



Preparation, structural characterization of a novel egg-shell palladium sulfide catalyst and its application in selective reductive alkylation reaction

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Received 2 May 2012

Available online 23 September 2012

Abstract

A novel egg-shell Pd–S catalyst with palladium metal as the core and a membrane of palladium sulfide as the surface has been prepared by sulphidizing Pd/C with H₂S. This catalyst is effective for the reductive alkylation of *p*-amino diphenylamine (PADPA) and methylisobutyl ketone (MIBK) to afford *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (DBPPD) with conversion up to 99.42% and selectivity to 97.46%. Comparing with the other common palladium sulfide catalysts, the membrane of palladium sulfide on the surface and the core of palladium metal cause the Pd on the surface of the new catalyst in a lower sulfur coordination, which improves its activity. Our result indicates that this new egg-shell Pd–S/C is an efficient hydrogenation catalyst.

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Keywords: H₂S; Palladium sulfide; Egg-shell; Reductive alkylation

Precious metal catalysts are widely used in the various reductive reactions for their high activity, easy separation and reusability. But the high activity of these catalysts always brings poor selectivity for the organic compounds with multiple reducible functionalities. In recent years, precious metal sulfides have attracted much attention as an excellent catalyst for the reductive reaction due to their high catalytic selectivity [1–6]. For example, platinum sulfide and ruthenium sulfide are applied to hydrogenation of halogen-containing nitro compounds to amines with high selectivity and no dehalogenation [2,3] and reductive alkylation [1,7]. However, the application of palladium sulfide catalyst is limited for its lower activity leading to harsh reaction conditions and poor conversion during the hydrogenation reactions [1,7]. It is desirable to design new structure of precious metals sulfides catalysts with high reactivity and selectivity. Here we report the preparation and structural characterization of a novel egg-shell Pd–S catalyst with palladium metal as the core and a membrane of palladium sulfide as the surface. This catalyst can catalyze the reductive alkylation of *p*-amino diphenylamine (PADPA) and methylisobutyl ketone (MIBK) to afford

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N-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (DBPPD) with high selectivity and higher activity. Our result suggests that the special catalyst can efficiently promote chemoselective hydrogenations.

1. Experimental

Preparation of egg-shell Pd–S/C catalyst: 10% Pd/C and water were mixed in the weight ratio of 1 to 20, then an excess of H₂S was passed into the slurry solution at 40 °C. The resulting catalyst was washed with water until the pH to 7 and then dried in the vacuum at 110 °C for 10 h. Preparation of PdS/C catalyst: a desired volume of H₂PdCl₄ aqueous solution with the nominal Pd loading of 10 wt% was added into an aqueous suspension of activated carbon in a weight ratio of activated carbon to water at 1:20, then an excess of H₂S was passed into the slurry solution at 40 °C. The resulting catalyst was washed with water until the pH is 7. The obtained product was dried in the vacuum at 110 °C for 10 h and then treated with 10% H₂S in hydrogen at 200 °C for 2 h.

Reductive alkylation was carried out at 3 MPa of hydrogen for 4 h in a 75 mL stainless steel autoclave (Parr Instruments), which contained PADPA (3.7g, 0.02 mol) and MIBK (10 mL, 0.08 mol) and 0.037 g catalyst. The final products were analyzed by a gas chromatography (Shimadzu GC-14B) equipped with an SE-30 capillary column and an FID.

2. Results and discussion

The novel egg-shell Pd–S/C catalyst has been characterized by EDS. The structure of the catalyst has been determined by XRD and XPS. The EDS data (Table 1) showed that the catalyst contained a certain amount of S. According to our preparation method, we induced that the S of the egg-shell Pd–S/C catalyst should be combined with Pd strongly, and not be just a physical adsorption on the activated carbon.

The egg-shell Pd–S/C catalyst was further examined by XRD and XPS to determine its structure. The XRD patterns (Fig. 1) showed that there were only diffraction peaks of Pd, and no peaks of palladium sulfides or other sulfides were observed. This result indicated that S did not enter the bulk to form palladium sulfide as a crystal. Considering the content of S in the egg-shell Pd–S/C catalyst was 1.43%, we suggested that S should just covered Pd particles as a membrane. Our conjecture was further confirmed by XPS spectra of the egg-shell Pd–S/C catalyst (Fig. 2). The peaks

Table 1
Elemental composition of egg-shell Pd–S/C catalyst.

Element	C	O	S	Pd
Content (%)	81.64	7.31	1.43	9.62

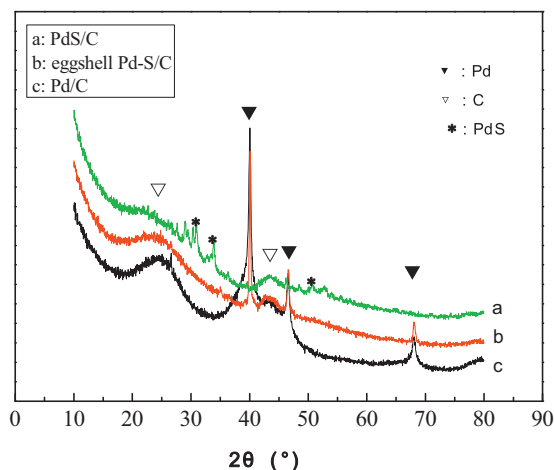


Fig. 1. XRD pattern of catalysts.

