In Situ Zeolitic Imidazolate Framework (ZIF-67) Nanocrystal Encaged Heteropolyacid: An Efficient Heterogeneous Catalyst for Friedel-Crafts Acylation

Muhammad Ammar,[a,b,]***** **Sai Jiang,**[a] **Muhammad Waqas,**[c] **Shangfu Ji,**[a]
[a]*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, China*
[b]*Department of Chemical Engineering, Government College University Faisalabad, Faisalabad, 38000,Pakistan*
[c]*University of Chinese Academy of Sciences, Beijing, 100049, China*
**Corresponding author: E-mail address ammar2354@gmail.com (M. Ammar)*

Abstract: A new strategy was developed for the encapsulation of the phosphotungstic acid (PTA) into zeolite imidazolate framework-67 (ZIF-67) cage and the PTA@ZIF-67 samples with different PTA content were prepared. The samples were characterized and results showed that 14.6-31.7wt% PTA were encapsulated in the ZIF-67 cage. The PTA@ZIF-67 samples had good catalytic activity for Friedel-Crafts acylation of anisole with benzoyl chloride. The conversion of anisole can reach ~100% and the selectivity of the product can reach ~94% over 26.5wt% PTA@ZIF-67 as catalyst. The catalyst can be easily separated from the reaction mixture and can be reused five times with the selectivity of product more than 90%.
Keywords: Heteropoly acids, Zeolite Imidazolate Framework, Friedel-Crafts acylation.

1. Introduction

The production of various chemical products at industrial scale involves the synthesis and further transformation of aromatic ketones and Friedel-Crafts acylation of aromatic compounds is an essential route for their synthesis [1]. Traditionally Lewis acid and Brönsted acid catalysts had been significantly used in the acylation reactions [2] and incessant investigation for appropriate heterogeneous catalyst has led to growth of catalysts. However, there is ambit to develop heterogeneous acid catalysts for the acylation reaction. Heteropoly acids (HPAs) have been used in excess for the acylation of activated aromatic compounds. Nevertheless, HPAs in unsupported form present poor stability, fast deactivation and low efficiency. A variety of supports have been employed to build up the stability and effectiveness of HPAs [3]. ZIFs classified as a novel subclass of Metal organic frameworks (MOFs), have fascinated important attention as they unite advantages from both zeolite and conventional MOFs [4]. However, there are a small number of applications of ZIFs in catalysis as compare to conventional MOFs [5].

In this work, we wish to report a direct encapsulation of PTA into ZIF-67 cage by following the one-pot synthesis approach. PTA@ZIF-67 samples have utilized as catalyst for the acylation reaction of anisole with benzoyl chloride. Excellent performance and reusability are achieved with PTA@ZIF-67 samples.

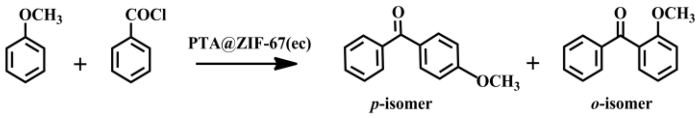
2. Experimental

For the synthesis of ZIF-67, $Co(NO_3)_2.6H_2O$ and 2-methylimidazole were dissolved in methanol. 2-methylimidazole solution was slowly added to $Co(NO_3)_2.6H_2O$ solution and was stirred for 2h. The obtained solids were collected and washed with methanol and acetone. Then solids were dried. For the encapsulation of PTA into ZIF-67, PTA was dissolved in DI water and added to $Co(NO_3)_2.6H_2O$ solution followed by same steps. PTA@ZIF-67 samples with PTA loading 46.4wt % to 14.6wt % according to ICP-AES were achieved.

The Friedel-Crafts acylation of anisole with benzoyl chloride using PTA@ZIF-67 as catalyst and n-Dodecane as internal standard was carried out into round-bottom flask with continuously stirring. After certain time, the reaction mixture was quenched with an aqueous NaOH solution. The organic components were extracted using diethyl ether, dried over anhydrous Na_2SO_4 and the product was analyzed by GC. The structure of the product was defined by GC-MS.

