Direct utilization of crude and waste H\textsubscript{2} via CO-tolerant hydrogenation

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H\textsubscript{2} tends to be a crucial medium in the foreseeable future as it is not only a green and renewable energy source for vehicles but also a fundamental feedstock for the chemical industry. For instance, selective hydrogenation, one of the catalytic processes used to produce fine compounds, is of vital importance because it enables the selective and efficient conversion of a variety of functional groups under mild reaction conditions. Catalytic hydrogenation of liquid organic hydrogen carriers (LOHCs, eg, methylbenzene) is a safe and economic approach for H\textsubscript{2} storage. At present, H\textsubscript{2} is mainly produced from the reforming of fossil fuels and industrial waste H\textsubscript{2}. Notably, both crude H\textsubscript{2} from reforming and industrial waste H\textsubscript{2} contain a notable amount of CO as an impurity, which can poison the noble-metal-based catalysts due to the strong and preferential adsorption of CO, inducing the blockage of active sites. Crude H\textsubscript{2} and waste H\textsubscript{2} need to be purified through various routes such as pressure swing adsorption, palladium, or polymeric membrane stack before being used; however, the purification processes are estimated to cause a significant extra cost of about 10%–20%. Consequently, developing CO-tolerant selective hydrogenation catalysts makes it possible for the direct utilization of crude H\textsubscript{2} and waste H\textsubscript{2} in the production of fine chemicals. What’s more, if the LOHCs can be hydrogenated with crude H\textsubscript{2} or even industrial waste H\textsubscript{2}, the purification of H\textsubscript{2} can be realized through a catalytic process, as the pure H\textsubscript{2} can be obtained from the dehydrogenation of the corresponding organic compound of LOHCs (eg, methyl-cyclohexane). The cycle of “hydrogenation by crude/waste H\textsubscript{2} – dehydrogenation to produce pure H\textsubscript{2}” can bring promising economic and environmental benefits (Figure 1), though other impurities like chlorine hydrogen sulfide and oxygen in waste H\textsubscript{2} may be an obstacle at the current stage.

The strong adsorption of CO on noble metal (eg, Pt) is resulted from the electron transfer of the d orbital electrons from metal to the 2\pi* anti-bonding orbital of CO molecules. Decreasing the d electron density of noble metal via the confinement of noble-metal species to an atomically dispersed motif has been demonstrated to be a useful method to reduce the strong adsorption of CO.\textsuperscript{1} Although the trade-off between CO-tolerant property and hydrogenation capability has brought harsh requirements for designing noble-metal catalysts, there have been some successful catalysts for the challenging process.

Single-atom alloy (SAA) catalysts are stable under hydrogenation reaction conditions. The Pt–M bond maintains the metallic property of noble-metal single atoms, making it possible to reduce the adsorption of CO and catalyze the hydrogenation reaction simultaneously. Flytzani–Stephanopoulos et al. reported the Pt\textsubscript{0.008}Cu\textsubscript{0.992}–SAA catalyst for CO-tolerant hydrogenation of acetylene.\textsuperscript{2} The authors demonstrated that the adsorption of CO on the Pt\textsubscript{0.008}Cu–SAA catalyst was weaker than that on the Pt nanoparticles. Moreover, they uncovered that the activation of H\textsubscript{2} was less affected by CO over the SAA catalysts through the H\textsubscript{2}–D\textsubscript{2} exchange experiment. In the authors’ view, weak adsorption of CO on the Pt\textsubscript{0.008}Cu–SAA catalyst led to more “CO-free” Pt sites under H\textsubscript{2}/CO atmosphere and further superior ability for H\textsubscript{2} activation. As a result, when the two catalysts were applied to catalyze selective hydrogenation of acetylene with simulated crude H\textsubscript{2} containing 200 ppm CO, the Pt\textsubscript{0.008}Cu–SAA catalyst exhibited 15 times higher activity.

![Figure 1. Illumination for CO-tolerant H\textsubscript{2} hydrogenation and storage](image-url)
than the Pt nanoparticles did. The existence of Pt–M is the key for the CO-tolerant hydrogenation activity of the SAA catalyst. Therefore, tuning the coordination environment of atomically dispersed Pt catalysts is crucial for CO-tolerant hydrogenation.

As is discussed above, Pt SAA catalysts with a Pt–M bond can be potential catalysts for CO-tolerant hydrogenation reaction. Our group discovered that Pt could be confined into single atoms with a Pt–Mo bond because of the strong interaction between noble metal and α-MoC. Moreover, the Pt–Mo coordination endows the Pt single atom on α-MoC with metallic properties, leading to the partially positive-charge Pt species (Pt$^{a+}$). The atomically dispersed Pt/α-MoC (Pt$_{a}$/α-MoC) was developed as a successful CO-tolerant catalyst for selective hydrogenation of nitrobenzene and its derivatives. The commercial Pt/C catalyst could catalyze the hydrogenation of nitrobenzene in pure H$_2$ at room temperature. However, once 0.1% CO (1000 ppm) was added, the commercial Pt/C catalyst was poisoned directly. By contrast, the Pt$_{a}$/α-MoC catalyst showed unprecedented CO tolerance for this reaction, whose turnover frequency remained 50%, reaching about ~3500 h$^{-1}$. Moreover, the catalyst could keep the activity and selectivity unchanged after eight cycles. Spectroscopic studies and theoretical calculations indicated the weakened adsorption of CO on a Pt$^{a+}$ single atom by decreasing the back donation of the Pt to CO, which was resulted from strong interactions between the α-MoC and supported Pt species. The interface structure of the Pt$_{a}$/α-MoC catalyst enabled a new reaction pathway for the hydrogenation of a nitro group by involving both Pt$_{a}$ and α-MoC sites. Water served as an H donor and thus facilitated the hydrogenation reaction, then the adsorption of CO on Pt sites reacted with the abundant $^*$OH on the surface to help extract H from water and regenerate active sites at room temperature in the assistance of the hydrogenation reaction. From this work, the choice of support of the atomically dispersed catalyst is drastically important for the CO-tolerant hydrogenation reaction because the support can not only tune the coordination environment of atomic noble-metal species but also participate in catalyzing the hydrogenation reaction. Very recently, Yang et al. reported that intermetallic Pt$_3$Mo nanocrystals with twin boundaries on mesoporous carbon (Pt$_3$Mo/C) were also active and stable for CO-tolerant hydrogenation of nitro-benzene and its derivatives. The Pt$_3$Mo/C catalyst also had a Pt–Mo bond, and the twin boundaries were demonstrated to be the key factor to weaken the adsorption of CO.

