Chemoselective Hydrogenation

Enhancing Metal–Support Interactions by Molybdenum Carbide: An Efficient Strategy toward the Chemoselective Hydrogenation of α , β -Unsaturated Aldehydes

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Abstract: Metal–support interactions are desired to optimize the catalytic turnover on metals. Herein, the enhanced interactions by using a Mo₂C nanowires support were utilized to modify the charge density of an Ir surface, accomplishing the selective hydrogenation of α,β -unsaturated aldehydes on negatively charged Ir^{δ–} species. The combined experimental and theoretical investigations showed that the Ir^{δ–} species derive from the higher work function of Ir (vs. Mo₂C) and the consequently electron transfer. In crotonaldehyde

Introduction

Metal-support interactions play essential roles in the catalytic applications of supported nanocatalysts, which affect the size, morphology, and valence state of active species through mass transport and interfacial charge redistribution.^[1-3] The combined effect of the above-mentioned factors would facilitate the achievement of high catalytic conversion with satisfied selectivity.^[3,4] Due to the possession of noble-metal-like electronic property because of d-band contraction in metal-carbon alloys,^[5,6] transition-metal carbides are recently discovered as promising supports.^[7] They serve as excellent supports for the dispersion of metal catalysts.^[8-11] And more importantly, they can also modify the reactivity of a supported metal through electronic perturbations, which has been proven by Rodriguez

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et al. for Cu/TiC and Au/TiC catalysts in hydrodesulfurization reactions, CO_2 conversion to methanol, O_2 dissociation, and water gas shift. $^{[12-18]}$

Chemoselective hydrogenation of α , β -unsaturated aldehydes to unsaturated alcohols is an important step toward valueadded chemicals.^[19-23] Because saturated aldehydes instead of the desired unsaturated alcohols are the thermodynamically favored products,^[20,24] selective catalysts are highly demanded to hydrogenate the carbonyl group from the conjugated ethylenic (C=C) and carbonyl (C=O) groups. Although supported iridium (Ir) with a large d band is considered as one of the efficient catalysts according to the semi-empirical extended Hückel calculation,^[21] the selectivity is unsatisfied in experimental reports.^[25-27] Commonly, good activity but poor selectivity is observed in liquid-phase hydrogenation,[25-27] owing to the highdensity unoccupied d orbitals adsorbing/activating both the C=C and the C=O group. In this regard, electron regulation on the Ir is required. For example, the excessive electrons in the Ir species would enhance the repulsive force with the C=C group,^[28] and also promote an electron feedback to the π^* orbital in the polar C=O group,^[21] resulting in the selective hydrogenation of the C=O moiety. Such regulation is expected to be achieved on metal-carbide supports through electronic metal-support interactions, which drive the charge transfer between the carbides and the Ir due to their variation in work functions.^[1,29,30]

Hydrogenating crotonaldehyde (CRAL) to crotyl alcohol (CROL) remains the main challenge of chemoselective hydrogenation,^[21,31] which is limited by the low selectivity associated with the negligible steric hindrance and electronic effects of a small methyl group at the γ -sites. Herein, we develop Mo₂C-

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nanowire-supported Ir (Ir/Mo₂C) for the selective hydrogenation of CRAL in an aqueous system. The combined experimental and theoretical investigations show that the negatively charged $Ir^{\delta-}$ species stems from the higher work function of Ir (5.22 vs. 5.00 eV of Mo₂C) and the consequent electron transfer, which promotes the adsorption and activation of the polar C= O group towards the enhanced production of unsaturated alcohol. As expected, the selectivity as high as 80% is superior to that of SiO₂-supported Ir (23%), and comparable to the best of the current Pt-group catalysts.^[32-37] Similar metal-support interactions affecting the selectivity are also confirmed for Mo₂Csupported Pt and Au, illustrating their efficient regulation over reaction pathways. Noticeably, the high selectivity as well as the good activity for a wide range of substrates verifies our Ir/ Mo₂C system as a promising catalyst for the chemoselective hydrogenation of α , β -unsaturated aldehydes.

