Highly Chemoselective Reduction of Nitroarenes Using a Titania-Supported Platinum-Nanoparticle Catalyst under a CO Atmosphere

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The discovery that supported gold catalysts can promote CO/H_2O-mediated reduction at ambient temperatures is important to chemoselective synthesis and has gained significant attention in recent years. Whether the alternative Pt group metal (PGM) catalysts can exhibit such exceptional performance is thus an interesting research issue. So far, no PGM catalyst shows activity for CO/H_2O-mediated reduction at ambient temperatures. Here, we demonstrate that it is possible to transform nonactive into highly active and selective catalysts for CO/H_2O-mediated reduction by modulating the interfacial structure and electronic properties at the metal-support interfaces. Thus, highly active and chemoselective hydrogenation Pt, Ir, Rh and Pd catalysts can be prepared by decorating the exposed metal faces with partially reduced support species by means of a simple catalyst activation procedure. In this way, it has been possible to dramatically facilitate the previously unappreciated PGM-catalyzed activation of CO molecules under mild conditions, which can make a significant contribution not only to reveal the intrinsic catalytic potential of supported PGMs but also to establish a more sustainable and industrially-relevant process.

Keywords   nitroarenes, reduction, carbon monoxide, PGM catalysts, strong metal-support interactions

Introduction

Selectivity is one of the key issues in chemical transformations especially when molecules present two or more reacting groups and only one of them has to be transformed.[1] This is, for instance, the case for chemoselective hydrogenations, for which Pt group metal (PGM) is frequently used as catalysts.[2] Nevertheless, it is difficult to control the chemoselectivity of PGM catalysts due to their inherently high hydrogenation activity.[3] An alternative approach that can achieve a higher degree of selectivity control is via transfer hydrogenation (TH) in the presence of various hydrogen donors.[4] In this regard, abundantly available CO/H_2O couple has emerged as a promising hydrogen source particularly suitable for controlled reduction of polar unsaturated bonds.[5] Even more appealing is the fact that using CO directly as a reductant offers distinct advantages as the current practice of multistep high-temperature H_2 gas production process would potentially be simplified into an energy-efficient single step.[6] Despite of these envisioned benefits, the implementation of such a convenient approach for selective reductions remains challenging, largely due to the lack of effective catalyst capable of activating the CO/H_2O couple under mild conditions as well as the perceived problems of the CO-poisoning effect on the traditional PGM catalysts.[7]

In recent years, there has been tremendous interest in developing more benign chemical synthesis facilitated by supported gold nanoparticles (NPs), in part due to the unique capability of this class of catalytic materials to subtly activate a range of industrially important small molecules under mild and clean conditions.[8] As part of our continued efforts to develop innovative catalysis for green synthesis, we recently discovered the outstanding catalytic ability of supported Au NPs for the deoxygenation of nitroaromatics to their corresponding anilines using CO/H_2O as a reducing reagent.[5a] In such CO-mediated reductions, an Au-hydride species was generated in situ from the reaction of H_2O with CO, which led to the highly chemoselective reduction. In short, this provides an efficient alternative that can circumvent the limited hydrogen delivery rate associated with previous Au-catalyzed hydrogenation processes. Essentially, the distinct capability of Au to enable CO/H_2O-activation lies in the much lower adsorption strength of CO on Au than on PGM.[8d] Considering that the adsorption affinity of CO might be tuned in favor of a weaker condition by a rational regulation of the metal-support interaction (MSI) in the PGM catalyst sys-

tem,[9,10] we were motivated to explore Pt NPs deposited on titania bearing tailored MSIs as a possible catalyst for chemoselective reduction of nitro compounds.

Experimental

Catalyst preparation

Pt/SiO$_2$, Pt/Al$_2$O$_3$, Pt/TiO$_2$, Rh/TiO$_2$, Ir/TiO$_2$ and Pd/TiO$_2$ samples were prepared by incipient wetness technique at the desired metal contents. Chloroplatinic acid hexahydrate (H$_2$PtCl$_6$•6H$_2$O, Pt$\geqslant$37.5 wt%), palladium chloride (PdCl$_2$, Pd$\geqslant$60.0 wt%), rhodium chloride hydrate (RhCl$_3$•xH$_2$O, Rh$\geqslant$38.5 wt%), and iridium chloride (H$_2$IrCl$_6$, Ir$\geqslant$35.0 wt%) precursors were used to impregnate the Al$_2$O$_3$ (Evonik, Aluminum oxide C), SiO$_2$ (Evonik, Aerosil 380), and TiO$_2$ (Evonik, P25) supports. As an example, 1.0 g TiO$_2$ was added to 10 mL of an aqueous solution containing 5.3 mg H$_2$PtCl$_6$•6H$_2$O. After a perfect mixing of the slurries, samples were dried at 80 ℃ overnight and then reduced under 5 vol% H$_2$/Ar flow at 300 or 600 ℃ for 2 h to give the corresponding 0.2% Pt/TiO$_2$-300 and 0.2% Pt/TiO$_2$-600 catalysts.

