ultrasonication for 0.5 h. The mixture was then added into a 50 mL Teflon-lined stainless steel autoclave, heated to 493 K and kept for 72 h. A white powder of Rh@MIL-53 (Al) was collected by filtration, washed three times with H₂O and ethanol, and dried at 333 K overnight. The dried Rh@MIL-53 (Al) was first calcined at 873 K for 5 h with a heating rate of 5 K·min⁻¹ in an Ar flow of 30 mL·min⁻¹ and then reduced at 573 K for 3 h with a heating rate of 2 K·min⁻¹ in a 10 vol% H₂/Ar flow of 30 mL·min⁻¹. After being cooled to room temperature, a black powder was obtained and denoted as Rh@Al₂O₃@C material. The content of carbon in the Rh@Al₂O₃@C is determined to be 36.5 wt% On the basis of thermogravimetric (TG) analysis results (Fig. S1, see electronic supporting information, the same below). The Rh loading in the Rh@Al₂O₃@C was 0.1 wt%, as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The Rh/γ-Al₂O₃ catalyst was prepared via a wet impregnation method. γ-Al₂O₃ (1 g, 9.8 mmol, Aladdin, 99.99%), RhCl₃·3H₂O (1 mg, 3.8 × 10⁻³ mmol, Tianjin Sailboat Chemical Reagent Technology Co., Ltd., 99%) and H₂O (2.130 mL) was first mixed at room temperature. After ultrasonication for 30 min, the slurry was stirred vigorously at room temperature for 12 h, and then dried at 333 K overnight. The Rh loading in Rh/γ-Al₂O₃ was 0.1 wt%, as detected by ICP-OES.

The Rh/C catalyst was prepared via a wet impregnation

method. Activated charcoal (1 g, 83.3 mmol, Aladdin, AR), $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (1 mg, 3.8×10^{-3} mmol, Tianjin Sailboat Chemical Reagent Technology Co., Ltd., 99%) and H_2O (2.175 mL) was first mixed at room temperature. After ultrasonication for 30 min, the slurry was stirred vigorously at room temperature for 12 h, and then dried at 333 K overnight. The Rh loading in Rh/C was 0.1 wt%, as detected by ICP-OES.

2.2. Catalyst characterizations

Powder X-ray diffraction (PXRD) was carried out using the PW3040/60 X'Pert Pro powder X-ray diffractometer from PANAnalytical, the Netherlands. The diffraction source was Cu $K\alpha$ ray ($\lambda = 1.5432 \text{ \AA}$), Ni filtered, LynxExe array detector, tube voltage and tube current were 40 kV, 40 mA, respectively. The scanning step is 0.02° . The crystalline phase was identified with reference to the ICDD PDF-2 database.

TG was studied on SETSYS 16/18 DSC 114 (SETARAM), and the heating rate is $10 \text{ K} \cdot \text{min}^{-1}$ under 10 bar Air atmosphere.

The actual Rh loading of the rhodium catalyst was determined by ICP-OES on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation) with a sensitivity line of 349.8 nm and a detection range of 1–10 ppm.

N_2 physisorption isotherms were obtained at 77 K using a Micromeritics ASAP 2460 instrument, all samples were outgassed for 12 h at 473 K in a nitrogen flow prior to the physisorption measurements.

Samples for transmission electron microscopy (TEM) inspection were prepared by dispersing the catalyst powder on a porous carbon film supported by a 200 mesh copper TEM grid by ultrasonic dispersion in ethanol. Scanning transmission electron microscopy (STEM) images were obtained with a JEOL JEM-2100F microscope operated at 200 kV. For atomic resolution images, AC-HAADF-STEM images were obtained using JEM ARM-200F STEM operating at 200 kV.

Infrared spectroscopy using CO as the probe molecule (CO-IR) was recorded on a BRUKER Equinox 55 spectrometer equipped with an MCT detector, and each spectrum is consist of 32 scans and recorded at a resolution of 4 cm^{-1} . Self-supported catalyst wafers were pressed at 3 kbar pressure for 10 s. The wafer was placed inside a self-designed cell with a CaF_2 window. The cell was evacuated and the sample was subsequently reduced at 523 K ($5 \text{ K} \cdot \text{min}^{-1}$) for 1 h under 10 vol% H_2/He flow. The cell was cooled down to 303 K, evacuated again and connected to a gas chamber that permits adjustment of the pressure of CO injected into the cell. CO adsorption was studied at 303 K at stepwise increasing exposure time of CO with the $\text{Rh@Al}_2\text{O}_3$, derived from burning off the carbon species of the $\text{Rh@Al}_2\text{O}_3/\text{C}$ in the air at 873 K for 5 h.

^{27}Al MAS NMR measurements were performed on a Bruker Advance III 400WB spectrometer using a 4 mm probe head. The probe was tuned to 104.3 MHz for ^{27}Al . Magic angle spinning at 10 kHz was employed. A single-pulse spectrum was obtained at 9.4 T with a radio frequency of 62.5 kHz. The corresponding relaxation delay and pulse length were 0.1 s and 1 μs , respectively.

X-ray photoelectron spectroscopy (XPS) characterization

was performed on a Thermo fisher ESCALAB 250Xi equipped with an Al $K\alpha$ anode ($h\nu = 1486.6 \text{ eV}$). The energy shift due to electrostatic charging was subtracted using the graphitic carbon C 1s band at 284.6 eV.

Temperature-programmed desorption of NH_3 (NH_3 -TPD) was carried out on a Micromeritics AutoChem 2920 II instrument. Before measurement, 50 mg of sample loaded in a U-shaped quartz reactor was treated at 473 K under He gas flow for 2 h to remove adsorbed species. After cooling down to 300 K, the flowing gas was switched to a 10 vol% NH_3/He flow and kept at 493 K for 1 h for adsorption. The extra NH_3 in gas phase was removed by purge with He and then NH_3 -TPD was performed in a He flow by heating the sample up to 973 K at a rate of $10 \text{ K} \cdot \text{min}^{-1}$.