Results and Discussion

Hierarchical nanowires composed of Mo₂C nanoparticles (\approx 15–20 nm in size, Figure S1 in the Supporting Information) are used as the catalyst support. They possess a rich nanoporosity and a large surface (\approx 40 m²g⁻¹) free from carbon deposition.^[38] After an impregnation procedure and a following reduction by using 5 vol% H₂/Ar at 300°C, a series of Ir/Mo₂C with different Ir loading was harvested (Figure 1 a and Table S1 in the Supporting Information). With the increased Ir loading, the diffraction peaks assigned to the cubic phase Ir (JCPDS NO. 87-0715) emerge in the X-ray diffraction (XRD) patterns (Figure 1 a), along with the characteristic peaks of α -Mo₂C (JCPDS NO. 31-0871). Taking 3.7% Ir/Mo₂C as the model sample, nanowires with a length of several micrometers and a width of 80–



Figure 1. a) XRD patterns of Mo_2C and Ir/Mo_2C with various Ir loading, and b) typical SEM and c) typical TEM images of 3.7 % Ir/Mo_2C .

150 nm are well observed in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figures 1 c and d). And the attached energy dispersive spectrum (EDS, Figure S2 in the Supporting Information) identifies the successful loading of Ir on Mo_2C , whose size is determined as approximately 2–3 nm by a high-resolution TEM (HRTEM) investigation (Figure 1 c).

In order to elucidate the interactions between the Ir and the Mo₂C support, hydrogen temperature-programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS) analysis are conducted. As shown in the H₂-TPR results (Figure 2a), Ir/Mo₂C presents a promoted reducibility of Ir³⁺ species at lower



Figure 2. a) H₂-TPR and b) XPS results of the Ir/Mo₂C and Ir/SiO₂ systems. The dash lines in b) indicate the theoretical values of standard Ir $4f_{7/2}$ and $4f_{5/2}$. Charge distribution of Ir on c) Mo₂C and d) SiO₂ surfaces determined by the Bader charge analysis. The blue and yellow isosurfaces represent positive and negative charges, respectively, and only the absolute isovalues greater than 0.008 e bohr⁻³ are shown. The purple, green, gray, red, white, and blue balls represent Ir, Mo, C, O, H, and Si atoms, respectively.

temperature (200 °C) than Ir/SiO₂ (260 °C). Given the similar size of Ir on both Mo₂C and SiO₂ (see Figures 1 b and S3 in the Supporting Information), the strong metal–support interactions between Ir and Mo₂C are reasonably suggested. As further validated by XPS (Figure 2 b), the Ir 4f_{7/2} and 4f_{5/2} peaks in Ir/Mo₂C are red shifted to 60.3 and 63.2 eV, respectively, in comparison with those of metallic Ir (Ir 4f_{7/2}=60.9 eV, Ir 4f_{5/2}=63.9 eV)^[39,40] on inert SiO₂. This observation well indicates the negatively charged Ir (Ir^{δ -}) on the Mo₂C surface.^[41]

Generally, the variation in the work functions of metals and supports usually contributes to the electronic metal–support interactions in heterogeneous catalysts.^[29,30] Owing to the lower work function of Mo₂C (5.00 eV) than that of Ir (5.22 eV),^[42,43] the formation of Ir^{δ -} on Mo₂C should be ascribed