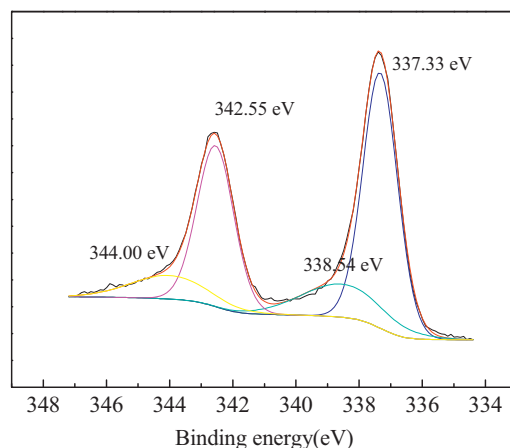


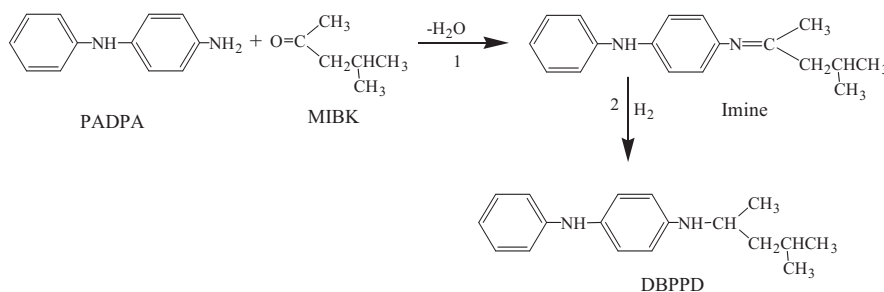
Fig. 2. Pd 3d XPS spectra of the egg-shell Pd-S/C.

Table 2
Properties of Pd/C, PdS/C and egg-shell Pd-S/C catalysts.

Catalyst	CO chemisorption uptake (ml/g)	Surface area (m ² /g)	Average pore radius (nm)
Pd/C	3.5	1517	0.94
PdS/C	0	1460	0.93
Egg-shell Pd-S/C	0	1476	0.94

of Pd 3d_{5/2} spectra at 338.84 eV and 337.33 eV of the XPS spectra showed that there was interaction between S and Pd, and the states of Pd should be +4 and +2, which indicated that Pd existed as palladium sulfide complex on the surface of the egg-shell Pd-S/C catalyst. Furthermore, no binding energy peak of Pd(0) was found at 3d_{5/2} spectra, which indicated that there was no Pd(0) on the surface of the catalyst. The result was also proved by the CO chemisorption uptake (Table 2). The CO chemisorption uptake showed that the egg-shell Pd-S/C catalyst could not absorb CO anymore, suggesting that there was no Pd(0) on the surface as well. The surface area and average pore radius of Pd/C, PS/C and egg-shell Pd-S/C are similar. All these results demonstrated that egg-shell Pd-S/C catalyst had such a structure with palladium metal as the core and a membrane of palladium sulfide as the surface.

In order to investigate the reactivity of the novel egg-shell Pd-S catalyst, it was applied to reductive alkylation reaction of PADPA and MIBK. The reaction started from a condensation reaction between PADPA and MIBK, affording imine as an intermediate, and then imine was hydrogenated in the presence of catalyst to form DBPPD (Scheme 1). PADPA, imine and DBPPD were easy to undergo hydrogenolysis to some small molecule by-products, such as aniline, using ordinary Pd catalysts. And a part of imine remained and could not be hydrogenated completely in the case of lowly active hydrogenation catalyst.



Scheme 1. Reaction pathways.

Table 3
Reductive alkylation over Pd/C, PdS/C and egg-shell Pd–S/C catalysts.

Catalysts	Reaction temperature (°C)	Conversion ^a (%)	Selectivity (%)		
			DBPPD	Imine	Others
Pd/C	160	100	62.81	0	37.19
	200	100	36.53	0	63.47
PdS/C	160	54.33	60.87	37.54	1.59
	200	90.17	97.03	0.87	2.10
Egg-shell Pd–S/C	160	65.27	72.43	25.95	1.62
	200	99.42	97.64	0.32	2.04

^a The reaction time is 4 h.

The catalytic performance of the egg-shell Pd–S/C catalyst was tested comparing with the traditional Pd/C and PdS/C catalysts in reductive alkylation to DBPPD. The results were summarized in Table 3. We can see that the egg-shell Pd–S/C showed both high activity and high selectivity. The novel catalyst not only kept the high selectivity as the normal palladium sulfide catalyst but also improved the activity in chemoselective reductive reaction.

3. Conclusion

An egg-shell Pd–S/C catalyst with palladium metal as the core and a membrane of palladium sulfide as the surface was prepared by sulphidizing Pd/C with H₂S. The palladium sulfide on the surface of the new kind of Pd–S/C catalyst provides high selectivity as common palladium sulfide catalysts, and its core of palladium metal causes the Pd on the surface in a lower sulfur coordination than common palladium sulfide catalysts, which improves its activity. The egg-shell Pd–S/C is expected to be an excellent hydrogenation catalyst with combination of high selectivity and good activity.

Acknowledgments

This work was financially supported by Zhejiang Provincial Natural Science Foundation of China (No. LY12B03009) and Program from Science and Technology Department of Zhejiang Province (No. 2011R09020-03).

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