All Spin-polarized periodic density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP 5.4.4) with a generalized gradient-approximated (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [28,29]. The electron-ion interactions were described with the projected augmented waves (PAW) method and the energy cutoff was set to 400 eV [30]. For structural optimizations, calculations were finished until the total energy was converged to 10^{-5} eV and the convergence criterion of force was less than $0.05 \text{ eV/\AA}$. The van der Waals (vdW) interactions were included by using Grimme's DFT-D3 (BJ) method [31]. The transition states were searched using the climbing-image nudged elastic band (CI-NEB) method [32], four to eight NEB images generated by the image-dependent pair potentials (IDPP) method [33], and each transition state was re-confirmed with only one imaginary frequency. In all calculations, two layers in the bottom of models were fixed and the rest atoms were allowed to fully relax, and a $15 \text{ \AA}$ vacuum layer was used along the c direction to avoid periodic interactions. A $2 \times 2 \times 1$ Monkhorst-Pack k -points were used to sample the Brillouin zone. The adsorption energies of Rh_n ($n = 1-4$) clusters on the $\gamma\text{-Al}_2\text{O}_3(100)$ were calculated according to the equation $E_{\text{ads}} = E_{(\text{surface} + \text{adsorbate})} - E_{(\text{surface})} - E_{(\text{adsorbate})}$, where $E_{(\text{surface} + \text{adsorbate})}$ represents the total energy of the $\gamma\text{-Al}_2\text{O}_3(100)$ surface slab and the adsorbed Rh_n cluster, $E_{(\text{surface})}$ is the energy of the pure $\gamma\text{-Al}_2\text{O}_3(100)$ surface, and $E_{(\text{adsorbate})}$ is the energy of the optimized Rh_n cluster in the gas phase.

2.3. Catalytic tests and product analysis

The selective hydrogenation of m -chloronitrobenzene ($m\text{-CNB}$) was carried out in a 10 mL Teflon-lined autoclave reactor. For a typical reaction, $m\text{-CNB}$ (78.8 mg, 0.5 mmol), toluene (2 mL), different catalyst samples (30 mg) was mixed in the autoclave reactor. Tetradecane (Aladdin, 99.5%) was also added as an internal standard. The reactor was then sealed, purged three times with N_2 and charged with 20 bar of H_2 . Then the reactor was heated to 313 K in a water bath and kept at this temperature for 0.5–12 h under vigorous stirring. After reaction, the autoclave was cooled to room temperature, H_2 was released. The catalyst was collected by filtration, washed with toluene and dried overnight at 333 K. For the recycling experiment, the dried catalyst was transferred back to

Scheme 1. Schematic illustration for the synthesis of the Rh@Al₂O₃@C.

the reactor and a new batch of substrate was added under standard reaction conditions for a new catalytic run. The reaction products were analyzed using an Agilent GC (7890B) gas chromatograph and identified with an Agilent GC-MS (7890B-5977A MSD), both equipped with an Agilent HP-5 (30 m × 0.32 mm × 0.25 μm) column and a flame ionization detector (FID).

3. Results and discussion

3.1. Synthesis and characterizations of catalysts

The Rh@Al₂O₃@C is fabricated via a two-step process utilizing MIL-53 (Al) as a scaffold, as illustrated in Scheme 1. First, a solution of RhCl₃ is introduced during the assembly process of MIL-53 (Al), to graft Rh atoms into MIL-53 (Al) and form Rh@MIL-53 (Al). Atomic distribution of Rh species is thus achieved by dispersing mononuclear Rh precursors into the MIL-53 (Al). The obtained Rh@MIL-53 (Al) is followed by pyrolysis at 873 K under Ar atmosphere and subsequently reduced in diluted H₂, to form the Rh@Al₂O₃@C. Compared to the MOF-based materials, the obtained material after pyrolysis shows an improved stability under hydrothermal conditions, thus more suitable as catalyst.

The XRD patterns of the MIL-53 (Al), Rh@MIL-53 (Al), Al₂O₃@C and Rh@Al₂O₃@C materials are shown in Fig. 1. The XRD pattern of Rh@MIL-53 (Al) shows similar diffraction reflection positions as that of MIL-53 (Al) [34], indicating that the addition of RhCl₃ has limited impact on the assembly of MIL-53 (Al) framework. After the thermal pyrolysis process, the Rh@Al₂O₃@C shows new diffraction peaks at 2θ = 37.6°, 45.8°, 60.9° and 67.0°, corresponding to the (311), (400), (511) and (440) lattice planes of γ-Al₂O₃ (JCPDS Card 10-425). Meanwhile, the Al₂O₃@C obtained after pyrolysis of MIL-53 (Al) shows no crystallized phase in the XRD patterns, pointing to the amorphous phase of Al₂O₃ and carbon. Compared to the Al₂O₃@C, the Rh@Al₂O₃@C shows a crystallized phase of γ-Al₂O₃, indicating that the addition of Rh possibly benefits the crystallization of Al₂O₃. Additionally, no apparent Rh-phase reflections are observed for the Rh/γ-Al₂O₃, Rh/C and Rh@Al₂O₃@C at this low metal loading of 0.1 wt% in the XRD patterns (Fig. 1 and Fig. S2), indicating a good dispersion of Rh on the support.

Fig. 1. XRD patterns of the MIL-53 (Al), the Rh@MIL-53 (Al), the Al₂O₃@C and the Rh@Al₂O₃@C.