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to the charge transfer through the interfaces. We further examined the charge redistribution of Ir on Mo₂C and SiO₂ supports by using periodic spin-polarized calculations in the framework of density functional theory (DFT) implemented within the Vienna ab initio simulation program (VASP).^[44,45] The Ir/Mo₂C and Ir/SiO₂ systems were modeled by adding a three-layer strip of metal Ir on the $Mo_2C(121)$ and the $SiO_2(001)$ surfaces (Figure S4 in the Supporting Information), respectively. The most stable facet of (121) in α -Mo₂C is mainly observed in Mo₂C nanowires (Figure 1 c), which provides a rational modeled surface for active Ir. It is clearly showed that electronic transfer occurs at the interfaces between Ir and Mo₂C, which is however negligible in Ir/SiO₂. The average charges per Ir atom achieved from Mo₂C is 0.21 e, as shown in the isosurfaces of charge density (Figure 2c). This well indicates the enhanced electronic metal-support interactions between Ir and Mo₂C due to the difference of their work functions, in which the higher Fermi energy level in Mo₂C promotes the electron transfer to Ir. The similar electronic interactions on carbide surface was ever evidenced on TiC-supported Cu and Au by DFT calculation, which showed the significant electronic perturbations of metals due to the strong Cu-C and Au-C interactions.^[12, 13, 17] In comparison, only 0.02 e per Ir atom are observed on SiO₂ (Figure 2d), which is attributed to the lower Fermi energy level of the nanoparticles compared to the bulk.^[46] The enhanced electronic density in Ir would increase the repulsive four-electron interactions with the C=C moiety, and favor a d-electron feedback into the π^* orbital of the polar C=O group.^[21,28] We anticipate that such electronic metal-support interactions in Ir/Mo₂C would benefit the selective hydrogenation of α , β -unsaturated aldehydes to unsaturated alcohols.

In this work, the selective hydrogenation of CRAL to CROL is investigated, whose reaction pathways are shown in Figure 3a. The desired CROL can be produced through the direct hydrogenation of the C=O double bond, namely, a 1,2-addition.[47] The undesired butanal (BUAL) generates from either the direct hydrogenation of the C=C double bond undergoing a 3,4-addition mechanism, or the indirect 1,4-addition to but-1-en-1-ol (ENOL) followed by a swift tautomerization.[47] The above-described partial hydrogenation products, including CROL, BUAL, and even ENOL, can be further hydrogenated to saturated butanol (BUOL). As expected, the catalyst comprising 3.7% Ir/ Mo₂C presents the prominent performance. In the time courses of the reaction (Figure 3b), the desired CROL is the main product, and the byproducts BUAL and BUOL are limited to a low level. As CRAL is almost completely converted (>120 min), the further hydrogenation of BUAL to BUOL is obvious, but that of CROL is negligible, suggesting the favored hydrogenation of the C=O double bond. Such performance is confirmed by three catalytic tests showing good degrees of reproducibility (Figure S5 in the Supporting Information). Considering the poor CRAL conversion and the CROL yield over bare Mo₂C under the same condition (Figure 3 c), highly dispersed Ir is believed as the main active species in Ir/Mo₂C for CRAL hydrogenation. By contrast, Ir/SiO₂ with a similar Ir loading (3.5%) displays the undesired hydrogenation routes to BUAL (Figure 3 d).

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Figure 3. a) Reaction pathways for the hydrogenation of CRAL, and time-dependent profiles over b) 3.7 % Ir/Mo₂C, c) Mo₂C, and (d) 3.5 % Ir/SiO₂.

Table 1. Hydrogenation results of CRAL over supported Ir catalysts. ^[a]											
Entry	Catalysts	<i>t</i> [min]	Conv. [%]	Select CROL	. [%] BUAL	Initial r _{c=0}	rate ^[c] r _{C=C}				
1	3.7 % lr/Mo ₂ C	150 ^[b]	>99	80	2	502	77				
2	3.5 % Ir/SiO ₂	150	88	23	60	134	419				
3	3.8 % lr/Mo ₂ C(c)	150	51	60	32	175	105				
4	0.9 % lr/Mo ₂ C	240 ^[b]	83	69	17	589	316				
5	2.4 % lr/Mo ₂ C	240 ^[b]	>99	75	7	544	141				
6	5.0 % lr/Mo ₂ C	210 ^[b]	>99	73	6	327	119				
7	6.3 % lr/Mo ₂ C	240 ^[b]	>99	69	8	242	153				
[a] Reaction condition: catalyst (25 mg), CRAL (2 mmol), H ₂ O (50 mL), temperature (373 K), H ₂ (2 MPa), stirring rate (600 rpm). [b] Values corresponding to the maximum yield of CROL. [c] In [μ mol s ⁻¹ g _µ ⁻¹].											

