1. PRF#: 57580-ND5
2. Project Title: A New Class of Heterogeneous Catalysts Based on Single Layer Nanosheets
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Heterogeneous catalysts play an important role in many petrochemical reactions because of their advantages in product separation and catalyst recycling. We aim to design and create a new group of heterogeneous catalysts supported on single-layer nanosheets, in contrast to the ones supported on porous materials or nanoparticles. Particularly, we proposed to use α-zirconium phosphate (ZrP) single-layer nanosheets as the support, which contain a high density of surface hydroxyl groups and can be easily prepared from the exfoliation of ZrP layered compounds. Because of their unique structure and morphology, such ZrP nanosheets based heterogeneous catalysts are expected to be readily accessible and separated, and thus exhibit advantages of both heterogeneous catalysts (recyclability) and homogeneous catalysts (high accessibility).

During the first stage of this project, we synthesized two types of catalysts supported on ZrP nanosheets: (1) supported solid acid; (2) supported ionic liquid. For both catalysts, we started from the synthesis and exfoliation of ZrP to prepare ZrP single-layer nanosheets. ZrP macro-crystals were first synthesized by a hydrothermal method (6.0 g of $ZrOCl_2 \cdot 8H_2O$ in 60.0 mL of 6.0 mol/L H_3PO_4 at 200 °C for 24 h). Subsequently, the synthesized ZrP macro-crystals were exfoliated by propylamine or tetra-*n*-butylammonium hydroxide to form single-layer ZrP nanosheets, as shown in Figure 1.

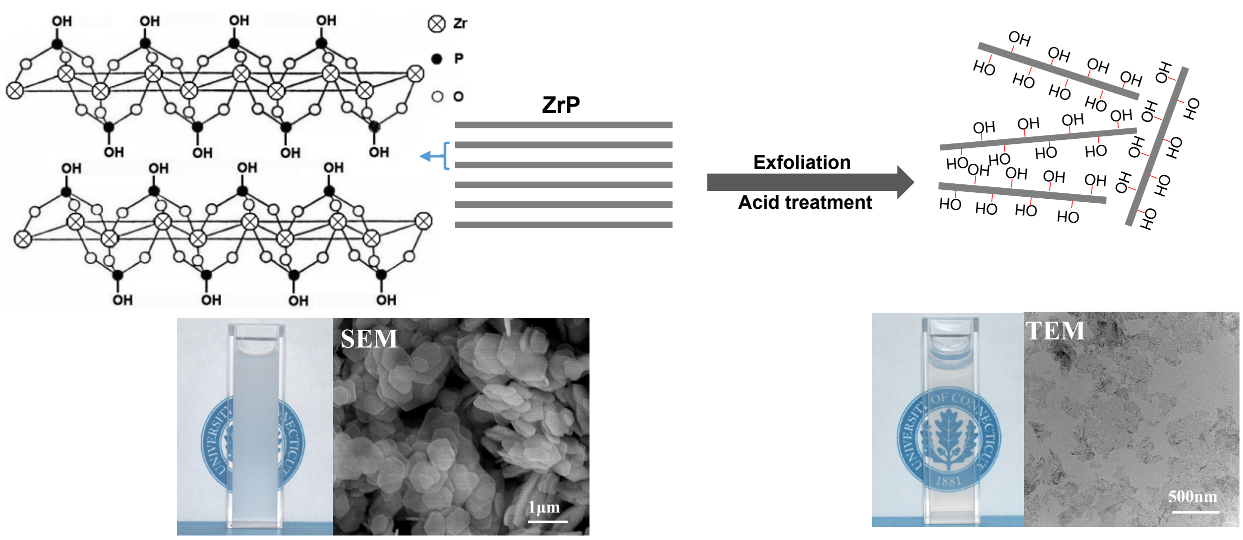
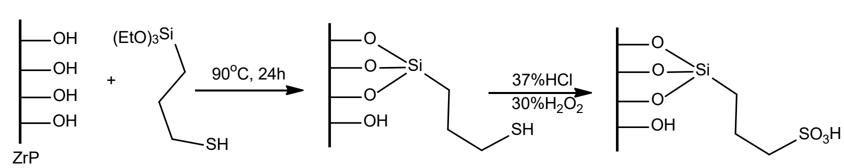