Surface areas and pore size distributions for different materials were determined by N₂ physisorption (Fig. 2 and Table 1). Prior to testing, the MIL-53 (Al) and Rh@MIL-53 (Al) samples were pretreated at 573 K for 72 h to remove terephthalic acid remaining in the pores. Both of them show typical type-I isotherms with microporous structure (Fig. 2(a)). Compared to MIL-53 (Al) material, the Rh@MIL-53 (Al) shows a slight decrease in the BET surface area from 1451 to 1109 m²·g⁻¹ (Table 1). Besides, the diameter of pore size also decreased from 0.72 to 0.62 nm (Fig. 2(b)), referring to the successful encapsulation of Rh species into the micropores of MIL-53 (Al). After thermal pyrolysis, the obtained Rh@Al₂O₃@C shows a significant drop

Fig. 2. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of the MIL-53 (Al), the Rh@MIL-53 (Al) and the Rh@Al₂O₃@C.

Table 1

Physicochemical properties of different samples under study.

Catalysts	BET surface area (m ² ·g ⁻¹)	Micropore surface area ^a (m ² ·g ⁻¹)	External surface area ^a (m ² ·g ⁻¹)	Micropore volume ^a (cm ³ ·g ⁻¹)	Rh loading (wt%)
MIL-53 (Al)	1451	1001	450	0.498	—
Rh@MIL-53 (Al)	1109	770	338	0.402	—
Rh@Al ₂ O ₃ @C	219	78	141	0.040	0.1 ^d
Rh@Al ₂ O ₃ @C (spent) ^b	180	58	122	0.031	0.1 ^d
Rh/γ-Al ₂ O ₃	174	— ^c	178	— ^c	0.1 ^d
Rh/C	1472	598	875	0.309	0.1 ^d

^a Obtained by the t-plot method.^b After one catalytic run.^c Below the detection limit of N₂ physisorption isotherms.^d Determined by ICP-OES analysis.

in porosity (BET surface area from 1109 to 219 m²·g⁻¹, Table 1), pointing to the decomposition of the linkers of MIL-53 (Al). Meanwhile, The BET surface area of the benchmark catalysts is 174 m²·g⁻¹ for Rh/γ-Al₂O₃, and 1472 m²·g⁻¹ for Rh/C respectively (Table 1).

The STEM images of the Rh@MIL-53 (Al) and the Rh@Al₂O₃@C are shown in Fig. 3. Clearly, the Rh@MIL-53 (Al) presents smooth-surfaced diamond-shaped particles with a diameter of about 1 μm (Fig. 3(a) and 3(b)), in line with the reported structure of the MIL-53 (Al) [34]. After pyrolysis, the obtained Rh@Al₂O₃@C transfers to a spindle-shaped morphology with a rough surface (Fig. 3(c) and 3(d)), owing to the de-

Fig. 3. STEM images of the Rh@MIL-53 (Al) (a,b) and the Rh@Al₂O₃@C (c-f).

construction of MIL-53 (Al) structure during pyrolysis, consistent with previous reports [35,36]. Notably, at the higher magnification, an aligned fibrous structure is visualized for the Rh@Al₂O₃@C (Fig. 3(e) and 3(f)). No appreciable Rh nanoparticles were detected for the Rh@Al₂O₃@C in STEM, indicating a highly dispersed Rh species in the Rh@Al₂O₃@C. In contrast, the average Rh particle size is visualized to be ~1.0 nm for the Rh/γ-Al₂O₃ and ~2.1 nm for the Rh/C respectively (Fig. S3).

To obtain insights into the structural information of the Rh species in the Rh@Al₂O₃@C, AC-STEM was conducted in the HAADF. Clearly, well-dispersed isolated Rh atoms as bright dots (circled by white rounds) are readily visualized in different regions of the Rh@Al₂O₃@C (Fig. 4). Combining with no detected Rh clusters or nanoparticles in STEM, the domain presence of single-atom Rh sites in the Rh@Al₂O₃@C is thus confirmed. In addition, an interplanar spacing of 0.2 nm is also observed from AC-HAADF-STEM images, associated with the (400) lattice plane of γ-Al₂O₃ [37]. To confirm the validity of the single-atom feature of Rh sites, FT-IR spectra of CO adsorption were measured for the Rh@Al₂O₃ (Fig. 5(a)), obtained by removing the amorphous carbon species of the Rh@Al₂O₃@C by thermal pyrolysis at 873 K for 5 h in the air flow. Spectra with good quality are thus obtained without the interference of carbon materials at a temperature of 303 K. The spectra show no development of features of bridged-CO species on Rh (around 1860 cm⁻¹) over time, indicating the absence of Rh clusters or particles [38], in line with AC-HAADF-STEM results that Rh species are present as isolated sites on the Rh@Al₂O₃@C. Two primary features at 2016 and 2087 cm⁻¹ appear with the increase of CO exposing time, corresponding to the symmetric and asymmetric stretching of *gem*-dicarbonyl species on positively charged Rh atoms respectively [39,40]. Notably, the location of features remains unchanged as the increase of CO exposing time, again pointing to the single-atom feature of Rh species [41]. A feature at 2060 cm⁻¹ develops after a CO exposing time of 2 min, associated with the linear-CO species on Rh^{δ+} sites [42,43]. The two broad features at around 2120 and 2170 cm⁻¹ are assigned to the gaseous CO [44]. The CO-IR data reveals the atomic dispersion of Rh^{δ+} on the Al₂O₃ even after burning-off the carbon species, indicating a strong interaction between Rh^{δ+} and Al₂O₃.