The detailed hydrogenation results over the supported catalysts of Ir are summarized in Table 1. At a reaction time of 150 min, when the maximum yield of CROL is achieved, 3.7% Ir/Mo₂C shows a CROL selectivity as high as 80% with an almost complete CRAL conversion (entry 1 in Table 1). The CROL selectivity is obviously higher than that observed for Ir/ SiO₂ (23%) with a similar Ir loading (entry 2 in Table 1), and comparable to the best of the current Pt-group catalysts.^[32–37] This situation is also confirmed by the initial formation rates of CROL (r_{C=0}) and BUAL (r_{C=C}). Remarkably, 3.7% lr/Mo₂C presents a higher $r_{C=0}$ value of 502 μ mol s⁻¹ g_{lr}⁻¹ than $r_{C=C}$ value (77 μ mol s⁻¹ g_{lr}⁻¹), whereas 3.5% Ir/SiO₂ only displays a lower $r_{C=O}$ value than $r_{C=C}$ value. TEM (Figures 1 b and S3 in the Supporting Information)) and the CO-uptake (Table S2 in the Supporting Information) analyses were conducted to identify the particle size and the active-site amounts of Ir on Mo₂C and SiO_2 , in which the difference is negligible. It is reasonable to ascribe the obviously improved CROL selectivity on Ir/Mo₂C to the enhanced electronic metal-support interactions. The nega-



tively charged $Ir^{\delta-}$ on Mo_2C , distinguished from the metallic Ir^0 on inert SiO₂, would prefer the adsorption and activation of the polar $C^{\delta+}=O^{\delta-}$ bond due to the enriched d electrons in Ir, which is commonly accepted in the chemoselective hydrogenation by using Pt-group metals.^[21,28,48]

Furthermore, the selective hydrogenation on Ir/Mo₂C is influenced by the nature of the Mo₂C and the Ir loading, as a result of the Ir-Mo₂C interactions. When commercial Mo₂C is employed as supports [denoted as Ir/Mo₂C(c)], the CRAL conversion (51%) and the CROL selectivity (60%) are lower than those on Ir/Mo₂C under the same condition (entry 3 in Table 1), which can be ascribed to the small surface of bulky Mo₂C (Figure S6 in the Supporting Information). And the evolving catalytic performance associated with the Ir loading from 0.9 to 6.3% (entries 4-7 in Table 1) suggests the optimized loading around 3.7%. The slightly low selectivity at high and low Ir loading should be ascribed to the prohibited metal-support interactions by excessive Ir and the unselective hydrogenation on Mo₂C, respectively. Additional tests show the satisfied cycleability of Ir/Mo₂C (Figure S7 in the Supporting Information), and its high selectivity and activity in aqueous systems superior to those in organic solvents (Table S3 in the Supporting Information), pointing out a promising candidate for the environmentally clean reduction of unsaturated aldehydes.^[49]

In Mo_2C -supported Pt and Au catalysts, the metal–support interactions are also observed. The similar preparation was employed for the metals on Mo_2C and SiO_2 , in which the similarities in the particle size and the active-site amounts of the metal on the different supports were confirmed by TEM and

CO-uptake analyses (Figure S8 and Table S2 in the Supporting Information), respectively. In XPS measurements (Figure 4a), the peaks of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ are red shifted to 70.3 and 73.8 eV, respectively, on Mo₂C, in comparison with those of metallic Pt on SiO₂ (71.4 and 74.6 eV).^[50] This indicates the formation of negatively charged $Pt^{\delta-}$ owing to the electron transfer from Mo₂C to Pt, which possesses a higher work function of 5.66 eV than Mo_2C .^[42,43] In the same way, Au with a higher work function of 5.10 eV^[42] accumulates electrons from Mo₂C, as verified by the obviously red shifted Au $3d_{7/2}$ and $3d_{5/2}$ peaks in the XPS (Figure 4b).^[51] Meanwhile, these metal-support interactions are consistent with the results of the H₂-TPR analysis (Figure S9 in the Supporting Information). Furthermore, the Bader charge analysis by DFT calculations clearly displays the different charge density of the metals on Mo₂C and SiO₂. As for Pt/Mo₂C and Au/Mo₂C, the average charges per metal atom achieved from Mo₂C are 0.23 and 0.16 e (Figures 4 c and e), respectively. However, the charges of the metals in the Pt/SiO₂ and Au/SiO₂ systems are negligible (Pt: 0.05 e and Au: 0.03 e, Figures 4d and f). These are in good agreement with the trend suggested by the difference of the work function between bulk metals and supports, in which the lower Fermi energy level the metal has, the more electrons are transferred from Mo₂C with the high Fermi energy level.

