Thermochemically Stable Poison-Containing Polymer Support for Highly Selective Partial Alkyne Hydrogenation[1]

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Abstract: In this work, we supported Pd catalysts on a thermochemically stable covalent organic polymer containing diphenyl-sulfide moieties, which can simultaneously act as a catalyst support and a "permanent" selectivity modifier. The entire Pd surfaces were ligated by sulfur groups of polymer framework, which behaved like a "molecular gate" that enabled exceptionally discriminative adsorption of alkynes over alkenes. This led to highly selective partial hydrogenation of various alkynes to alkenes with minimal conversion of other functional groups. The catalytic performance was retained over a long reaction period due to the high thermochemical stability and suppressed coke formation.

Keywords: Chemoselectivity, Hydrogenation, Polymer.

1. Introduction

Partial hydrogenation of alkynes to alkenes is an important model reaction for studying chemoselectivity, and also a key transformation in fine chemical synthesis. Various modifiers such as carbon monoxide and heteroatom-containing (N, S, P) organic molecules are introduced to enhance the alkene selectivity of unmodified Pd catalyst. However in order to maintain selectivity, the molecular modifiers should be continuously supplied to the reaction feeds because they are readily leached out during reaction.

In the present work, we supported Pd catalysts on a thermally stable covalent organic polymer containing diphenyl sulfide moieties, which can act as a 'permanent' selectivity modifier as well as a catalyst support (Figure 1). The sulfide groups in the polymer can ligate (or poison) the surfaces of the Pd clusters and act as a 'molecular gate' that enable the discriminative adsorption of alkynes over alkenes. This leads to highly selective hydrogenation of various alkynes to alkenes with minimal conversion of other functional groups.

2. Experimental

A sulfur-containing covalent organic polymer (COP) was synthesized by nucleophilic substitution of cyanuric chloride with 4,4'-thiobisbenzenethiol (Figure 1). 1 wt% Pd catalysts supported on the COP (Pd/COP) and γ-Al_2O_3 (Pd/γ-Al_2O_3) were synthesized by conventional impregnation followed by hydrogen reduction. Gas phase alkyne selective hydrogenation reactions were carried out in a stainless plug-flow reactor. The alkene selectivity was compared at similar conversion level (88% – 95%).

3. Results and discussion

EXAFS indicated that the Pd/COP catalyst possesses not only Pd-Pd but also Pd-S coordination. It means that Pd clusters are effectively ligated by the sulfur groups

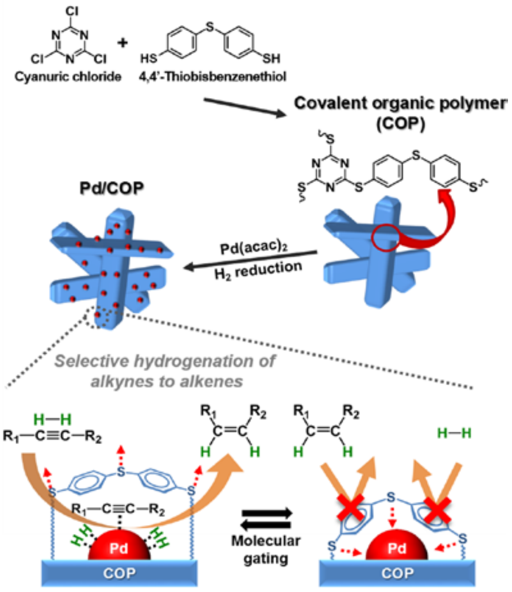


Figure 1. Synthesis of Pd/COP and its hydrogenation mechanism

of the polymer framework. COP has remarkably high thermal stability up to 503 K even under catalytically relevant condition (*i.e.*, in the presence of embedded Pd catalyst and under H_2 atmosphere) due to its highly cross-linked aromatic structure.