It has been reported that the unsaturated five-coordinated aluminum species (Al^V), providing anchor sites for metal atoms, plays a pivotal role in the formation of single-atom metal sites on alumina supports [45,46]. Solid-state ²⁷Al MAS NMR measurements were therefore performed for inspecting the presence of such species in the Rh@Al₂O₃@C SAC. The Rh/γ-Al₂O₃

Fig. 4. AC-HAADF-STEM images of the Rh@Al₂O₃@C in grey (a,b) and in color (c,d).

Fig. 5. (a) FT-IR spectra of CO adsorption over the Rh@Al₂O₃/C; (b) ²⁷Al MAS NMR spectra of the Rh@Al₂O₃/C.

nanocatalyst and Al₂O₃/C support, prepared by pyrolysis of MIL-53 (Al) under the same condition of Rh@Al₂O₃/C were also employed as contrast catalysts. As shown in Fig. 5(b) and Fig. S4, three resonances, with an isotropic shift of around 5, 35, and 67 ppm, are visualized for both of the Rh@Al₂O₃/C and the Al₂O₃/C, representing four-coordinated (Al^{IV}), five-coordinated (Al^V) and six-coordinated (Al^{VI}) aluminum species respectively [45]. The Al^V sites are probably derived from thermal pyrolysis of MIL-53 (Al) at elevated temperatures, serving as the anchoring sites for isolated Rh atoms via a strong interaction. Notably, a significant amount of Al^V (23%) is indeed present in the Al₂O₃/C, which is much higher than that in the Rh@Al₂O₃/C (9%). This is also in line with the XRD results of the lower crystallinity of Al₂O₃/C compared to Rh@Al₂O₃/C (Fig. 1). Instead, no Al^V species is observed for the Rh/γ-Al₂O₃ (Fig. S5). Combining with the observed Rh nanoparticles of about 1.0 nm in the Rh/γ-Al₂O₃ by STEM and previous reports of the significant contribution of Al^V species for the preparation of single-atom catalysts (SAC) [47], it is highly rational to ascribe the successful preparation of SAC to the presence of the Al^V species in the Rh@Al₂O₃/C, providing unsaturated anchoring sites for metal atoms.

DFT calculations were conducted to further validate the critical role of the Al^V species for anchoring Rh single atoms. The employed surface model of γ-Al₂O₃(100), which is the only

facet exposing Al^V species, was based on previously established models [48,49] (Fig. S6). The stability of Rh atoms is mainly related to the structural evolution including adsorption, migration, and aggregation of Rh_n clusters on the support. As shown in Table S1 and Fig. S7, the Rh single atoms and clusters adsorb strongly on the γ-Al₂O₃ surface with adsorption energies in the range from -3.86 to -2.79 eV, indicating the strong bond in Rh-Al^V pairs [50]. High migration energy barriers (Fig. 6(a)) indicate that it is very thermodynamically and kinetically unfavorable for the migration of isolated Rh atoms from the most stable adsorption sites. Furthermore, the first step of the nucleation from single Rh atoms needs the formation of Rh dimers (Fig. 6(b)) [51], which is endothermic by 0.35 eV, indicating the unfavorableness of the nucleation of the isolated Rh atoms on the Al^V sites. Indeed, DFT calculations confirm a stable and strong interaction between Rh single atoms and Al^V sites, which is unfavorable for structural migration and aggregation on the γ-Al₂O₃ support.

3.2. Selective hydrogenation of *m*-chloronitrobenzene into *m*-chloroaniline

The catalytic performance of the Rh@Al₂O₃/C SAC was evaluated in selective hydrogenation of *m*-chloronitrobenzene (*m*-CNB) into *m*-chloroaniline (*m*-CAN) under batch conditions

Fig. 6. (a) The migration energetic diagram of single Rh atoms on the γ-Al₂O₃(100) surface; (b) nucleation energies *E*_{nuc} of the aggregation from Rh₁ to Rh₄ on the γ-Al₂O₃(100) surface. Red, pink and dark cyan balls represent O, Al, and Rh atoms, respectively.

at 313 K and 20 bar P_{H_2} . The contrast experiments were also performed with the Rh/ γ - Al_2O_3 and Rh/C nanocatalysts as benchmark catalysts. The time-on-line concentration profiles of substrates and products under different catalysts and reaction scheme are depicted in Fig. 7. The Rh@ Al_2O_3 @C SAC achieved a quantitative conversion of *m*-CNB and a *m*-CAN yield of 99% within 2.5 h, indicating an excellent performance in both activity and selectivity (Fig. 7(a)). Furthermore, the yield of *m*-CAN could retain at 99% even with an extended reaction time of 12 h. Additionally, this SAC can afford a significant *m*-CNB turnover frequency (TOF) of $2317 \text{ mol}_{m\text{-CNB}} \cdot \text{mol}_{Rh}^{-1} \cdot h^{-1}$, which is the highest value to date, in heterogeneous catalyst systems at such a mild temperature of 313 K [22,24,52–60]. At the early stage of *m*-CNB (1) hydrogenation, *m*-chlorophenylhydroxylamine (3) and 3, 3'-dichloroazoxybenzene (4), formed by coupling of *m*-nitrosochlorobenzene (2) and (3), were observed as the primary intermediates for the Rh@ Al_2O_3 @C (Fig. 7(d)). For the Rh/ γ - Al_2O_3 nanocatalyst, an inferior activity is observed with a TOF of $661 \text{ mol}_{m\text{-CNB}} \cdot \text{mol}_{Rh}^{-1} \cdot h^{-1}$, with a *m*-CNB conversion of 99% and a *m*-CAN yield of 91% at a reaction time of 4 h (Fig. 7(b)). A significant amount of cyclohexylamine (7) (30%) via an intermediate of aniline (6) was formed as a by-product, at the expense of *m*-CAN (5), by consecutive hydrogenation reactions (Fig. 7(d)). Similar observation of over-hydrogenation has also been demonstrated with other nanocatalysts for the selective hydrogenation of *m*-CNB to *m*-CAN [25,53]. Comparatively, the Rh/C nanocatalyst shows a low activity, with an *m*-CNB conversion of 61% and an *m*-CAN yield of 59% in 12 h (Fig. 7(c)). This corresponds to a TOF of $122 \text{ mol}_{m\text{-CNB}} \cdot \text{mol}_{Rh}^{-1} \cdot h^{-1}$, comparable with the values of reported Pd/C and Pt/C nano-

catalysts [61,62].

