

# Size Dependence of Pyrrole Hydrogenation over Monodisperse Platinum Nanoparticles Supported on Mesoporous Silica

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## Introduction

During fuel processing, heteroatoms are commonly removed from heteroatom aromatic molecules by hydrotreating.<sup>[1]</sup> If not removed to low enough levels, heteroatom aromatic molecules poison downstream catalysts, which consist of precious metals and/or zeolites, and pollute the environment. Here, we report the influence of Pt nanoparticle (NP) size on the activity for hydrogenation of pyrrole and subsequent ring opening of pyrrolidine.

## Materials and Methods

Hydroxyl terminated polyamidoamine dendrimers (4th generation) were used as the templating and capping agent for the synthesis of ultrasmall Pt NPs (0.8, 1.0, and 2.0 nm).<sup>[2]</sup> Pt NPs (1.5, 2.9, and 5.0 nm) were synthesized with polyvinylpyrrolidone.<sup>[3,4]</sup> After loading onto mesoporous silica, Pt loadings and dispersions were measured by elemental analysis (ICP-MS, Galbreath Laboratories) and H<sub>2</sub> chemisorption isotherms (Autosorb-I), respectively. Pt NPs and Pt/SBA-15 catalysts were also characterized by TEM (FEI Tecnai G2 S-Twin). Catalytic activities for ethylene and pyrrole hydrogenation were measured in a laboratory scale flow reactor with the gas composition analysis by gas chromatography (HP 5890 Series II).

**Table 1. Strategy for Pt NP size control and description, characterization, and initial ethylene hydrogenation activity of Pt/SBA-15 catalysts.**

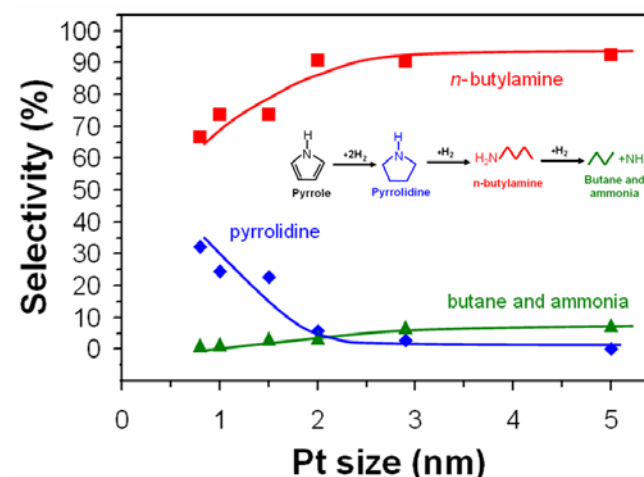
	0.8 nm	1.2 nm	1.5 nm	2.0 nm	2.9 nm	5.0 nm
	dendrimer	dendrimer	PVP	dendrimer	PVP	PVP
Pt size (nm)	atoms per NP	% Pt	Dispersion (%)	TOF (s <sup>-1</sup> ) <sup>(a)</sup>		
0.8	20	0.6	100	3.5		
1.0	40	0.6	100	2.7		
1.5	127	0.2	34	12.6		
2.0	282	0.6	58	11.4		
2.9	926	0.3	25	14.5		
5.0	4747	0.3	21	15.3		

<sup>(a)</sup> Initial activity acquired at 295 K in 10 torr C<sub>2</sub>H<sub>4</sub> and 100 torr H<sub>2</sub> with a He balance.

## Results and Discussion

Sizes, Pt loadings, and dispersions of the Pt NPs are presented in Table 1. Additionally, ethylene hydrogenation rates, as expected for a structure insensitive reaction<sup>[5]</sup>,

were similar to Pt single crystals. The slightly lower activities of the ultrasmall Pt NPs are believed to be caused by increased difficulty in reduction and this phenomenon is currently under greater investigation. For pyrrole hydrogenation, ring hydrogenation was similar (TOF ~ 70 ks<sup>-1</sup>) regardless of size. Selectivity differences (Figure 1) were caused by ring opening (n-butylamine formation) occurring more slowly over Pt NPs smaller than 2 nm. This observation was correlated to the N of n-butylamine binding strongly to the surfaces of smaller NPs and is consistent with the reducibility and/or the coordination of the Pt surface atoms decreasing with particle size. Pt NP shape (e.g., cubic and nanopolyhedra) also influenced the selectivity of pyrrole hydrogenation with the (100) surface of the Pt nanocubes promoting the ring opening to n-butylamine.



**Figure 1.** Pyrrole hydrogenation selectivity (color coordinated to Scheme 2) as a function of Pt NP size (T = 413 K and 11 ± 2% conversion). Feed was 4 torr of pyrrole and 400 torr of H<sub>2</sub> with a He balance.

## Significance

Removal of N-containing aromatic molecules is important to fuel processing. Moreover, poisoning of downstream precious metal catalysts is important when removal is ineffective.

## References.

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