Accordingly, the CRAL hydrogenation is affected by the electronic metal-support interactions in the above-described catalysts. Focusing on the performance at a reaction time of 120 min, the CRAL conversion and the CROL selectivity are summarized in Figure 5 a. The activity of the Mo₂C-supported



Figure 4. XPS results of a) Pt and b) Au supported by Mo_2C and SiO_2 . Charge distribution of c,d) Pt and e,f) Au on Mo_2C (c and e) and SiO_2 (d and f) surfaces determined by the Bader charge analysis. The blue and yellow isosurfaces are positive and negative charges, respectively, and only the absolute isovalues greater than 0.008 e bohr⁻³ are shown. The cyan, golden, green, gray, red, white, and blue balls represent Pt, Au, Mo, C, O, H, and Si atoms, respectively.

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metals outperforms that of their counterparts on SiO₂. More importantly, the varied CROL selectivity for each metal depends on the charge distribution on the interfaces. Pt/Mo₂C with detectable Pt^{$\delta-$} species presents a remarkably higher CROL selectivity of 66% than Pt/SiO₂ (32%), which is consistent with the previously reported Pt^{$\delta-$} that benefits the C=O hydrogenation.^[28,48] Correspondingly, Au/Mo₂C delivers a slightly higher selectivity of CROL (53%) than Au/SiO₂ (49%).^[52]

In the hydrogenation of CRAL to CROL, a high activity and selectivity are usually difficult to achieve at the same time on



Figure 5. Comparison of a) the CRAL conversion and the CROL selectivity after a reaction time of 120 min and b) the initial reaction rates in the CRAL hydrogenation on a series catalysts of 3.7% Ir/Mo₂C, 3.5% Ir/SiO₂, 3.0% Pt/Mo₂C, 3.4% Pt/SiO₂, 3.8% Au/Mo₂C, and 3.8% Au/SiO₂.

metals without electronic metal–support interactions,^[53] as illustrated by the initial performance on SiO₂-supported Ir, Pt, and Au (Figure 5 b). Ir and Pt with large unoccupied d orbitals and thus, a high hydrogenation activity, usually give a low C= O selectivity, whereas Au catalysts, presenting a good selectivity, are limited by their low activity. Employing the electronic metal–support interactions from Mo₂C, the C=O selectivity of Ir and Pt can be remarkably improved (Figure 5 b), and both the activity and the selectivity of Au are slightly increased. Significantly, our Ir/Mo₂C system successfully fulfils the high selectivity as well as a good activity among these catalysts, as confirmed by the outstanding performance in the initial reaction (Figure 5 b) and after a reaction time of 120 min (Figure 5 a).

Our Ir/Mo₂C catalyst can be considered in a sense as a universal catalyst for the selective hydrogenation of $\alpha_{i\beta}$ -unsaturated aldehydes. The performance for various substrates is summarized in Table 2, in which the activity and selectivity are discussed at the beginning of the reaction (10 min) and after the time required for the maximum yield of products. Beside the prominent performance for CRAL (entry 1 in Table 2), the selective routes for 3-methyl-2-butenal and 2-pentenal are also achieved (entries 2 and 3 in Table 2, respectively). For 3-methyl-2butenal, the C=O selectivity is maintained around 82-83%. And a high activity (conversion of $\approx 80\%$ after only 40 min) with a C=O selectivity of approximately 55% is observed for 2pentenal. Remarkably, Ir/Mo₂C shows a highly selective hydrogenation for cinnamaldehyde and citral (entries 4 and 5 in Table 2, respectively), and the higher selectivity (\approx 90%) in comparison with CRAL should be ascribed to the steric hindrance and electronic effects of the substituents at the γ carbon atom.^[21] For cinnamaldehyde, the selectivity of approximately 90% over Ir/Mo₂C is superior to those of previously reported Ir catalysts (Ir/SiO2: 57%, Ir/CNT: 68%, Au-Ir/TiO2: 83%) and Pt-on-Au nanostructures (<80%),[25,54-56] and comparable