As shown in Fig. 7(d), two different routes from *m*-CNB to *m*-CAN are depicted, involving sequential hydrogenation, hydrogenolysis, dehydration and dechlorination reactions, which require a good combination of different function sites (metal and acid sites). Therefore, the chemical state of metal and the acid amount of the catalyst materials are essential for the catalytic performance. To explore insight into the enhanced performance of the Rh@ Al_2O_3 @C, XPS (Fig. 8) and NH_3 -TPD (Fig. S8) measurements were performed for the Rh@ Al_2O_3 @C SAC and two contrast nanocatalysts (Rh/ γ - Al_2O_3 and Rh/C). In the Rh 3d signal, a feature at a binding energy of 308.5 eV, assigned to the positively charged $Rh^{\delta+}$ species, is mainly present in the Rh@ Al_2O_3 @C [63], in line with the CO-IR results. Notably, the NH_3 -TPD results show a largest amount of total acidity for the Rh@ Al_2O_3 @C ($0.054 \text{ mmol} \cdot g^{-1}$) among the three catalysts. Compared to the Rh/ γ - Al_2O_3 , the increased acid amount of the Rh@ Al_2O_3 @C, is associated with the aligned fibrous shape of γ - Al_2O_3 in the well-defined structure, which can significantly enhance the acid accessibility of the material. Based on the time-on-line profiles and reaction mechanism (Fig. 7(a) and 7(d)), the excellent activity and selectivity of the Rh@ Al_2O_3 @C originate from the combination of modulated hydrogenation sites ($Rh^{\delta+}$) and the good accessibility of the acid sites. The single-atom sites are normally with positively charged chemical state, showing weakened hydrogenation ability compared to their nanoscale counterparts. Such modulation of hydrogenation ability has shown to be an advantage in efficiently avoiding over-hydrogenation [20,21]. Additionally, the reaction intermediates of *m*-chlorophenylhydroxylamine (3) and 3,

Fig. 7. Time profiles of selective hydrogenation of *m*-chloronitrobenzene using the Rh@ Al_2O_3 @C (a), the Rh/ γ - Al_2O_3 (b) and the Rh/C (c) as the catalysts; (d) catalytic routes of selective hydrogenation of *m*-chloronitrobenzene to *m*-chloroaniline. Reaction conditions: $T = 313 \text{ K}$, $P_{H_2} = 20 \text{ bar}$, 30 mg catalyst, 0.5 mmol *m*-chloronitrobenzene, 2 mL toluene.

Fig. 8. Rh 3d XPS spectra of the Rh/C, the Rh/ γ -Al $_2$ O $_3$ and the Rh@Al $_2$ O $_3$ @C.

3'-dichloroazoxybenzene (**4**) are often observed when the metal sites are with decreased hydrogenation ability [64]. The acid sites can facilitate the dehydration reactions involved in the reaction scheme, especially at this relatively low temperature of 313 K. For the Rh@Al $_2$ O $_3$ @C SAC, the over-hydrogenation is efficiently avoided owing to the proper modulation of hydrogenation metal by forming SAC, and the presence of a significant amount of acid sites enhances the formation of the target *m*-CAN. Instead, the Rh/ γ -Al $_2$ O $_3$ shows a combination of active nanoparticles (~ 1 nm) and a medium amount of acid sites (0.036 mmol·g $^{-1}$), and the main issue of this nanocatalyst is the lack of control on consecutive hydrogenation reactions, resulting in a significant decrease in selectivity at the extended reaction time. Comparatively, the formation of a large nanoparticles (~ 2.1 nm) is observed for the Rh/C at this relatively low Rh loading of 0.1 wt%, together with a small amount of acid site (0.006 mmol·g $^{-1}$). Owing to the significant decrease in active sites, the Rh/C displays a much lower activity, with reactions staying primarily in the early stage. Therefore, a proper modulation of electronic structure of hydrogenation metal by forming SAC, together with an enhanced accessibility of acid sites, has been achieved for the Rh@Al $_2$ O $_3$ @C via an in-situ synthesis approach, providing an enhanced chemoselectivity for the selective hydrogenation of *m*-CNB to *m*-CAN.

The stability of the Rh@Al $_2$ O $_3$ @C SAC was further examined by performing multiple recycling tests under the applied conditions. Catalytic activity and selectivity were compared at different *m*-CNB conversion levels. As shown in Fig. S9, the activity and *m*-CAN selectivity are sustained over this SAC at a *m*-CNB conversion of 65% upon three multiple reuse. Additionally, even at a prolonged reaction time of 12 h, this SAC could be reused for at least five consecutive runs without an apparent drop in activity and *m*-CAN selectivity ($\sim 98\%$, without the occurrence of over-hydrogenation), indicating no occurrence of deactivation for the catalyst during the reuse runs (Fig. 9(a)). According to the ICP-OES results in Table 1, no appreciable Rh leaching is detected. While the BET surface area of Rh@Al $_2$ O $_3$ @C SAC slightly decreases from 219 to 180 m 2 ·g $^{-1}$ (Table 1), possibly because of the deposition of carbonaceous

