

# Experimental and Theoretical Study on Hydrogenolysis of Diphenyl Ether over Supported Pt Catalysts

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Name

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Title (担持白金触媒を用いたジフェニルエーテルの水素化分解に関する実験的および理論的研究)

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## 論 文 内 容 の 要 旨

## Thesis Summary

Lignin is an aromatic biopolymer composed of phenylpropanoid subunits and is the only relevant renewable feedstock for aromatic chemicals. A common strategy for the lignin valorization is the depolymerization of lignin into low-molecular-weight compounds, which are then upgraded to form useful chemicals and fuels. Catalytic hydrogenolysis is regarded as an efficient method to make use of lignin. The key issue for lignin utilization is to screen out highly efficient catalysts, which can selectively cleave the ubiquitous C-O bonds while remaining aromatic rings. Catalytic hydrogenolysis of lignin-derived aryl ethers is generally studied as the first step in developing new catalysts for lignin valorization. Besides, insight on the hydrogenolysis mechanisms of model compounds is of great importance for directionally regulating the products selectivity.

In this study, with using diphenyl ether (DPE) as a typical model compound of lignin 4-O-5 linkage, we successfully achieved the production of two sharply contrasting products with very high selectivity from DPE hydrogenolysis by tuning the support and reaction conditions. Detailed 2-propanol dehydrogenation experiments demonstrated that the amounts of H\* species played an important role in governing product selectivity during DPE hydrogenolysis. Namely, Pt/TiO<sub>2</sub> showed high activity for 2-propanol dehydrogenation, resulting in ~99% selectivity toward saturated aromatic products with the full conversion of DPE. In contrast, Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> displayed inferior activity for 2-propanol dehydrogenation, efficiently impeding the hydrogenation of aromatic compounds and obtaining 95.7% selectivity for aromatics with a conversion of 98.7%. Our Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was one of the heterogeneous catalysts that displayed this reactivity and was by far the most selective catalyst known to date. The first principle calculations unveiled that the Pt/Ti<sub>5c</sub> and Pt/Al<sub>3c</sub> sites at the interfacial boundary were identified to be particularly active sites toward 2-propanol adsorption and dissociation, and stronger interaction between interfacial Pt atom and H atom on defect Pt<sub>24</sub>/TiO<sub>2-x</sub>(101) surface was responsible for the highly efficient dehydrogenation of 2-propanol, which providing a deep understanding of experimental observation. Based on a combination of experiments and AIMD simulations, we found the directional dissociation of DPE into aromatics was the main pathway over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, whereas the C-O bond cleavage of DPE followed by the hydrogenation of aromatics was the main pathway over Pt/TiO<sub>2</sub>. The deep investigation into the nature of selectivity control during DPE hydrogenolysis without molecular H<sub>2</sub> is highly valuable for the selective hydrogenolysis of other aryl ethers into aromatics.

Cl-modified Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by treatment with ammonium chloride. The Pt/Cl(8)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst displayed higher selectivity than unmodified Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> for aromatic products in C-O bond cleavage reactions of DPE. The high selectivity of aromatics was mainly ascribed to the following two factors: (1) Pt/Cl(8)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibited inferior activity in 2-propanol dehydrogenation due to the reduced number of active sites available after Cl addition. The decrease in the amount of H\* produced by 2-propanol dehydrogenation suppressed deep hydrogenation of aromatics. (2) Characterization and DFT calculations implied that Cl atoms preferentially occupied the terrace sites of Pt NPs. Due to the decrease in available active sites

and the repulsive interaction between the phenyl ring and the negatively charged Cl, DPE adsorbed at the low coordination sites, which increased the distance between the phenyl ring and the metal surface, and inhibited the hydrogenation reaction. Although the DFT calculations indicated that the energy barrier for breaking the C-O bond of DPE at a corner site was lower than that at a terrace site, the process was still inhibited by the low proportion of corner sites. In addition, phenol dehydroxylation was effectively promoted at low-coordination sites owing to the low energy barrier, which provided a plausible explanation of the high selectivity for benzene. Insights into the impact of Cl species on the high selectivity for aromatics based on experimental results and theoretical calculations provide a fundamental understanding for developing highly active and selective catalysts for lignin valorization.

The nature of metal-support interaction for Pt atoms anchored on the stoichiometric  $\text{TiO}_2(101)$  and reduced  $\text{TiO}_{2-x}(101)$  surfaces was studied by using the DFT calculations. For stoichiometric  $\text{TiO}_2$  surface, the interaction between Pt atoms and  $\text{TiO}_2$  was localized at Pt- $\text{TiO}_2$  interface accompanied by the formation of Pt-O bonds. The Pt atoms adjacent to the two-coordination O atoms were positively charged. As the sizes of Pt clusters increased, more electrons were transferred from Pt cluster to the surface and *d*-band center gradually decreased. The states of Pt atoms traversed the Fermi level leading to the disappearance of band gap according to the DOS analysis. For reduced  $\text{TiO}_{2-x}$  surface, by taking  $\text{Pt}_1/\text{TiO}_{2-x}$  as an example, the Pt atom could accept electrons from the surface on the basis of various electronic structures analyzes, and the remaining electrons shifted into 3d orbitals of  $\text{Ti}^{4+}$  resulting in the formation of  $\text{Ti}^{3+}$  cations. Deep understanding of interaction between Pt clusters and different  $\text{TiO}_2$  surface is helpful to investigate the reactive sites in experimental catalysts.