Significance of surface oxygen-containing groups and heteroatom P species in switching the selectivity of Pt/C catalyst in hydrogenation of 3-nitrostyrene

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Abstract: The selectivity of 3-nitrostyrene (NS) hydrogenation over 0.5 wt.-% Pt/activated charcoal (ACH) can be switched simply by changing reduction temperature. When the reduction temperature was 150 ℃, the 93% selectivity to 1-ethyl-3-nitrobenzene (ENB) was obtained at 95% conversion. When it was 450 ℃, 96% selectivity was switched to 3-aminostyrene (AS) at 91% conversion. For low-temperature, surface acidic groups interact with $–NO_2$ and make C=C more likely to interact with Pt, which facilitates the hydrogenation of C=C. For high-temperature, P interact with Pt and form Pt-POx complex, on which $–NO_2$ was likely to be adsorbed, facilitating the selective production of AS.

Keywords: Pt/C, Nitrostyrene, Selectivity.

1. Introduction

For carbon-supported metal catalysts, the surface oxygen functional groups (SOFGs) and heteroatom dopants[1] of carbon materials could influence the dispersion of metal nanoparticles thereon[2], the adsorption of organic substrates[3] and metal precursors[4]. Selective hydrogenation of 3-nitrostyrene (NS) is a useful model reaction for investigation of the catalysis of supported metal catalysts[5]. Some results indicate that the product selectivity of NS ($-NO_2$ or C=C) can be controlled by reaction conditions for the same supported metal catalysts but those catalytic systems need complicated catalyst synthesis procedures and unfavorable additives. Herein, we expect that the product selectivity of conventional carbon-supported metal catalysts could be modified by changing the amount and nature of SOFGs and heteroatom of the supports, which would contribute directly or indirectly to the substrate adsorption and the catalytic performance of metal active species on their surface.

2. Experimental

A 0.5 wt.-% Pt was loaded on carbon supports by incipient wetness method. The catalysts were characterized by using TEM, FTIR, TPR and CO-DRFT. The hydrogenation was carried out with a 50 mL autoclave, and the products were analyzed by using GC with a flame ionization detector.

3. Results and discussion

At first, for examining the influence of SOFGs and heteroatom on the catalytic performance of Pt/C catalyst, the catalysts were reduced under different temperatures and the carbon supports treated with HNO_3. As shown in Table 1, the product selectivity is significantly different between the catalyst reduced at 150 ℃ and those at 450 ℃, but the sizes of Pt nanoparticles are comparable among these catalysts. Hence, the size of supported Pt nanoparticles is not a factor responsible for the selectivity switching by the reduction temperature as observed. This switching of the product selectivity may be ascribed to actions of surface SOFGs and surface hetero P species. For the low-temperature reduced catalyst, surface acidic groups present close to Pt nanoparticles (~ 2 nm) would interact with the nitro group of a NS molecule and make its vinyl group more likely to interact with the surface active metal species of Pt nanoparticles; this facilitates the hydrogenation of the latter and produces ENB selectively. For the high-temperature reduced catalyst, however, a NS molecule is likely to be adsorbed with its nitro group, facilitating the selective production of AS via its hydrogenation. The $Pt^{\delta+}/Pt^0$ ratio is larger for Pt on HNO_3-treated carbon than on untreated one for either Pt/ACH or Pt/AC samples (entry 1-4). That is, the surface of supported Pt nanoparticles becomes likely to expose more $Pt^{\delta+}$ species by the HNO_3 treatment of carbon supports. This suggests the existence of metal-support interactions affecting the chemical state of exposed Pt species. The XPS results demonstrated the interactions between Pt and P species at the high reduction temperature of 450 ℃, that Pt-POx composites were formed and promoted the selective adsorption/activation of polar nitro group, resulting in an enhanced selectivity to product AS. Simultaneously, the surface of supported Pt nanoparticles is partially covered by Pt-POx composites and the total activity is decreased significantly. As illustrated in Figure 2, the supported Pt nanoparticles could cooperate with SFOGs and hetero P atoms in the low-temperature and high-temperature reduced Pt/C catalysts, which causes the switching of the product selectivity in NS hydrogenation.

Table 1. Catalytic performances of Pt/ACH-T catalysts in 3-nitrostyrene hydrogenation.

Entry	Catalyst	Time (min)	Conversion (%)	Selectivity (%)				Particle Size(nm)	$Pt^{\delta+}/Pt^0$	Acid groups (Num/nm^2)	P wt.%
				AS	ENB	EA	Others				
1	Pt/ACH-150	5.0	95	0	93	4	3	2.1	0.8	0.15	1.68
2	Pt/(ACH-HNO_3)-150	180	97	1	97	0	2	2.6	2.6	0.82	0.455
3	Pt/AC-150	5	94	5	53	35	7	1.7	0.5	0.08	0.034
4	Pt/(AC-HNO_3)-150	240	85	2	95	2	1	3.5	2.3	-	0.034
5	Pt/ACH-450	1440	91	96	0	1	3	2.5	2.5	0.04	1.68
6	Pt/(ACH-HNO_3)-450	60	98	0	68	24	8	2.5	2.3	0.27	0.455
7	Pt/AC-450	60	99	35	0	56	9	0.5	0.5	0.03	0.034
8	Pt/(AC-P)-450	360	99	83	0	9	8	0.9	0.9	-	1.700

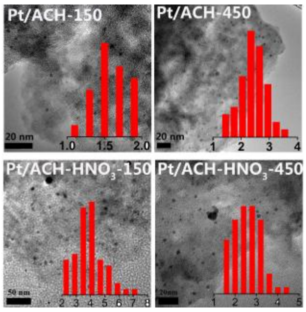

Figure 1. TEM images of catalysts.

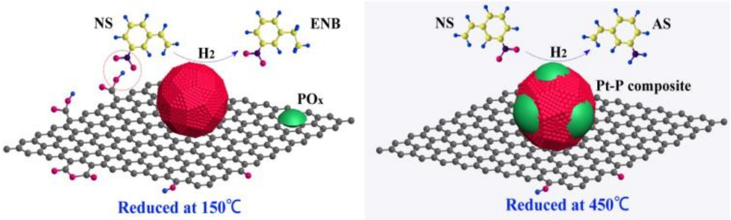

Figure 2. Schematic illustration of the selective hydrogenation of NS on Pt/ACH

4. Conclusions

The present work demonstrates the significance of SOFGs and heteroatom P species on the catalytic performance of carbon-supported 0.5 wt.-% Pt catalysts in the selective NS hydrogenation. It is interesting that the product selectivity can be completely switched by the reduction temperature. The cooperation of Pt nanoparticles with SOFGs and the heteroatom P can adjust the selective adsorption/activation of NS on the surface of Pt/C catalysts reduced at different temperatures. These results provide useful knowledge for design and synthesis of heterogeneous metal catalysts for selective hydrogenation or other reactions with organic substrates including two or more functional groups in different nature like vinyl and nitro groups of NS.

References

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