論文の内容の要旨
Thesis Summary

論文題目　Kinetic and Spectroscopic Studies of Catalytic Mechanisms: Hydrodeoxygenation of γ-Valerolactone on Transition Metal Phosphide Catalysts
(遷移金属リン化触媒を用いたγバレロラクトンの水素化脱酸素反応における触媒反応機構の速度論的および分光学的研究)

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Bio-oil derived from biomass is being considered as a sustainable source for the production of a variety of chemicals and fuels [1]. A major barrier in the application of the bio-oil is that it consists contains large levels of oxygen containing compounds (35 ~ 40 wt. %) which result in low heating value and chemical instability [2]. Hydrodeoxygenation (HDO) is a key process to lower the oxygen content of biomass streams, analogous to hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes that lower sulfur and nitrogen levels in petroleum feedstocks [3]. The development of effective HDO catalysts is critical to unearthing the full potential of biomass-derived compounds. Transition metal sulfide catalysts (CoMoS and NiMoS) have been widely tried as candidates due to their hydrogenation ability in commercial HDS and HDN processes, which are closely related to HDO processes in the removal of a heteroatom with direct bonding to carbon [4]. However, a major problem of the sulfides is that they are deactivated in the absence of sulfur, which is not normally present in the bio-oil. Noble metals have also been tried as they are active in hydrogenation reactions at mild conditions. As a result, transition metal phosphide catalysts (metal-rich compounds, MP or M_2P), which have combined physical properties of both metals and ceramic [5], are considered as alternative catalysts for HDO. Recently, a plethora of studies on HDO over phosphide catalysts have been reported showing their higher activity and stability compared to commercial catalysts [6,7].

Although studies of HDO of real bio-oil feeds have merits, they do not provide detailed insights into factors controlling catalyst performance because of the complexity of the bio-oil, so that model compound studies are required to give greater understanding of catalyst behavior. In addition, in situ spectroscopies such as FTIR and EXAFS are extensively used for identification of the active phase of catalysts and elucidation of reaction mechanism by providing information on the working state of the catalysts.

This thesis deals with the catalytic HDO on the cyclic five-membered ester γ-valerolactone (GVL-$C_5H_8O_2$) on a series of supported metal phosphide catalysts. The compound GVL is found in bio-oil, and indeed, it is a so-called platform chemical because it is formed in large amounts in the degradation of cellulose and has potential use as a liquid fuel, an intermediate for fine chemicals, and a solvent. Furthermore, in order to understanding fundamental information about the manner of oxygen removal, the reaction pathways for HDO of GVL were investigated by kinetic, spectroscopic, and transient studies.

Chapter 1 describes the general motivation of this research, which is the use of biomass as a sustainable energy resource to replace petroleum liquid fuels. Then, literature review provides information including strategies for biomass upgrading and catalyst development for bio-oil.

Chapter 2 describes the catalytic HDO of GVL on a series of supported metal phosphide catalysts (Ni_2P/MCM-41, CoP/MCM-41, MoP/MCM-41, WP/MCM-41) and a commercial Pd/Al_2O_3 catalyst. Highly dispersed phosphide catalysts were successfully synthesized, which were characterized by Brunauer-Emmett-Teller, X-Ray diffraction, X-ray absorption fine-structure and CO-chemisorption measurements. Comparison of activities was based on turnover frequencies calculated from surface metal atoms determined from the chemisorption of CO at 50 ^{o}C. It was found that catalytic activity followed the order: Ni_2P/MCM-41 >> CoP/MCM-41 >> Pd/Al_2O_3 ≈ MoP/MCM-41 > WP/MCM-41. On all catalysts ring opening of the lactone to produce pentanoic acid was the main initial step with subsequent hydrogenation to form pentanal. The product distribution on the iron-group phosphides (Ni_2P/MCM-41 and CoP/MCM-41) and Pd/Al_2O_3 differed from that on group 6 metal phosphides (MoP/MCM-41 and WP/MCM-41), especially in the selectivity to hydrocarbons. The main hydrocarbon product was butane on Ni_2P/MCM-41, CoP/MCM-41, and Pd/Al_2O_3 and was n-pentenes on MoP/MCM-41 and WP/MCM-41. This indicates that iron group phosphide catalysts and Pd/Al_2O_3 follow a decarbonylation pathway to produce CO and saturated C4 hydrocarbons whereas group 6 phosphides follow an HDO pathway to produce unsaturated C5 hydrocarbons in the removal of oxygen. The iron group phosphides and Pd/Al_2O_3 showed high hydrogenation ability to form saturated hydrocarbons. Based on the product selectivity, all applied catalysts followed a similar initial reaction sequence from GVL to pentanal involving ring-opening and hydrogenation. After formation of pentanal the main reaction was decarbonylation on Ni_2P/MCM-41, CoP/MCM-41 and Pd/Al_2O_3 and was hydrodeoxygenation on MoP/MCM-41 and WP/MCM-41.

