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Hydrodesulfurization of dibenzothiophene using Pd-promoted Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃ catalysts coupled with ionic liquids at ambient operating conditions†

Yaseen Muhammad,^{ab} Ata Ur Rahman,^b Haroon Ur Rashid,^a Maria Sahibzada,^c Sidra Subhan^{ab} and Zhangfa Tong^{id}*^a

Sulfur compounds in fuel oils are a major source of atmospheric pollution. This study is focused on the hydrodesulfurization (HDS) of dibenzothiophene (DBT) via the coupled application of 0.5 wt% Pd-loaded Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃ catalysts with ionic liquids (ILs) at ambient temperature (120 °C) and pressure (1 MPa H₂). The enhanced HDS activity of the solid catalysts coupled with [BMIM]BF₄, [(CH₃)₄N]Cl, [EMIM]AlCl₄, and [(*n*-C₈H₁₇)(C₄H₉)₃P]Br was credited to the synergism between hydrogenation by the former and extractive desulfurization and better H₂ transport by the latter, which was confirmed by DFT simulation. The Pd-loaded catalysts ranked highest by activity *i.e.* Pd–Ni–Mo/Al₂O₃ > Pd–Co–Mo/Al₂O₃ > Ni–Mo/Al₂O₃ > Co–Mo/Al₂O₃. With mild experimental conditions of 1 MPa H₂ pressure and 120 °C temperature and an oil : IL ratio of 10 : 3.3, DBT conversion was enhanced from 21% (by blank Ni–Mo/Al₂O₃) to 70% by Pd–Ni–Mo/Al₂O₃ coupled with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br. The interaction of polarizable delocalized bonds (in DBT) and van der Waals forces influenced the higher solubility in ILs and hence led to higher DBT conversion. The IL was recycled four times with minimal loss of activity. Fresh and spent catalysts were characterized by FESEM, ICP-MS, EDX, XRD, XPS and BET surface area techniques. GC-MS analysis revealed biphenyl as the major HDS product. This study presents a considerable advance to the classical HDS processes in terms of mild operating conditions, cost-effectiveness, and simplified mechanization, and hence can be envisaged as an alternative approach for fuel oil processing.

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1. Introduction

Organosulfur compounds leading to the production of deleterious and hazardous sulfur oxides, *i.e.* SO_x, from the combustion of fuel oils has led to the permissible limits of sulfur becoming much more stringent over the years.¹ Among the many desulfurization approaches, such as oxidative desulfurization,² biodesulfurization³ and extractive desulfurization,⁴ hydrodesulfurization (HDS) ranks higher, attributed to its diverse nature, high practicability and efficiency.⁵ HDS generally utilizes a Co or Ni sulfide phase added to Mo impregnated over Al₂O₃-supported catalysts.^{6–8} Furthermore, incorporation of a third promoter metal, *i.e.* Pt, Pd, and Ir, can further enhance the HDS activity of classical catalysts.^{5,9,10} Despite its efficient and versatile nature, HDS suffers from complex mechanization,

poor safety and harsh temperature (380–400 °C) and pressure (8 MPa) operating conditions.^{11–13} Similarly, expensive catalytic promoters like Pt, Pd, and Ir further add to the uncontrolled process costs. Thus, an HDS process operated at mild temperature and pressure over a low-cost catalyst without compromising on the process efficiency could offer an alternative route for fuel oil processing.

Apart from HDS, a newer approach to fuel oil desulfurization research is extraction using ionic liquids (ILs).^{14,15} Aspects such as ease of synthesis, high recycling ability, low volatility, high thermal stability and environmental friendliness are credited for the widespread application of ILs.¹⁶ However, few studies on the integrated application of ILs with solid catalysts have been reported in hydrogenation reactions,¹⁷ which emphasizes that ILs coupled with solid catalysts should be tested for HDS of fuel oils.

In previous work, we reported 52% dibenzothiophene (DBT) conversion in a HDS process with a mild operating temperature and pressure by the coupled application of selected ILs with Ce–Ni–Mo/Al₂O₃ catalysts.¹⁸ However, to further improve the efficiency of solid catalyst-coupled ILs HDS processes, more exploration is required for new types of catalysts and ILs.

^aSchool of Chemistry and Chemical Engineering, Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, Guangxi University, Guangxi, 530004, P. R. China. E-mail: zhtong@sina.com

^bInstitute of Chemical Sciences, University of Peshawar, Peshawar, 25120, KP, Pakistan

^cDepartment of Chemistry, Umea University, Umea, Sweden

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Pd has been reported as a more promising promoter for classical HDS catalysts than many of its counterparts, *e.g.* Ir and Ru.^{19,20} However, to our knowledge, no studies on the HDS of DBT coupled with ILs using Pd-promoted Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts at mild operating conditions have been reported so far. Extractive desulfurization by ILs can augment the hydrogenation by solid catalysts in their blended application at mild operating conditions. Low Pd loading and mild operating conditions can concomitantly lead to cost-effectiveness and process safety. Thus, in this work, HDS of DBT was performed at 120 °C temperature and 1 MPa H₂ pressure over low (0.5 wt%) Pd-loaded Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ sulfide phase catalysts coupled with selected ILs. The fresh and spent catalysts were characterized by X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM),

inductively coupled plasma mass spectrometry (ICP-MS), energy dispersive X-ray (EDX), X-ray diffraction (XRD) and BET surface area techniques. The reaction products were quantitatively and qualitatively analyzed *via* high-pressure liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC-MS), respectively, and a suitable reaction mechanism was proposed.