Entry	Substrate	Product	<i>t</i> [min]	Conv. [%]	Select. [%]
	0 	ОН	10	44	77
1 ^[a]			150 ^[c]	>99	87
		н П П	10	11	83
2 ^[a]		H	180 ^[c]	>99	82
	0 II	ОН	10	44	55
3 ^[a]			40 ^[c]	80	55
	o II	ОН	10	35	88
4 ^[b]	Н	Н	150 ^[c]	> 99	90
	Ĩ I	Ĭ I	10	19	91
5 ^[b]		+ OH	240 ^[с] `он	95	94



to metal–organic-framework-confined Pt (91%) and ligand-capped PtFe (94%).^[57,58] And in citral hydrogenation, the C=O selectivity of 94% outperforms those of Ir (Ir/SiO₂: 47–68%),^[59] and other metals (Pt/Ti-doped mesoporous silica): \approx 35%, Zn-Pt/mesoporous silica: \approx 75%, Pt/TiO₂-H₂: \approx 80%, Au/CNT (CNT = carbon nanotube): \approx 50%, Au/Nb₂O₅: \approx 70%, Ag/SiO₂ and Ag-In/SiO₂: \approx 80%).^[48,60–65]

Conclusion

We have developed Ir/Mo₂C catalysts with enhanced metalsupport interactions for the chemoselective hydrogenation of α , β -unsaturated aldehydes, in which the Ir^{δ -} active species resulting from an electron transfer at the interfaces contributes to the selective routes. Showing the prevailing influences on various metals by Mo₂C supports, this work opens up new opportunities for the design of selective catalysts through interface engineering. It is envisioned that the future work with a better control over the electron and surface properties of carbide supports^[66,67] would further boost the relevant catalytic applications.

Experimental Section

Catalyst preparation: The synthesis of the Mo₂C nanowires was conducted according to our previous report.^[38] Ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O] (2.48 g) was dissolved in distilled water (40 mL) and aniline (3.34 g) was added to this solution. Afterwards, a 1 m aqueous solution of HCl was dropwise added with magnetic stirring at room temperature until a white precipitate appeared (pH 4–5). After stirring at 50 °C in an oil bath for approximately 2–6 h, the precursor of Mo₃O₁₀(C₆H₈N)₂·2 H₂O was received. Finally, the Mo₂C nanowires were harvested after calcining Mo₃O₁₀(C₆H₈N)₂·2 H₂O at 775 °C for 5 h under an Ar flow.

An impregnation procedure was introduced to prepare the supported catalysts of Ir and Pt. Typically, the catalyst supports (Mo₂C or SiO₂) were impregnated with an aqueous solution containing the relevant metal ions (i.e., HIrCl₄ or H₂PtCl₆), and then the solutions were stirred for 4 h at 80 °C. The solids were dried at 50 °C overnight, followed by a careful reduction with a stream of 5 vol% H₂/Ar at 300 °C for 2 h. Meanwhile, a typical deposition–precipitation procedure was employed to prepare the Au/Mo₂C and Au/SiO₂ catalysts. Briefly, Mo₂C or SiO₂ was dispersed with an aqueous solution of HAuCl₄, and the pH was adjusted to 9.0 by dropwise addition of a 0.25 M aqueous solution of NH₃-H₂O. After stirring for 6 h and aging for another 2 h, the catalysts were washed with deionized water and then dried at 50 °C for 2 h.