Characterization

Transmission electron microscopy (TEM) observations were carried out using a JEOL 2011 electron microscope operating at 200 kV. High-resolution transmission electron microscopic (HRTEM) images were carried out using Tecnai G2 F20 S-Twin at 200 kV. The size distribution of the metal clusters was determined by measuring about 200 random particles on the images. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization was performed with a ThermoFisher Nicolet 6700 FT-IR spectrometer equipped with a DRIFTS cell. The catalyst (20 mg) was pretreated with He at 250 ℃ for 1h before being cooled down to 25 ℃ to collect the background spectra. Subsequently, the sample was exposed to a flow (20 mL•min^{-1}) of 1 vol% CO/He for 1 h followed by purging with pure He for 30 min to remove the gas phase CO. Water-gas shift temperature programmed surface reaction (WGS-TPSR) was run in a Micromeritics AutoChem HP 2950 instrument equipped with a mass spectrometer. For each experiment, the catalyst was stabilized in 1 vol%CO-3 vol%H$_2$O-He for 20 min at 40 ℃ before being heated up to 300 ℃ at 10 ℃•min^{-1}.

General procedure for the reduction of nitroarenes with CO/H$_2$O

A 25-mL Hastelloy-C high pressure Parr reactor was used to carry out the liquid phase reduction reaction. A mixture of 4-nitrostyrene (0.5 mmol), supported metal catalysts (metal 0.5 mol%), organic solvent (2 mL), water (1 mL) was loaded into the reactor. The reactor was stirred at a rate of 800 r•min^{-1} under 1 MPa CO for a specific reaction time at a given temperature. After reac-

tion, the conversion and product selectivity were periodically determined by GC analysis (Agilent GC-6820 gas chromatograph equipped with a capillary column DB-Wax (30 m$\times$0.25 mm) and FID detector) using *n*-decane as an internal standard. The identification of the products was performed by using a GC-MS spectrometer.

Results and Discussion

To begin our studies on the effect of MSI on Pt catalysts for CO-mediated reduction, a series of Pt/TiO$_2$ catalysts have been prepared containing different amounts of Pt that reduced under different temperature in 5 vol% H$_2$/Ar atmosphere. As determined by TEM measurements, the average particle size of Pt NPs increases from 2.1 to 3.5 nm when the Pt content is increased from 0.2 to 2 wt%. Notably, in the case of 0.2 wt% Pt/TiO$_2$, small size distributions of Pt NPs were kept when the reduction temperature increased from 300 to 600 ℃, while a significant aggregation of Pt NPs to 7 nm was observed for 2 wt% Pt/TiO$_2$ under elevated reduction temperature. The electron microscopic results have been complemented with a structural characterization of the Pt metal surface by CO adsorption combined with DRIFTS measurements. This was done in order to gain information about the available CO adsorption sites on these different Pt/TiO$_2$ samples (Figure 1). A significant coverage of CO on Pt is indicated by linear CO species with peaks at 2088 and 2034 cm^{-1} and bridged CO species of a broad band around 1840 cm^{-1} was observed in the 2 wt% Pt/TiO$_2$-300 catalyst.[11] The dominant IR band at 2088 cm^{-1} is related to extended Pt crystal faces while IR band at 2034 cm^{-1} corresponds to
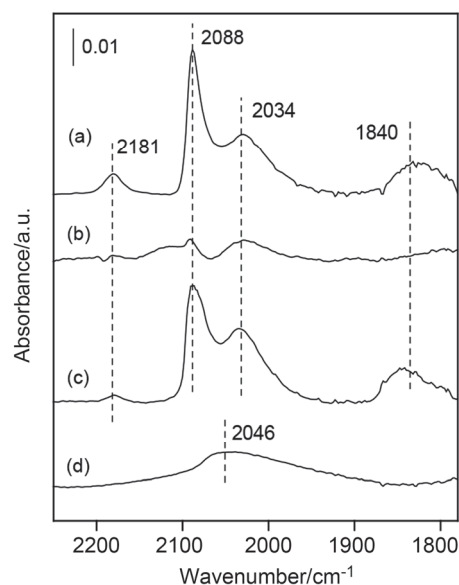
Figure 1 DRIFT spectra of CO desorption of (a) 2% Pt/TiO$_2$-300, (b) 2% Pt/TiO$_2$-600, (c) 0.2% Pt/TiO$_2$-300, (d) 0.2% Pt/TiO$_2$-600.