For acetylene partial hydrogenation in an ethylene-rich feedstock (ethylene/acetylene = 82), Pd/COP showed 70 – 80% ethylene selectivity even at a complete acetylene conversion level (>99%) and its performance did not significantly decrease over a long reaction period (>15 days) due to remarkably high thermochemical stability of the polymer (Figure 2). This catalyst also showed higher chemoselectivities in converting alkynes to desired alkenes with minimal over-hydrogenation, isomerization, and hydrogenolysis of various side functional groups (Table 1).

Interestingly, Pd/COP does not adsorb H_2 according to our hydrogen chemisorption experiment. It means that Pd/COP lacks H_2 activation ability because the entire Pd surface is 'poisoned' by the sulfur groups. H_2-D_2 exchange experiments showed that only alkyne could adsorb on the Pd surface and enable 'cooperative' adsorption of H_2. It means that alkyne can compete with sulfur groups of COP for the adsorption on Pd surface, while alkene with weaker adsorption strength cannot. In other words, the sulfur groups of COP ligating the Pd surface act as a 'molecular gate' that selectively enables the adsorption of alkynes over alkene (Figure 1).

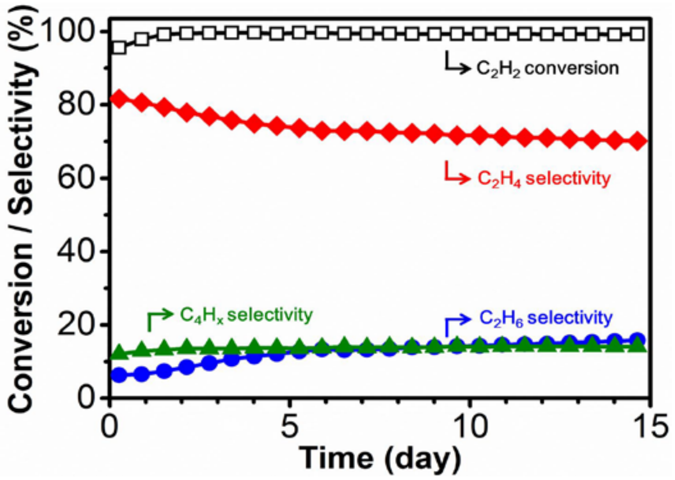
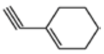
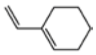
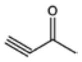
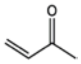
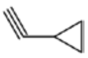
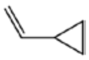
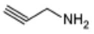
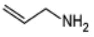


Figure 2. Acetylene conversion and product selectivities during hydrogenation reaction in an ethylene-rich stream (reaction condition: 0.6 kPa C_2H_2, 0.9 kPa H_2, and 49.3 kPa C_2H_4 in N_2 balance at 393 K).

Reaction	Substrate	Desired product	Pd/COP		Pd/γ-Al_2O_3	
			TOR[a]	Sel[b]	TOR[a]	Sel[b]
1			0.18	85.6	2.69	37.4
2			0.19	85.1	0.97	20.3
3			0.19	89.0	0.98	42.5
4			0.19	93.7	0.94	21.6
5			0.19	91.9	0.98	12.4
6			0.04	94.3	0.89	40.8

[a] TOR: $mol_{reactant}\ mol_{Pd}^{-1}\ sec^{-1}$

[b] Sel: selectivity (%) is compared at similar conversion level

Table 1. Hydrogenation of various alkyne compounds

4. Conclusions

In the present work, we demonstrated that the Pd catalysts supported on a thermally stable crosslinked polymer containing diphenyl sulfide linkages can be used as a highly chemoselective catalyst for partial hydrogenation of various alkynes to desired alkenes products. Discriminative adsorption behaviors of the reactant/intermediate on the sulfur poisoned Pd catalysts surface led to the high alkene production selectivity. It is reasonably expected that thermally stable polymers containing various poison-like functional groups can be used as a unique catalyst support for diverse chemoselective reactions.

References

1. S. Yun, S. Lee, S. Yook, H. A. Patel, C. T. Yavus, M. Choi, *ACS Catal.* 2016, 6, 2435-2442.