Catalyst characterization: XRD analysis was performed on a Bruker D8 diffractometer by using Cu_{Ka} radiation ($\lambda = 1.54056$ Å). SEM and TEM investigations were taken on a ZEISS ULTRA55 and a JEOL JEM 2100F, respectively. EDS attached on TEM was carried out on a JEOL JEM 2100F. XPS was processed on a Perkin–Elmer PHI X-tool, by using C 1s (B.E. = 284.6 eV) as a reference. The metal loading was determined by using inductively coupled plasmaatomic emission spectroscopy (ICP-AES). The Brunauer–Emmett– Teller (BET) specific surface areas were determined by adsorption– desorption measurements of nitrogen at the liquid nitrogen temperature, by using a Micromeritics TriStar 3000 equipment, degassing at 300 $^\circ\text{C}.$ The H_2-TPR and CO chemisorption measurements were both conducted on a XianQuan instrument TP 5076.

Catalytic performance measurement: CRAL hydrogenation was carried out in a 100 mL stainless steel autoclave (Parr 4598), in which the catalyst (25 mg), CRAL (2 mmol), and H₂O (50 mL) were loaded. The reactor was sealed and purged with H₂ to remove the air for five times, and then the reactor was heated to the desired temperature. H₂ (2 MPa) was purged into the reactor after the desired temperature was reached and the stirrer was started. The products were analyzed by using a Shizumadu GC-2014C with a FID detector.

Density functional theory calculations: The periodic spin-polarized calculations in the framework of the density functional theory implemented within the Vienna ab initio simulation program (VASP)^[44,45] were performed to model the supported metal catalysts for understanding the charge transfer between the metal and the supports. The projector-augmented-wave (PAW) pseudopotentials^[68] were utilized to describe the core–electron interactions. The generalized gradient approximation (GGA) exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE)^[69] form was utilized to describe the exchange–correlation interaction. The cut-off energy of the plane wave basis set was set to 400 eV.

The most stable hydroxylated cleaved stoichiometric (001) surface of α -quartz, which is the most stable phase of silica at the reaction temperature,^[70] was modeled by a p(3×2) unit cell of $14.85 \times$ 9.90 $Å^2$ with a 12 Å vacuum between the slabs in the z direction. The slab contains 18-layer SiO₂, corresponding to 36 units of SiO₂ per slab. The Brillouin zone was sampled with 2×3×1 Monkhorst-Pack k-point mesh. For Mo₂C, the α -phase according to the experimental result was researched. The crystal structure of this phase has a hexagonal structure with the space group Pbcn. The most stable (121) surface of this phase was modeled by a $p(3 \times 2)$ unit cell of 18.29×11.41 Å² with a 12 Å vacuum between the slabs in the z direction. The slab contains 9-layer Mo₂C, corresponding to 36 units of Mo₂C per slab. The Brillouin zone was sampled with $2 \times$ 3×1 Monkhorst–Pack k-point mesh. The metal/SiO₂ and metal/ Mo₂C systems were modeled by adding a three-layer strip of metal Ir, Pt, or Au on the SiO₂(001) or Mo₂C(121) surface, respectively. During all the optimization processes, the bottom nine layers of SiO₂ and three layers of Mo₂C were fixed in the slab, whereas the upmost layers of the supports and metal strips were relaxed. For each metal-support system, the five lowest energy structures from the results of Nose thermostat molecular dynamics simulation (T = $150\,^\circ\text{C}\text{,}\ 1$ fs per step, 2000 steps) were selected to be further optimized by conjugate gradient methods. Geometry optimization was performed until all the remaining forces on each relaxed atom were lower than 0.02 eV $Å^{-1}$. The structure with the lowest energy was utilized for the charge population analysis. The charge difference in the scheme of the Bader charge analysis was constructed by subtracting the charges of the metal-support systems from the charges of the metal and the support with each in the same structure. The isosurfaces of the charge density differences were also constructed by subtracting the charge densities of the metal-support systems from the charge densities of the metal and the supporter with each in the same structure.

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