Pt sites of low surface coordination. A very weak band is detected at higher frequency of 2181 cm^{-1} indicating the presence of oxidized Pt species in such low-temperature reduced catalyst. Similar IR bands are also observed in 2% Pt/TiO$_2$-600 inspite of a sharp decrease of the intensity of CO adsorption due to the observable growth of Pt particles after high temperature (HT) reduction. In the case of 0.2% Pt/TiO$_2$-300, the intense linear CO adsorption at low-coordinated Pt sites (2034 cm^{-1}) reflects the smaller particle size at a low Pt content. Dramatically, with the HT-reduced 0.2% Pt/TiO$_2$-600 catalyst, only one band at 2046 cm^{-1} related to Pt-Ti interface sites is observed without the observation of linear or bridged CO adsorption on Pt aggregates.[12a]
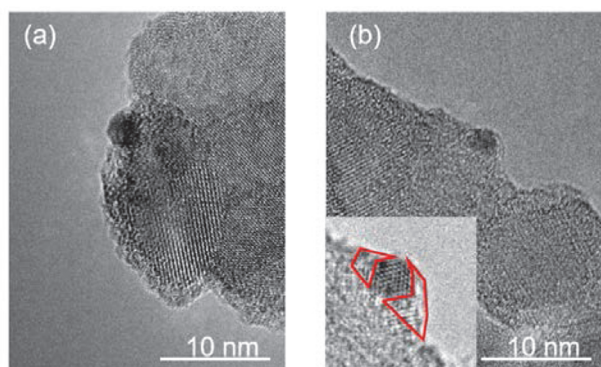
**Figure 2** HRTEM images of (a) 0.2% Pt/TiO$_2$-300 and (b) 0.2% Pt/TiO$_2$-600.

It has been reported that high reduction temperatures of Pt/TiO$_2$ catalysts produce a decoration of Pt NPs with TiO$_x$ species that increases the interface between Pt and TiO$_2$,[12,13] which is consistent with the CO adsorption results given above. This was further confirmed by HR-TEM measurement. According to the HRTEM image of 0.2% Pt/TiO$_2$-600 (Figure 2b), Pt NPs were partially covered by a thin layer of TiO$_x$ while the encapsulation was not observed in 0.2% Pt/TiO$_2$-300. From all these evidences, we can infer that a strong metal-support interaction (SMSI) occurs between Pt NPs and TiO$_2$ support. The formation of SMSI has been proved to significantly alter the geometrical arrangement[10h] and electronic property[9] of metal NPs. In our case, the SMSI between Pt and TiO$_2$ effectively stabilizes Pt NPs from sintering under relatively high reduction temperature. Such geometrical encapsulation and the electronic modification of Pt NPs by reduced TiO$_x$ nanolayers lead to a significant suppression of CO chemisorption on active Pt sites, which might help Pt tolerate CO thus promoting the Pt catalyzed CO-mediated reduction.

To check this hypothesis, we choose the selective reduction of 4-nitrostyrene (**1a**) to 4-aminostyrene (**2a**) as the reaction model. For these initial assays the conditions studied were 100 ℃, 1 MPa CO, and a catalyst loading of 0.5 mol% (the amount of the active metal species relative to the substrate). Notably, 0.2% Pt/TiO$_2$-600, in which a favorable SMSI formed under a rela-