3. Results and discussion

Figure 1A reveals that the PTA@ZIF-67 patterns showed hardly any difference and good agreement with the peaks of bare ZIF-67 up to a certain amount of PTA (14.6-31.7wt%) added in the synthesis mixture. While, the higher amount of PTA (46.4wt%) caused to lower the pH and prevented ligand from coordination with metal due to protonation result into demolishing the crystal structure. Figure 1B shows that ZIF-67 revealed well-shape, hexagonal nano-crystals having an average particle size of about 200 nm and as the amount of PTA encapsulated into the cage of ZIF-67 (14.6-31.7wt%) keep up the crystal shape and structure. Figure 1B shows that ZIF-67 revealed only tiny weight loss up to 350 ºC, concerning to the removal of guest molecules and un-reacted species, while the thermal stability of PTA@ZIF-67 samples were reduced in the range 200-350 ºC owing it to the introduction of PTA. Hence, the PTA encapsulation into ZIF-67 structure did not badly damage the thermal stability.



Scheme 1 Friedel-Crafts acylation of anisole with benzoyl chloride using PTA@ZIF-67.

The performance of the PTA@ZIF-67 samples as catalyst in the Friedel-Crafts acylation of anisole with benzoyl chloride was assessed (Scheme 1) and the results were graphically summarized in Figure 1C. PTA@ZIF-67 samples found much more active catalysts as compared to ZIF-67. The encapsulated PTA into ZIF-67 cage gave dramatic increment of strongly active sites on PTA@ZIF-67, which resulted in a boost in the reaction conversion. A conversion of 100% was achieved over 26.5wt% PTA@ZIF-67. Furthermore, the catalytic activity of 14.6wt% PTA@ZIF-67 was better than the 31.7wt% PTA@ZIF-67, which can be caused by active sites strongly, bonded with carrier and could not take part in the reaction efficiently. Consequently, the 26.5wt% PTA@ZIF-67 was probed for the reusability in the acylation reaction over five consecutive runs. It was observed that 26.5wt% PTA@ZIF-67 could be recovered easily and reused with a gradual decrease in activity. However, the selectivity was observed more or less unchanged (Figure 1D).

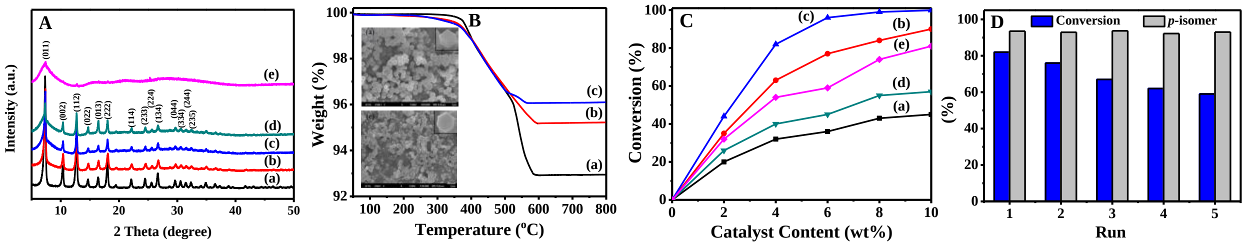


Figure 1. XRD patterns (A), SEM images and TGA (B), Catalytic performances (C) and Reusability (D) of ZIF-67 (a), 14.6wt% PTA@ZIF-67 (b), 26.5wt% PTA@ZIF-67 (c), 31.7wt% PTA@ZIF-67 (d), and 46.4wt% PTA@ZIF-67 (e)

4. Conclusions

The Friedel-Crafts acylation of anisole with benzoyl chloride is investigated over PTA@ZIF-67 samples. The PTA@ZIF-67 samples have been synthesized by direct addition of PTA to the synthesis mixture of ZIF-67 at room temperature. Among the 14.6-31.7wt% PTA@ZIF-67, 26.5wt% PTA@ZIF-67 reveals high activity, stability and reusability for acylation reaction. In conclusion, we have utilized ZIF structure as a support for PTA and develop a highly active, stable, reusable and environmentally friendly heterogeneous catalyst for the Friedel-Crafts acylation.

References

1. G.A. Olah, Friedel-Crafts Chemistry, Wiley New York, 1973.
2. S. Pivsa-Art, K. Okuro, M. Miura, S. Murata, M. Nomura, J. Chem. Soc. Perkin Trans. 1 (1994) 1703-1707.
3. C.Y. Sun, S.X. Liu, D.D. Liang, K.Z. Shao, Y.H. Ren, Z.M. Su, J. Am. Chem. Soc. 131 (2009) 1883-1888.
4. J. Gascon, U. Aktay, M.D. Hernandez-Alonso, G.P. van Klink, F. Kapteijn, J. Catal. 261 (2009) 75-87.
5. Y. Zhou, J. Song, S. Liang, S. Hu, H. Liu, T. Jiang, B. Han, J. Mol. Catal. A: Chem. 308 (2009) 68-72.