Chapter 3 describes the catalytic HDO of the GVL on a series of supported bimetallic NiMo phosphide catalysts. Alloy formation between Ni and Mo was indicated by X-ray diffraction analysis. Ni-rich samples such as Ni_2P/MCM-41, NiMo(3:1)P/MCM-41, and NiMo(1:1)P/MCM-41 presented small peaks corresponding to Ni_2P; however, the peaks were shifted to lower angles compared to those of the Ni_2P phase. Similarly, the Mo-rich samples such as NiMo(1:3)P/MCM-41 and MoP/MCM-41 exhibited a distinct peak corresponding to MoP, but the peaks of NiMo(1:3)P/MCM-41 were shifted to lower angle. The structure of NiMoP is hexagonal and is isomorphic with that of Ni_2P [8] with similar crystallographic index a, but considerably larger index c. This explains why the (101) and (201) reflexions above are shifted to lower angle but the (210) reflexion is hardly displaced. The number of active sites of each metal species was estimated by factor analysis combining CO-uptake measurements and infrared (IR) spectra of adsorbed CO. Deconvolution of the IR spectra of the bimetallic phosphide catalysts revealed contributions from Ni and Mo sites These results suggest that there was no surface enrichment in the alloys. The activity was related to the proportion of Ni in the catalyst, following the order: Ni_2P/MCM-41 > NiMo(3:1)P/MCM-41 > NiMo(1:1)P/MCM-41 ≅ (Ni_2P+MoP)/MCM-41> NiMo(1:3)P/MCM-41 > MoP/MCM-41, indicating that Ni was the major active site, while Mo was a diluent. This interpretation is confirmed by results of TOF normalized by accessible Ni sites which revealed that the effect of alloying on the activity was very small indicating a single Ni atom was involved in the rate-determining step. In contrast to TOF results, the presence of Mo sites had a significant effect on the product selectivity: Ni_2P/MCM-41 mostly produced butane, whereas Mo-containing catalysts produced higher amount of 1-pentanol and C5 hydrocarbons such as pentane and n-pentenes, suggesting that the product selectivity was strongly affected by the neighboring atoms of Ni. Therefore, while the proportion of Ni sites in the catalyst governed the activity, the Mo sites controlled the selectivity to C5 hydrocarbons. These results provide insights into the behavior of Ni and Mo sites during the HDO of γ-GVL: the Ni and Mo sites behaved independently, and as a result the HDO of GVL is structure-insensitive with regards to activity, but structure-sensitive with respect to selectivity. Interestingly, the NiMo(1:1)P/MCM-41 catalyst presented higher C5/C4 hydrocarbons selectivity ratio than the physical mixture of Ni_2P/MCM-41 and MoP/MCM-41. Thus, the formation of Ni-Mo led to a slight ligand effect between the individual Ni and Mo sites.

Chapter 4 describes determination of the reaction pathway and the estimation of the reaction constants of each step by a contact time study. There are two routes: the first route involves ring-opening of the lactone on the methyl-substituted side and the second route involves removal of the oxygen from the carbonyl group. Along the first route, which was proposed pentanoic acid is formed initially, which is then converted into pentanal. Following this, n-butene is produced by decarbonylation with the formation of CO, and the n-butene was further hydrogenated to n-butane. The pentanal could also be hydrogenated sequentially to n-pentane but this was not preferred. Simulated fitting results to a first-order network showed good agreement with the experimental results.

From partial pressure analysis, it was concluded that higher H_2 partial pressure favors hydrogenation and enhances the overall reaction rate. In situ infrared spectroscopy measurements indicated that an intermediate with greater number of CH_2 groups than GVL was formed at reaction conditions, and this gave support for the proposed reaction mechanism, in which the initial reaction led to the production of pentanoic acid which has more CH_2 bonds than GVL. In situ quick X-ray absorption fine structure (QXAFS) measurements confirmed that with increasing activity more reactant adsorbed on Ni sites, and as a result, the effect of GVL concentration exhibited the same behavior as that calculated from the coverage of C5 compounds. These include the GVL and pentanoic acid. Overall, the combined kinetic and spectroscopic results give a consistent picture of the mechanism of GVL hydrodeoxygenation on Ni_2P/MCM-41.

References

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[1] G.S. Foo, A.K. Rogers, M.M. Yung, C. Sievers, ACS catal., 6 (2016) 1292-1307

[2] H. Wang, J. Male, Y. Wang, ACS catal., 3 (2013) 1047-1070.

[3] A.Y. Bunch, U.S. Ozkan, J. Catal., 206 (2002) 177-187.

[4] R.C. Nelson, B. Baek, P. Ruiz, B. Goundie, A. Brooks, M.C. Wheeler, B.G. Frederick, L.C. Grabow, R.N. Austin, ACS catal., 5 (2015) 6509-6523.

[5] S.T. Oyama, T. Gott, H.Y. Zhao, Y.K. Lee, Catal. Today 143 (2009) 94-107.

[6] R.H. Bowker, M.C. Smith, M.L. Pease, K.M. Slenkamp, L. Kovarik, M.E. Bussell, ACS catal., 1 (2011) 917-922.

[7] H.Y. Zhao, D. Li, P. Bui, S.T. Oyama, Appl. Catal., A., 391 (2011) 305-310.

[8] P.R. Guirin, M. Serhent, Acta Crystallogr. Sect. B: Struct. Sci., B33 (1977) 2820-2823.