Table 1 Reduction of 4-nitrostyrene under a CO atmosphere in the presence of H$_2$O^a
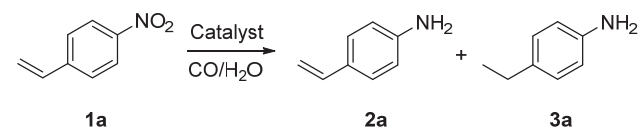
Entry	Catalyst	Temp./℃	CO/MPa	Conv./%	Select./% 2a	3a	azo
1	0.2%Pt/TiO$_2$-300	100	1	12	>99	—	—
2	0.2%Pt/TiO$_2$-600	100	1	66	>99	—	—
3	2%Pt/TiO$_2$-300	100	1	Trace	—	—	—
4	2%Pt/TiO$_2$-600	100	1	Trace	—	—	—
5	0.2%Pt/SiO$_2$-300	100	1	Trace	—	—	—
6	0.2%Pt/SiO$_2$-600	100	1	Trace	—	—	—
7	0.2%Pt/Al$_2$O$_3$-300	100	1	Trace	—	—	—
8	0.2%Pt/Al$_2$O$_3$-600	100	1	Trace	—	—	—
9	0.2%Pt/CeO$_2$-300	100	1	11	69	—	31
10	0.2%Pt/CeO$_2$-600	100	1	42	82	—	18
11^b	0.2%Pt/TiO$_2$-600	100	—	>99	—	>99	—
12	0.2%Pt/TiO$_2$-600	150	1	97	>99	—	—
13	0.2%Pt/TiO$_2$-600	80	1	15	>99	—	—
14	0.2%Pt/TiO$_2$-600	100	2	53	>99	—	—
15	0.2%Pt/TiO$_2$-600	100	0.5	40	>99	—	—

^{a} Reaction conditions: 4-nitrostyrene (0.5 mmol), catalyst (Pt: 0.5 mol%), ethanol (2 mL), water (1 mL), 2 h. ^{b} H$_2$ (1 MPa).

Scheme 1 Intermolecular competitive reaction of nitrobenzene and styrene using 0.2 Pt/TiO$_2$-600 in the presence of CO/H$_2$O.
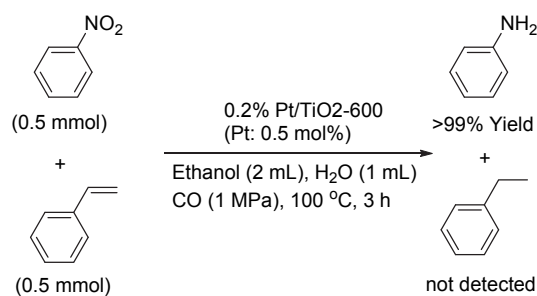
tively high temperature of 600 ℃, shows the best performance (Table 1, Entry 2). On the contrary, 0.2% Pt/TiO$_2$-300 has only very limited activity (Entry 1) while the reduction hardly occurs and no trace of **2a** could be detected using 2% Pt/TiO$_2$ catalysts (Entries 3, 4) as the strong adsorption of CO on Pt sites inhibited the further activation of substrate molecules. To further confirm the participation of SMSI in this CO/H$_2$O-mediated reduction, 0.2% Pt/CeO$_2$, 0.2 Pt/Al$_2$O$_3$, 0.2% Pt/SiO$_2$ catalysts were prepared and reduced at 300 ℃ and 600 ℃, respectively. For non-reducible oxides like SiO$_2$ and Al$_2$O$_3$ supported Pt NPs, there are no SMSI between Pt sites and support, which are consistently

inactive in such CO-mediated process (Entries 5−8). On the other hand, partially reducible CeO_2 shows similar behavior with TiO_2 that the high reduction temperature enhanced the activity of Pt/CeO_2 catalyst, although the selectivity decreases due to the formation of azo compounds (Entries 9, 10). These results confirm that the combination of small-size Pt NPs with a suitable TiO_2 support treated at high reduction temperature of 600 ℃ could achieve the best activity and selectivity. Raising the reaction temperature to 150 ℃ observably decreasing the reaction time while under a lower temperature of 80 ℃ the reaction can still occur at a moderate rate (Entries 12, 13). The effect of CO pressure shows a volcanic curve indicating that CO adsorption on catalyst surface is the key factor in this reaction (Entries 14, 15).