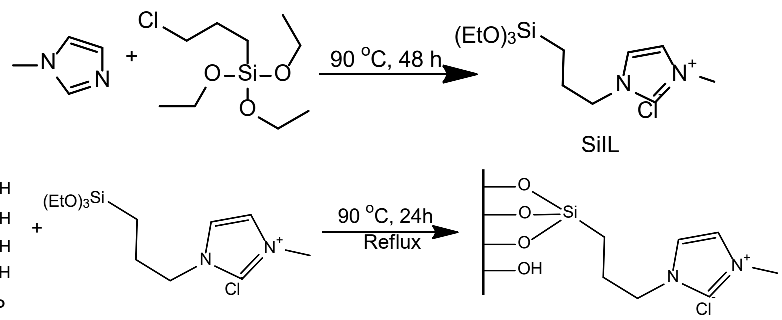
Figure 1. Preparation of ZrP single-layer nanosheets.

Based on the prepared ZrP single-layer nanosheets, we managed to graft sulfonic acid groups to synthesize supported solid acid (as shown in Scheme 1), and to graft methylimidazolium moieties (which was synthesized from the reaction of 1-methylimidazole and (3-chloropropyl) triethoxysilane) to form supported ionic liquid (as shown in Scheme 2).



Scheme 1. Procedures to prepare supported solid acid on ZrP single-layer nanosheets.

Both the supported solid acid and the supported ionic liquid exhibited excellent catalytic performance in terms of catalytic activity and recyclability. The supported solid acid was evaluated for the esterification of oleic acid with methanol and exhibited a higher catalytic activity than the commercial Amberlyst® 15 catalyst. An oleic acid conversion rate of 89% was achieved, and the solid acid also maintained a high activity for 5 cycles of reaction. The supported ionic liquid was applied in Knoevenagel condensation under solvent free conditions, and exhibited an outstanding performance (equivalent to the free 1-butyl-3-methylimidazolium chloride), and can be easily recycled and reused for eleven cycles of reaction without appreciable loss in catalytic activity. Overall, both catalysts demonstrated combined advantages of heterogeneous and homogeneous catalysts as designed.



Scheme 2. Step 1: synthesis of imidazole containing silane; step 2: preparation of supported ionic liquid on ZrP single-layer nanosheets.

In addition to ZrP nanosheets, we also explored to use another type of nanosheets, Zn-Al layered double hydroxide nanosheets, as the catalyst support, to immobilize $H_3PMo_{12}O_{40}$, and also achieved excellent catalytic results in degrading methyl orange under room temperature and ambient pressure.

So far, three journal papers (*Dalton Transaction*, **2017**, *46*, 13126; doi: 10.1039/c7dt01510k; *Catalyst* **2018**, *8*, 17; doi:10.3390/catal8010017; *Applied Catalysis A, General* **2018**, *550*, 206; doi: doi.org/10.1016/j.apcata.2017.11.012) have been published based on the results from this project, and two more are to be submitted.

This ACS PRF grant has had a huge impact on me and my students. When conducting the preliminary research to prepare for this proposal, I developed several new ideas on nanosheet research, which led to another two grants. Two graduate students, one visiting scholar, and four undergraduate students benefited a lot from working on this project. Mr. Hao Ding, a PhD student, has gained significant experience and confidence in the past one and a half years when working on this project and is on his track to complete his PhD. Another PhD student, Jingjing Liu, who did not receive stipend directly from this grant but worked on this project, has obtained her PhD and now works for the University of Texas Rio Grande Valley. Four undergraduate students were heavily involved in this project (they participated in this project through registering for a research course at the University of Connecticut and thus did not receive stipend directly from this grant). Throughout this project, these four undergraduate students received a wide spectrum of training, including basic chemical synthesis and separation skills, materials preparation and processing techniques, and various chemical, mechanical, and physical characterizations. One of the students is now working in chemical industry.