Palladium Catalysts for Selective Hydrogenation of Aromatic Hydrocarbons to Cycloolefins

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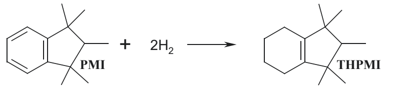
Introduction

Hydrogenation of aromatic hydrocarbons to cycloolefins is required in the production of numerous and diverse commodity and specialty chemicals. In the absence of efficient catalysts, the chemical, pharmaceutical and food industries are currently using multistep complex processes that involve hazardous and environmentally-unfriendly intermediates and byproducts. Replacement of the current multistep processes will significantly improve energy efficiency and make economically feasible commercial production of new chemicals with highly useful properties. Moreover, biomass-derived renewable chemical feedstocks contain large amounts of aromatic hydrocarbons, which can potentially be processed into high-value products using selective hydrogenation. Therefore, it is highly desirable for green chemistry and sustainability to develop new efficient catalysts for selective hydrogenation of aromatic hydrocarbons to cycloolefins without any byproducts.

Previous studies, for example [1-2], examined selective hydrogenation of aromatic hydrocarbons to cycloalkanes. In contrast, the current study focused on the development of improved catalysts for the selective production of cycloolefins and preventing further hydrogenation to cycloalkanes.

Materials and Methods

5 wt % Pd catalysts on multiple supports were prepared using the incipient wetness impregnation method. Effects of the support and catalyst pretreatments were examined. In addition to pure Pd, bimetallic Pd-Na, Pd-K and Pd-Ag catalysts were also evaluated. Reaction testing was performed in a batch Parr reactor at a constant pressure of 650 psi, which was maintained with an attached H_2 burette. The Parr reactor was equipped with a mixing impeller, which was rotating with an agitation speed of 700 rpm. Liquid samples from the reactor were analyzed using a gas chromatograph equipped with a flame ionization detector and a Carbowax HP-5 column. Hydrogenation of 1,1,2,3,3-pentamethyl indane (PMI) to 1,1,2,3,3-pentamethyl-tetrahydro indane (THPMI) (Scheme 1) was used as the probe reaction [3]. Decalin was used as the solvent with a 1 to 3 wt ratio of PMI to decalin. The catalysts were characterized with microscopy and H_2 temperature programmed desorption. The experimental study was combined with density functional theory (DFT) calculations for PMI adsorption and surface reactivity using the $DMol^3$ code in Materials Studio software by BIOVIA Corporation. The calculations used the double numerical with polarization (DNP) basis set and the generalized gradient-corrected Perdew−Wang (GGA PW91) functional.



Scheme 1. Probe reaction for selective hydrogenation of aromatics to cycloolefins: hydrogenation of pentamethyl indane (PMI) to pentamethyl-tetrahydro indane (THPMI).

Results and Discussion

5 wt % Pd supported on carbon was significantly more active than the catalysts with the same metal loading on silica, titania, alumina and silica-alumina in hydrogenation of PMI to THPMI (Figure 1). The selectivity to THPMI was unaffected by the support type. Acid washing of the carbon support prior to Pd deposition resulted in slightly improved activity and significantly better selectivities. The same selectivity improvement was observed when the carbon support was calcined at 623 K prior to metal deposition instead of being acid washed. Calcining the catalyst at the same conditions after metal deposition was detrimental to the activity without affecting the selectivity. Reducing the catalyst after metal deposition and prior to reaction testing at 423 K was detrimental to activity and, furthermore, detrimental to selectivity. Addition of Na significantly decreased the reaction rate. However, the reaction selectivity increased and remained practically constant at 90% up to 10% conversion. Addition of Ag had a similar but a less pronounced effect. The activity decreased, but the selectivity increased, remaining above 80% up to 50% conversion. In contrast, addition of K made the catalyst both more active and selective (Figure 1). Results of the DFT calculations indicate that the observed selectivity improvements are due to changes in the PMI and THPMI adsorption energies. The addition of the promoters destabilizes the cycloolefin relative to the initial aromatic hydrocarbon on Pd and, thus, allows the target cycloolefin product to desorb from the surface instead of undergoing further hydrogenation.

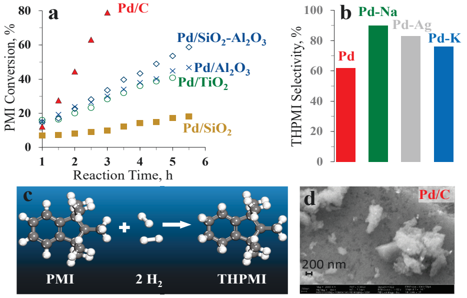


Figure 1. (**a**) PMI conversion in a batch reactor for 5 wt % Pd on multiple supports at 473 K; (**b**) Selectivity to THPMI for 5 wt % Pd without promoters and with Na (3:1 Pd:Na), Ag (6:1 Pd:Ag) and K (6:1 Pd:K) supported on C; (**c**) Evaluated probe reaction of selective hydrogenation of PMI (aromatic hydrocarbon) to THPMI (cycloolefin); (**d**) TEM image of 5 wt % Pd/C catalyst.

Significance

More active and selective catalysts for selective hydrogenation of aromatic hydrocarbons into cycloolefins were developed. Adsorption sites and surface species of PMI (aromatic hydrocarbon) and THPMI (cycloolefin) were determined on pure and promoted Pd catalysts. Selectivity improvements were attributed to changes in relative adsorption energies between the initial aromatic hydrocarbon and the cycloolefin product.

References

1. Dokjampa, S.; Rirksomboon, T.; Osuwan, S.; Jongpatiwut, S.; Resasco, D. E., *Catal. Today* 123, 218 (2007).
2. Yu, Y.; Gutiérrez, O. Y.; Haller, G. L.; Colby, R.; Kabius, B.; Rob Van Veen, J. A.; Jentys, A.; Lercher, J. A., *J. Catal.* 304, 135 (2013).
3. Podkolzin, S. G.; Chen, T.; Zheng, Y.; Yang, M.; Tadepalli, S. R.; Tampy, G. K.; Cherkauskas, J. P. *U.S. Patent 20200001274A1* (2020).