It is noteworthy that complete chemoselectivity for nitro groups in the presence of olefinic functionalities was achieved in such SMSI-induced $Pt-CO/H_2O$ reduction system. In sharp contrast, by using H_2 as reducing agent instead of CO/H_2O, we observed substantial formation of the over-reduced product of 4-ethylaniline (**3a**) (Table 1, Entry 11). This result is consistent with other reported $Pt-H_2$ reduction systems as the homolytic cleavage of H_2 often leads to unselective hydrogenation of polar and nonpolar unsaturated groups.[3] The high chemoselectivity of 0.2% Pt/TiO_2-600 for nitro functionalities was further investigated in the intermolecular competitive reaction of nitrobenzene and styrene. Interestingly, nitrobenzene was completely reduced to aniline while styrene remained unreacted (Scheme 1). These results clearly demonstrated that the $Pt-CO/H_2O$ catalytic system showed complete chemoselectivity for nitro functionalities in the presence of inter- and intramolecular olefinic functionalities. Together with the fact that no H_2 was detected in the gas phase after the CO/H_2O-mediated reduction, the $Pt-CO/H_2O$ reduction system is supposed to proceed through active polar hydrogen species generated by CO induced H_2O activation on the interface between Pt NPs and TiO_2, facilitating the desired reduction of the polar nitro groups.
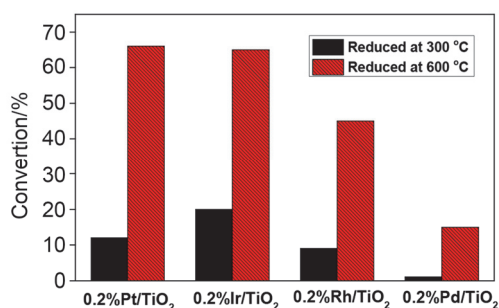
Figure 3 Results of CO/H_2O-mediated reduction of **1a** on PGM catalysts (conditions: **1a** 0.5 mmol, metal 0.5 mol%, ethanol 2 mL, H_2O 1 mL, 100 ℃, 2 h).

Given the encouraging results obtained in converting the "nonactive" Pt into a highly active and selective Pt catalyst for CO/H_2O-mediated reduction by modulating the metal-support interaction in the Pt/TiO_2 system, we were curious to find if the concept could be extended to other metals. Results from Figure 3 show that Ir, Rh and Pd, which are almost inactive for the CO/H_2O-mediated reduction of **1a**, can now be converted into active and selective catalysts by supporting them on TiO_2 and reducing at 600 ℃. To explain the strong effect of the catalyst activation conditions on Pt/TiO_2, as well as on the other PGM catalysts, we can assume that the SMSI occurred between metals and TiO_2 support can be manifested by modifying the electron density of small clusters by charge transfer from partially reducible supports, through the unique properties of metal-support borderline sites, and/or by decoration of the metal by mobile support.[9,10] To gain insight into the origin of the SMSI-enhanced CO/H_2O-mediated reduction activity of PGM catalysts, WGS-TPSR was performed for the typical 0.2% Pt/TiO_2-300 and 0.2% Pt/TiO_2-600. As shown in Figure 4, 0.2% Pt/TiO_2-300 is almost inactive below 200 ℃ in this TPSR mode, while the H_2 formation over 0.2% Pt/TiO_2-600 occurs at a lower temperature and a much higher rate. These results demonstrated that the CO-induced H_2O activation is the first and most important step in this CO/H_2O-mediated reduction. Together with HRTEM and DRIFTS results, the formation of SMSI between PGM and TiO_2 at high reduction temperature significantly changes the CO adsorption characteristics on active PGM sites, promoting the WGS pathway and sequential reduction process.
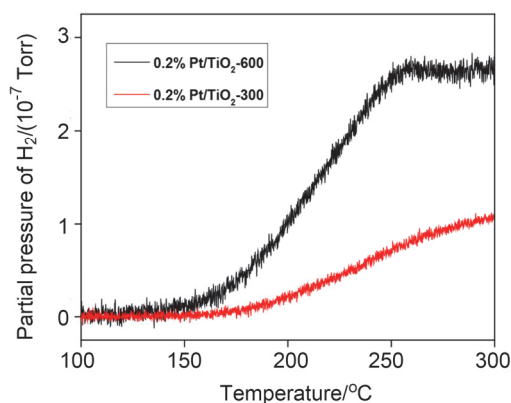
Figure 4 WGS-TPSR (1%CO-3%H_2O-He, 20 mL•min^{-1}; 100 mg sample) data for the H_2 produced.

Conclusions

In summary, we have demonstrated an efficient and chemoselective 0.2% Pt/TiO_2-600 catalyst for reduction of nitroarenes in the presence of other reducible functional groups to give the corresponding anilines in high yields using CO/H_2O as hydrogen source. The unusual performance of this catalyst can be attributed to the SMSI formed between small-size Pt NPs and TiO_2 under relatively high reduction temperature, which geometrically and electronically enhances the tolerance of

Pt to CO poisoning. We anticipate this conception potentially provides a general and simple design of PGM catalysts that can be applied to varied CO-mediated catalytic processes.

Acknowledgement

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