Fig. 9. (a) The recycling experiments of the Rh@Al $_2$ O $_3$ @C; (b–d) STEM images of the spent Rh@Al $_2$ O $_3$ @C after five consecutive runs. Reaction conditions: $T = 313$ K, $P_{H_2} = 20$ bar, $t = 12$ h, 30 mg catalyst, 0.5 mmol *m*-chloronitrobenzene, 2 mL toluene.

species derived from reactants or products. XRD pattern (Fig. S10) and STEM images (Fig. 9(b) and (c)) of the spent catalyst after five consecutive runs show negligible change of the Rh@Al $_2$ O $_3$ @C SAC in crystal phase and morphology. Again, no nanoparticles or nanoclusters observed in the high-resolution STEM images (Fig. 9(d)) corroborates the maintenance of Rh single-atom feature in Rh@Al $_2$ O $_3$ @C, indicating no occurrence of metal sintering for the SAC during catalysis. Therefore, an excellent stability is demonstrated for the Rh@Al $_2$ O $_3$ @C SAC, consistent with the good stability of reported SACs for hydrogenation reactions in liquid phase and even under harsh conditions [35,36].

4. Conclusions

In summary, we have shown an in-situ synthesis approach for the successful preparation of the Rh@Al $_2$ O $_3$ @C SAC material, via utilizing MIL-53 (Al) as scaffold. AC-HAADF-STEM and CO-IR reveal an exquisite structure of the Rh@Al $_2$ O $_3$ @C, containing atomically dispersed Rh sites onto Al $_2$ O $_3$ confined by the amorphous carbon. A combined study of 27 Al MAS NMR and DFT calculation indicates the presence of the unsaturated Al IV species in the Rh@Al $_2$ O $_3$ @C, serving as the anchoring sites for metal and essential for achieving the atomic dispersion of Rh atoms. This Rh@Al $_2$ O $_3$ @C SAC has been evaluated and compared to the benchmark Rh/ γ -Al $_2$ O $_3$ and Rh/C nanocatalysts, for the selective hydrogenation of *m*-CNB to *m*-CAN at 313 K and 20 bar H $_2$. The SAC affords an excellent turnover frequency of 2317 mol $_{m\text{-CNB}}$ ·mol $_{Rh}^{-1}$ ·h $^{-1}$, the highest value to date in heterogeneous catalyst systems for the hydrogenation of *m*-CNB under such mild conditions, together with a sustained selectivity to *m*-CAN ($\sim 98\%$) during five consecutive runs. The advanced catalytic performance of the Rh@Al $_2$ O $_3$ @C is attributed to a proper modulation of electronic structure of hydrogenation metal by forming SAC, together with an enhanced accessibility of acid function sites. This work offers not only an efficient strategy for the fabrication of highly selective SAC via utilizing a metal-organic framework of MOF,

but also presents a good example of proper modulation of different function sites, for achieving an enhanced and sustained chemoselectivity in catalysis.

References

- [1] Peter F. Vogt and John J. Gerulis, Amines, Aromatic in Ullmann's Encyclopedia of Industrial Chemistry, Wiley, New Jersey, **2000**.
- [2] A. M. Alexander, J. S. J. Hargreaves, *Chem. Soc. Rev.*, **2010**, 39, 4388–4401.
- [3] N. Ono, The nitro group in organic synthesis, Wiley, New Jersey, **2003**.
- [4] P. Lara, K. Philippot, *Catal. Sci. Technol.*, **2014**, 4, 2445–2465.
- [5] D. Formenti, F. Ferretti, F. K. Scharnagl, M. Beller, *Chem. Rev.*, **2019**, 119, 2611–2680.
- [6] J. Song, Z. F. Huang, L. Pan, K. Li, X. Zhang, L. Wang, J. J. Zou, *Appl. Catal. B*, **2018**, 227, 386–408.
- [7] Z. Wei, F. Shao, J. Wang, *Chin. J. Catal.*, **2019**, 40, 980–1002.
- [8] R. A. Sheldon and H. van Bekkum, Fine Chemicals through Heterogeneous Catalysis, Wiley, New Jersey, **2008**.
- [9] G. Vilé, D. Albani, N. Almora-Barrios, N. López, J. Pérez-Ramírez, *ChemCatChem*, **2016**, 8, 21–33.
- [10] M. Pietrowski, *Curr. Org. Synth.*, **2012**, 9, 470–487.
- [11] W. Shi, B. Zhang, Y. Lin, Q. Wang, Q. Zhang, D. S. Su, *ACS Catal.*, **2016**, 6, 7844–7854.
- [12] M. Orlandi, D. Brenna, R. Harms, S. Jost, M. Benaglia, *Org. Process Res. Dev.*, **2018**, 22, 430–445.
- [13] A. Corma, P. Serna, *Science*, **2006**, 313, 332–334.
- [14] J. Wu, L. Qi, H. You, A. Gross, J. Li, H. Yang, *J. Am. Chem. Soc.*, **2012**, 134, 11880–11883.
- [15] L. Bu, N. Zhang, S. Guo, X. Zhang, J. Li, J. Yao, T. Wu, G. Lu, J. Y. Ma, D. Su, X. Huang, *Science*, **2016**, 354, 1410–1414.
- [16] C. Zhang, X. Wang, M. Li, Z. Zhang, Y. Wang, R. Si, F. Wang, *Chin. J. Catal.*, **2016**, 37, 1569–1577.
- [17] H. Wei, X. Wei, X. Yang, G. Yin, A. Wang, X. Liu, Y. Huang, T. Zhang, *Chin. J. Catal.*, **2015**, 36, 160–167.
- [18] J. Zhang, L. Wang, Y. Shao, Y. Wang, B. C. Gates, F. S. Xiao, *Angew. Chem. Int. Ed.*, **2017**, 56, 9747–9751.
- [19] F. Cárdenas-Lizana, S. Gómez-Quero, A. Hugon, L. Delannoy, C. Louis, M. A. Keane, *J. Catal.*, **2009**, 262, 235–243.
- [20] A. Wang, J. Li, T. Zhang, *Nat. Rev. Chem.*, **2018**, 2, 65–81.
- [21] L. Zhang, M. Zhou, A. Wang, T. Zhang, *Chem. Rev.*, **2020**, 120, 683–733.
- [22] L. Lin, S. Yao, R. Gao, X. Liang, Q. Yu, Y. Deng, J. Liu, M. Peng, Z. Jiang, S. Li, Y. W. Li, X. D. Wen, W. Zhou, D. Ma, *Nat. Nanotechnol.*, **2019**, 14, 354–361.
- [23] F. Chen, X. Jiang, L. Zhang, R. Lang, B. Qiao, *Chin. J. Catal.*, **2018**, 39, 893–898.
- [24] H. Wei, X. Liu, A. Wang, L. Zhang, B. Qiao, X. Yang, Y. Huang, S. Miao, J. Liu, T. Zhang, *Nat. Commun.*, **2014**, 5, 5634.
- [25] C. Wang, S. Mao, Z. Wang, Y. Chen, W. Yuan, Y. Ou, H. Zhang, Y. Gong, Y. Wang, B. Mei, Z. Jiang, Y. Wang, *Chem*, **2020**, 6, 752–765.
- [26] L. Shang, T. Bian, B. Zhang, D. Zhang, L. Z. Wu, C. H. Tung, Y. Yin, T. Zhang, *Angew. Chem. Int. Ed.*, **2014**, 53, 250–254.
- [27] S. Mitchell, J. M. Thomas, J. Perez-Ramirez, *Catal. Sci. Technol.*, **2017**, 7, 4248–4249.
- [28] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **1996**, 54, 11169–11186.
- [29] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77, 3865–3868.
- [30] G. Kresse, D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, **1999**, 59, 1758–1775.
- [31] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, **2011**, 32, 1456–1465.
- [32] G. Henkelman, B. P. Uberuaga, H. Jónsson, *J. Chem. Phys.*, **2000**,