CO-tolerant hydrogen storage is an appealing process, but it is even more challenging than the above-reviewed CO-tolerant selective hydrogenation. Specifically, the hydrogenation of a benzene ring requires a noble-metal catalyst with large particles. It means that atomically dispersed catalysts are less active for hydrogenation of benzene ring, so the above-mentioned strategy may be not suitable. Alternatively, if crude hydrogen can be purified in situ by means of parallel methanation reaction over a bifunctional catalyst, CO-tolerant hydrogenation of LOHCs with benzene ring may be achieved.

Very recently, our group reported the synthesis of RuNi/TiO$_2$ catalysts with bifunctional active sites for CO-tolerant hydrogenation of methylbenzene to methyl-cyclohexane. Commercial noble-metal catalysts and 2Ru/TiO$_2$ all exhibited drastically high activity toward methylbenzene hydrogenation in pure H$_2$, but once 0.1% CO was incorporated in the gas feed, the activity decreased by more than an order of magnitude. By contrast, although the reaction rate over the 5Ni/TiO$_2$ was much lower than that of 2Ru/TiO$_2$, it only decreased slightly with the incorporation of 0.1% CO. Significantly, the 2Ru5Ni/TiO$_2$ catalyst took the advantages of the 2Ru/TiO$_2$ and 5Ni/TiO$_2$ catalysts, reaching a reaction rate of 18.2 m$\text{mol}_{\text{cyclohexane}}$/mol$\text{metal}$.h in H$_2$ and 12.5 m$\text{mol}_{\text{cyclohexane}}$/mol$\text{metal}$.h in 0.1% CO/ H$_2$, respectively. Besides, high conversion of methylbenzene and CO were kept over 2Ru5Ni/TiO$_2$ during 24 h long-term tests. In other words, a crude H$_2$ storage process was realized over the 2Ru5Ni/TiO$_2$ catalyst. It was demonstrated that Ru was the active site for CO methanation, while Ni was the active site for methylbenzene hydrogenation. Moreover, the strong interaction between the RuO$_2$ and TiO$_2$ and Ni species led to the high dispersion of Ni sites. Therefore, the 2Ru5Ni/TiO$_2$ catalyst exhibited much better activity than the Snu/TiO$_2$ catalyst due to its small particle size. Overall, by rapid purification of CO through the methanation reaction, CO-tolerant crude H$_2$ storage in methylbenzene/methyl-cyclohexane was realized over the RuNi/TiO$_2$ catalyst. It is believed that the strategy of fabricating bifunctional catalysts can be generalized to other LOHC systems.

To sum up, direct utilization and storage of crude H$_2$ and industrial waste H$_2$ is a drastically attractive process in both academic and industrial fields, but there is only limited research focusing on this topic. Still, some successful strategies for the design of CO-tolerant hydrogenation catalysts have been raised as below. Construction of Pt-based SAs leads to atomic Pt species with metallic property thanks to the Pt–M coordination environment, which can decrease the adsorption of CO but keep the ability for hydrogenation reaction, leading to the feasibility for CO-tolerant hydrogenation. Moreover, support can also play an important role in CO-tolerant hydrogenation as it not only determines the coordination environment of supported noble-metal species but also participates in catalyzing the CO-tolerant hydrogenation. Finally, fabrication of bifunctional catalyst for the simultaneous hydrogenation of CO and organic substrate has been demonstrated a successful strategy for CO-tolerant crude H$_2$ storage process.

Until now, CO-tolerant hydrogenation has still been at the initial stage, where plenty of opportunities and challenges exist. To achieve a deeper understanding and progress in this field, there are several aspects to be improved. Firstly, many more catalysts should be designed for CO-tolerant hydrogenation and H$_2$ storage processes so that the underlying trends and mechanisms can be summarized. Some reported noble-metal catalysts based on strong metal-support interaction may be possible for this challenging process. Secondly, more kinds of organic substrates should be considered for CO-tolerant hydrogenation to meet the practical demand in the chemical industry. Last but not least, the industrialization of the above-reviewed CO-tolerant hydrogenation or H$_2$ storage processes should be pushed forward. The use and storage of crude H$_2$ that only contains a small amount of CO poison has been achieved at the laboratory scale, which may be realized in the industry in the near future. For industrial by-product H$_2$ containing other impurities, it is highly desired but challenging to develop multiple-poisons-tolerant catalysts. Motivated by the economic benefits of crude H$_2$/waste H$_2$ utilization, we believe more research will be devoted to this challenging area for extended hydrogen development.

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DECLARATION OF INTERESTS
The authors declare no competing interests.