

Catalytic Hydrodesulfurization of Dibenzothiophene Coupled with Ionic Liquids over Low Pd Incorporated Co-Mo@Al₂O₃ and Ni-Mo@Al₂O₃ Catalysts at Mild Operating Conditions

Authors : Yaseen Muhammad, Zhenxia Zhao, Zhangfa Tong

Abstract : A key problem with hydrodesulfurization (HDS) process of fuel oils is the application of severe operating conditions. In this study, we proposed the catalytic HDS of dibenzothiophene (DBT) integrated with ionic liquids (ILs) application at mild temperature and pressure over low loaded (0.5 wt.%) Pd promoted Co-Mo@Al₂O₃ and Ni-Mo@Al₂O₃ catalysts. Among the thirteen ILs tested, [BMIM]BF₄, [(CH₃)₄N]Cl, [EMIM]AlCl₄, and [(C₈H₁₇)(C₃H₇)₃P]Br enhanced the catalytic HDS efficiency while the latest ranked the top of activity list as confirmed by DFT studies as well. Experimental results revealed that Pd incorporation greatly enhanced the HDS activity of classical Co or Ni based catalysts. At mild optimized experimental conditions of 1 MPa H₂ pressure, 120 oC, IL:oil ratio of 1:3 and 4 h reaction time, the % DBT conversion (21 %) by Ni-Mo@Al₂O₃ was enhanced to 69 % (over Pd-Ni-Mo@ Al₂O₃) using [(C₈H₁₇) (C₃H₇)₃P]Br. The fresh and spent catalysts were characterized for textural properties using XPS, SEM, EDX, XRD and BET surface area techniques. An overall catalytic HDS activity followed the order of: Pd-Ni-Mo@Al₂O₃ > Pd-Co-Mo@Al₂O₃ > Ni-Mo@Al₂O₃ > Co-Mo@Al₂O₃. [(C₈H₁₇) (C₃H₇)₃P]Br could be recycled four times with minimal decrease in HDS activity. Reaction products were analyzed by GC-MS which helped in proposing reaction mechanism for the IL coupled HDS process. The present approach attributed to its cost-effective nature, ease of operation with less mechanical requirements in terms of mild operating conditions, and high efficiency could be deemed as an alternative approach for the HDS of DBT on industrial level applications.

Keywords : DFT simulation, GC-MS and reaction mechanism, Ionic liquid coupled HDS of DBT, low Pd loaded catalyst, mild operating condition

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