Graphical Abstract

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MIL-53 (Al) derived single-atom Rh catalyst for the selective hydrogenation of *m*-chloronitrobenzene into *m*-chloroaniline

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The Rh@Al₂O₃@C SAC, fabricated by utilizing a metal-organic framework of MIL-53 (Al), shows an excellent, sustained chemoselectivity for the hydrogenation of *m*-chloronitrobenzene.

- 113, 9901–9904.
- [33] S. Smidstrup, A. Pedersen, K. Stokbro, H. Jónsson, *J. Chem. Phys.*, **2014**, 140, 214106.
- [34] C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, G. Férey, *J. Am. Chem. Soc.*, **2002**, 124, 13519–13526.
- [35] W. Cao, W. Luo, H. Ge, Y. Su, A. Wang, T. Zhang, *Green Chem.*, **2017**, 19, 2201–2211.
- [36] W. Cao, L. Lin, H. Qi, Q. He, Z. Wu, A. Wang, W. Luo, T. Zhang, *J. Catal.*, **2019**, 373, 161–172.
- [37] D. Liu, F. Dai, Z. Tang, Y. Liu, C. Liu, *Mater. Res. Bull.*, **2015**, 65, 287–292.
- [38] J. C. Matsubu, V. N. Yang, P. Christopher, *J. Am. Chem. Soc.*, **2015**, 137, 3076–3084.
- [39] R. R. Cavanagh, J. T. Yates Jr., *J. Chem. Phys.*, **1981**, 74, 4150–4155.
- [40] J. T. Y. Jr., T. M. Duncan, S. D. Worley, R. W. Vaughan, *J. Chem. Phys.*, **1979**, 70, 1219–1224.
- [41] R. Lang, T. Li, D. Matsumura, S. Miao, Y. Ren, Y. T. Cui, Y. Tan, B. Qiao, L. Li, A. Wang, X. Wang, T. Zhang, *Angew. Chem. Int. Ed.*, **2016**, 55, 16054–16058.
- [42] I. Eswaramoorthi, A. K. Dalai, *Catal. Lett.*, **2009**, 131, 203–212.
- [43] F. Li, H. Ma, H. Zhang, W. Ying, D. Fang, *C. R. Chim.*, **2014**, 17, 1109–1115.
- [44] H. Tang, Y. Su, Y. Guo, L. Zhang, T. Li, K. Zang, F. Liu, L. Li, J. Luo, B. Qiao, J. Wang, *Chem. Sci.*, **2018**, 9, 6679–6684.
- [45] J. H. Kwak, J. Hu, D. Mei, C. W. Yi, D. H. Kim, C. H. F. Peden, L. F. Allard, J. Szanyi, *Science*, **2009**, 325, 1670–1673.
- [46] N. Tang, Y. Cong, Q. Shang, C. Wu, G. Xu, X. Wang, *ACS Catal.*, **2017**, 7, 5987–5991.
- [47] Z. Zhang, Y. Zhu, H. Asakura, B. Zhang, J. Zhang, M. Zhou, Y. Han, T. Tanaka, A. Wang, T. Zhang, N. Yan, *Nat. Commun.*, **2017**, 8, 16100.
- [48] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, *J. Catal.*, **2004**, 226, 54–68.
- [49] R. Wischert, P. Laurent, C. Copéret, F. Delbecq, P. Sautet, *J. Am. Chem. Soc.*, **2012**, 134, 14430–14449.
- [50] X. R. Shi, D. S. Sholl, *J. Phys. Chem. C*, **2012**, 116, 10623–10631.
- [51] M. C. Valero, P. Raybaud, P. Sautet, *Phys. Rev. B*, **2007**, 75, 045427.
- [52] G. Wienhöfer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar, M. Beller, *J. Am. Chem. Soc.*, **2011**, 133, 12875–12879.
- [53] F. Yang, M. Wang, W. Liu, B. Yang, Y. Wang, J. Luo, Y. Tang, L. Hou, Y. Li, Z. Li, *Green Chem.*, **2019**, 21, 704–711.
- [54] W. C. Cheong, W. Yang, J. Zhang, Y. Li, D. Zhao, S. Liu, K. Wu, Q. Liu, C. Zhang, D. Wang, Q. Peng, C. Chen, Y. Li, *ACS Appl. Mater. Interfaces*, **2019**, 11, 33819–33824.
- [55] C. Xu, Q. Li, Q. Zhang, K. Li, H. Yin, S. Zhou, *ACS Appl. Nano Mater.*, **2019**, 2, 5086–5095.
- [56] T. Schwob, R. Kempe, *Angew. Chem. Int. Ed.*, **2016**, 55, 15175–15179.
- [57] P. Zhang, C. Yu, X. Fan, X. Wang, Z. Ling, Z. Wang, J. Qiu, *Phys. Chem. Chem. Phys.*, **2015**, 17, 145–150.
- [58] C. Jiang, Z. Shang, X. Liang, *ACS Catal.*, **2015**, 5, 4814–4818.
- [59] R. V. Jagadeesh, A. E. Surkus, H. Junge, M. M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, *Science*, **2013**, 342, 1073–1076.
- [60] F. A. Westerhaus, R. V. Jagadeesh, G. Wienhöfer, M. M. Pohl, J. Radnik, A. E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brückner, M. Beller, *Nat. Chem.*, **2013**, 5, 537–543.
- [61] P. Luo, K. Xu, R. Zhang, L. Huang, J. Wang, W. Xing, J. Huang, *Catal. Sci. Technol.*, **2012**, 2, 301–304.
- [62] H. Goksu, H. Sert, B. Kilbas, F. Sen, *Curr. Org. Chem.*, **2017**, 21, 794–820.
- [63] J. Soria, A. Martinez-Arias, J. Fierro, J. Conesa, *Vacuum*, **1995**, 46, 1201–1204.
- [64] W. Liu, L. Zhang, W. Yan, X. Liu, X. Yang, S. Miao, W. Wang, A. Wang, T. Zhang, *Chem. Sci.*, **2016**, 7, 5758–5764.

