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TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

In-situ generation of Brönsted acidity in the Pd-I bifunctional catalysts for selective reductive etherification of carbonyl compounds at mild conditions

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### PURPOSE OF THE ABSTRACT

Ethers and its derivatives are widely used as solvent, surfactants, pharmaceuticals, polymers and liquid fuels. Traditional routes for the synthesis of ethers normally involve dehydration of alcohols and Williamson ether synthesis, which always need acidic catalyst at elevated temperatures (>150 °C) or environmentally harmful halides as intermediates [1]. Reductive etherification undergoes intermediate acetalization of carbonyl group over an acid catalyst with subsequent hydrogenolysis to ethers over metal site have been considered as an alternative way to valorize biomass feedstock [2]. However, catalytic conversion of biomass-derived feedstocks normally suffers from low selectivity due to occurrence of side reactions. Considering the efficient catalytic ability of iodine for acetalization, modification of metal-supported catalysts with iodine could be therefore, favorable for the reductive etherification. However, this strategy of catalyst design has not yet been explored given the well-known strong poisoning effect of iodine. Herein, we develop an extremely efficient Pd-I catalyst for reductive etherification. The catalyst can be prepared by in-situ modification of a commercially available Pd-supported catalyst with organic iodide. This substantially simplifies its preparation process.

As shown in Table 1, commercialized 5 wt% Pd/Al2O3 was demonstrated high activity with formation of THFA as the main product. Addition of traces of ethyl iodide (Etl) or pre-treatment with Etl (I-Pd/Al2O3) leads to total change of the reaction route, causing a favoured formation of ether (2-(isopropoxymethyl)furan) as the main product (92 % and 83% selectivity). Instead of Etl, addition of iodobenzene (IBen) also showed high selectivity to ether. And the analysis of the products from Pd/Al2O3 promoted with IBen showed the presence of benzene. Thus, the modification of the catalyst might be explained by the Etl reaction with hydrogen on the surface of Pd with intermediate formation of atomic iodine on the surface.

Extensive catalyst characterizations uncovered the presence of I species on the surface of Pd nanoparticles. STEM-EDS mapping image (Figure 1a) shows that most intense iodine EDS signals come from the same locations as Pd and only negligible iodine is detected on the alumina support. And CO-FTIR analysis (Figure 1b) also shows a set of CO absorption band on initial Pd/Al2O3 with linear at 2090 cm-1 and bridged and multiple species at 1976 cm-1 and 1913 cm-1, respectively. However, there are no peaks of CO over I-Pd/Al2O3. This observation suggests that most of iodine is adsorbed on the Pd surface and not on the support. Acetalization of carbonyl groups is usually considered as an acid catalyzed reaction, which takes place in the presence of Brönsted acid sites. Pyridine-IR analysis was carried out on Pd/Al2O3 and I-Pd/Al2O3 to verify the generation of acidity (Figure 1c). A peak at 1540 cm-1 assigned to Brönsted acid sites in I-Pd/Al2O3 appeared after release H2 and disappeared after removal of H2 in the cell. Interestingly, it could be recovered by dossing again hydrogen. This result indicates that the Brönsted acidity generation on the Pd-I catalysts is reversible and depends on partial pressure of hydrogen. A feasible reaction pathway was proposed (Figure 1d). First, Brönsted acid sites (H+) are produced on the Pd-I sites via hydrogen dissociation. Then, the acetal intermediates are produced on the

Brönsted acid sites followed by by hydrogenolysis over neighboured bare-Pd to produce ether.

To conclude, in-situ produced Brönsted acidity in Pd-I catalyt is responsible of the high catalytic efficiency in reductive etherification. The catalyst is easily prepared and could be extended to reactions between various carbonyl compounds and alcohols.

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 Table 1: Etherification reaction of furfural over Pd catalysts treated and non-treated by iodine (T=60 °C, 20 bar H<sub>2</sub>, 0.1 g furfural, 2 g isopropanol, 15 mg organic iodide if needed, 50 mg catalyst, 1h)

Fu		FA CH	C THFA	он + [	o +	Acetal	+ Hemiacetal	он
Entry	Catalytic system	Conversion,	Selectivity, %					
		%	FA	THFA	Ether	Acetal	Hemiacetal	Others
1	Pd/Al <sub>2</sub> O <sub>3</sub>	88	0	99	0	0	0	1
2	Pd/Al <sub>2</sub> O <sub>3</sub> + Etl	72	4	0	92	1	2	1
					0.2	12	4	4
3	I-Pd/AI <sub>2</sub> O <sub>3</sub>	36	0	0	83	12		



### FIGURE 1

Etherification reaction of furfural over Pd catalysts treated and non-treated by iodine

#### FIGURE 2

(a) STEM-EDS mapping image of I-Pd/Al2O3; (b)
CO-FTIR analysis of Pd/Al2O3 and I-Pd/Al2O3; (c)
Pyridine-FTIR analysis of I-Pd/Al2O3 and Pd/Al2O3;
(d) Proposed reaction pathway.

# **KEYWORDS**

Acidity generation | Surface modification | Biomass upgrading | Palladium and iodine

### **BIBLIOGRAPHY**

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