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Development of Heterogeneous Catalysts for Alcohol Transformations

This thesis entitled “Development of Heterogeneous Catalyst for Alcohol Transformations”, described the development of catalyst systemd using Co and Pd that can efficiently transform readily available simple alcohols to more complex chemicals including *N*-containing compounds. This thesis consists of four chapters.

Chapter 1 explains the importance of the greener approach to producing chemicals by transforming readily available and benign alcohols as starting materials to produce more complex chemicals. Their abundance, readily available, easy handling, and environmentally benign properties make alcohol convenient to be utilized for a greener synthesis approach. Thus, a variety of research has been dedicated to developing efficient catalysts for alcohol transformations. The study in this thesis investigates heterogeneous catalysts based on Co and Pd for the formation of C–C and C–N bonds using alcohols as starting materials. The demonstrated chemical products are greatly used in chemical industries such as for agrochemicals and pharmaceuticals. The main purpose of this thesis is to develop an efficient catalyst for green alcohol transformation protocols namely borrowing hydrogen and acceptorless dehydrogenative coupling protocols which are considered atom- and step-efficient protocols as well as environmentally friendly protocols.

In chapter 2, the formation of the C–C bond through α-alkylation of ketone with alcohols via borrowing hydrogen protocols over Co-MgO/TiO_2 was demonstrated. The developed Co-MgO/TiO_2 catalyst exhibited higher activity than the noble metal catalysts including Ru, Pd, and Pt. During the investigation, the co-deposited MgO turns to enhance the hydrogenation of alkene intermediate and the direct cooperation of Co, MgO, and

TiO_2 resulting in a high activity of the catalyst as well as highly selective to produce the desired alkylated product. The investigation of catalyst recyclability suggests that the stirring rate greatly affected the reuse experiment. In addition, the developed catalyst has successfully been applied for various scopes of ketones and primary alcohols with different functionalities generating a moderate to excellent yield of corresponding alkylated products.

Chapter three shows that the Co-MgO/TiO_2 catalyst is also applicable for the formation of C–N bond formation through direct amination of primary alcohols with NH_3 to give the corresponding primary amines in high selectivity under milder conditions than the reported heterogeneous Co catalysts. Moreover, the catalyst is allowed to selectively produce either primary, secondary, or tertiary amines by simply changing the reaction conditions.

In chapter 4, the synthesis of the *N*-heteroaromatics compound was carried out over Pd/TiO_2. The Pd/TiO_2 catalyst is revealed to be a very active catalyst for the synthesis of pyrazine compounds. Moreover, it has high stability as it can be used for four consecutive runs without a significant decrease in activity and selectivity. The catalyst has outperformed the previously reportedly work in terms of selectivity and relatively milder reaction conditions. The effectiveness of Pd/TiO_2 for the reaction was due to the ability of TiO_2 to absorb H_2 released during the reaction.

Finally, this research is summarized in chapter 5. The alternative catalysts based on Co and Pd have been developed to efficiently transform readily available alcohols to more complex chemicals through described greener protocols. It is concluded that in both reaction protocols, the catalyst surface modification of active metals is an important factor in obtaining a high-performance catalyst for alcohol transformation.