MIL-53 (Al)衍生的Rh单原子催化剂在间氯硝基苯选择性加氢制间氯苯胺反应中的应用

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摘要: 卤代苯胺是化学工业中重要的中间体, 主要用于制造药物、聚合物、染料等含氮化学品, 用多相金属催化剂催化卤代硝基芳烃加氢制备卤代苯胺是一种高效、绿色和可持续发展的生产工艺。该过程需要选择性加氢硝基基团, 同时避免卤素基团的脱卤副反应发生。然而, 化学选择性加氢存在巨大的挑战, 难点在于催化剂的精准设计, 一方面要求具备对硝基基团合适的加氢能力, 另一方面要阻止对卤素基团的脱卤副反应发生。基于此, 研制高效多相金属催化剂用于卤代硝基芳烃选择性加氢制备卤代苯胺反应引起了高度关注。近年来, 单原子金属催化剂受到越来越多的关注, 并在卤代硝基芳烃选择性加氢制备卤代苯胺反应中显现出极大的潜力。本文通过在金属有机骨架材料MIL-53 (Al)自组装的过程中将金属Rh原位嫁接其骨架结构中, 继而通过限域热解的方法制备了Rh@Al₂O₃@C单原子催化剂, 其在间氯硝基苯(*m*-CNB)加氢制间氯苯胺(*m*-CAN)反应中显现了高效催化选择性。球差校正高角度环形暗场模式的透射电镜, CO作为探针分子的红外光谱和X射线光电子能谱等结果发现, Rh是以单原子的形式均匀的分布在Al₂O₃上并被无定型碳包覆, 且Rh化学价态呈正价。而²⁷Al

固体核磁共振与密度泛函理论计算的结果则进一步确定 $\text{Al}_2\text{O}_3@\text{C}$ 载体中存在的五配位的Al物种(Al^{V})是锚定Rh单原子的主要位点, Al^{V} 的不饱和的配位结构可以有效地稳定Rh单原子, 对形成Rh位点的单原子分散至关重要. 在间氯硝基苯选择性加氢制间氯苯胺反应中, 与等体积浸渍法制备的Rh/C和Rh/ γ - Al_2O_3 纳米催化剂相比, $\text{Rh}@\text{Al}_2\text{O}_3@\text{C}$ 单原子催化剂表现出优异催化性能: 其在313 K, 氢气压力为20 bar的温和条件下转换频率(TOF)高达 $2317 \text{ mol}_{\text{m-CNB}} \cdot \text{mol}_{\text{Rh}}^{-1} \cdot \text{h}^{-1}$, 优于已报道的多相金属催化剂, 是目前最高值. 此外, 该催化剂展现出极佳的稳定性能, 经过五次循环后, 该催化剂对 m -CAN的选择性仍旧保持在98%左右. $\text{Rh}@\text{Al}_2\text{O}_3@\text{C}$ 单原子催化剂的优异催化性能源自于金属单原子结构的形成对于金属位点电子结构的有效调节, 进而调控催化剂加氢性能并实现对加氢脱卤副反应的抑制; 与此同时, $\text{Rh}@\text{Al}_2\text{O}_3@\text{C}$ 催化剂增进了酸位点的可及性, 从而促进了其串联步骤中包含的脱水反应的发生, 进而有效提高催化剂的反应活性.

关键词: 单原子催化剂; 铑; 金属有机骨架; 加氢反应; 化学选择性

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