2. Materials and methods

2.1. Chemicals

All the reagents used in this study were of analytical reagent grade and were used without further purification. DBT, *n*-octane, the Al₂O₃ support and Ni(NO₃)₂·4H₂O were purchased from Sinopharm Chemical Reagent Co. Ltd. Co(NO₃)₂·6H₂O

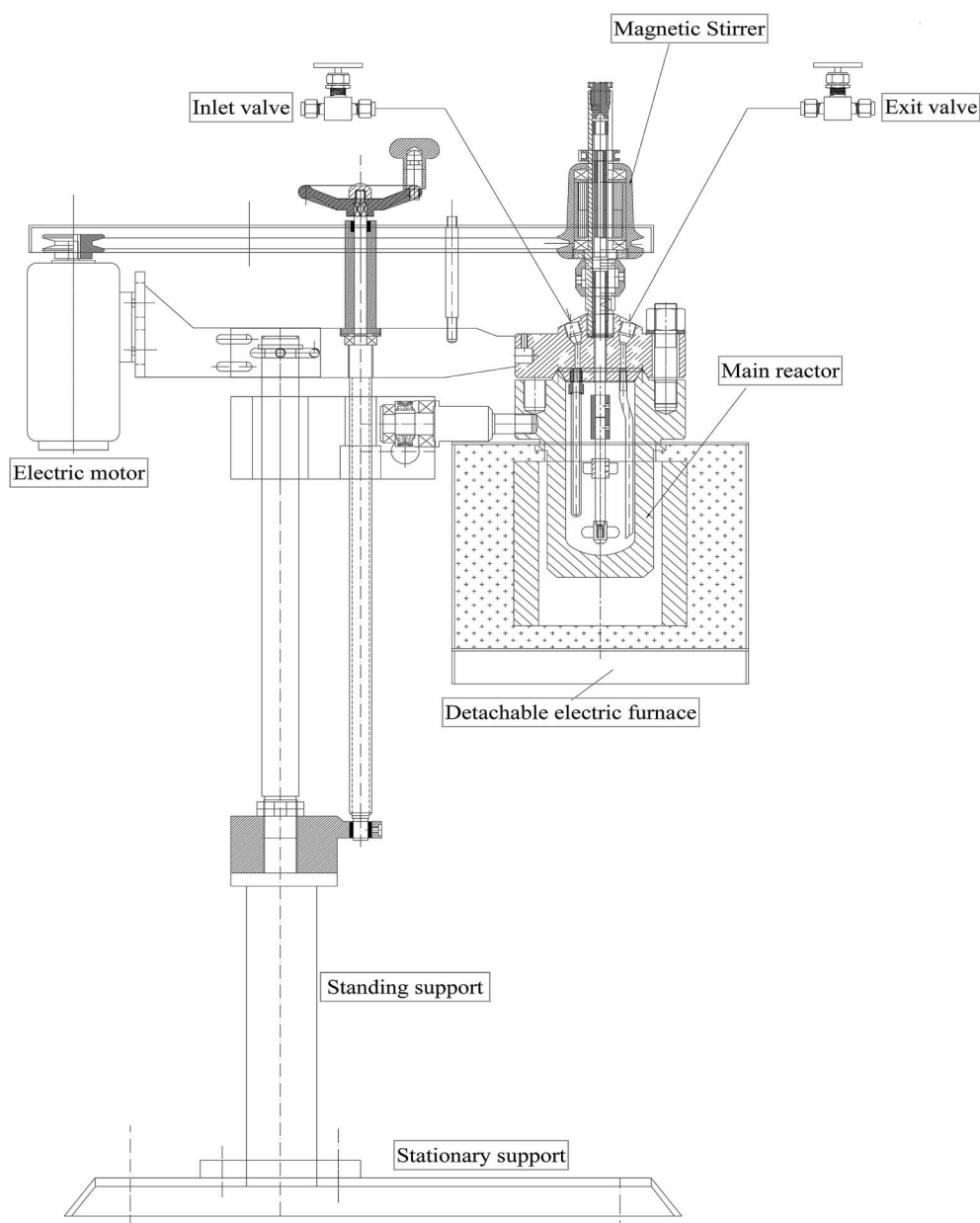


Fig. 1 Design of the batch autoclave reactor.



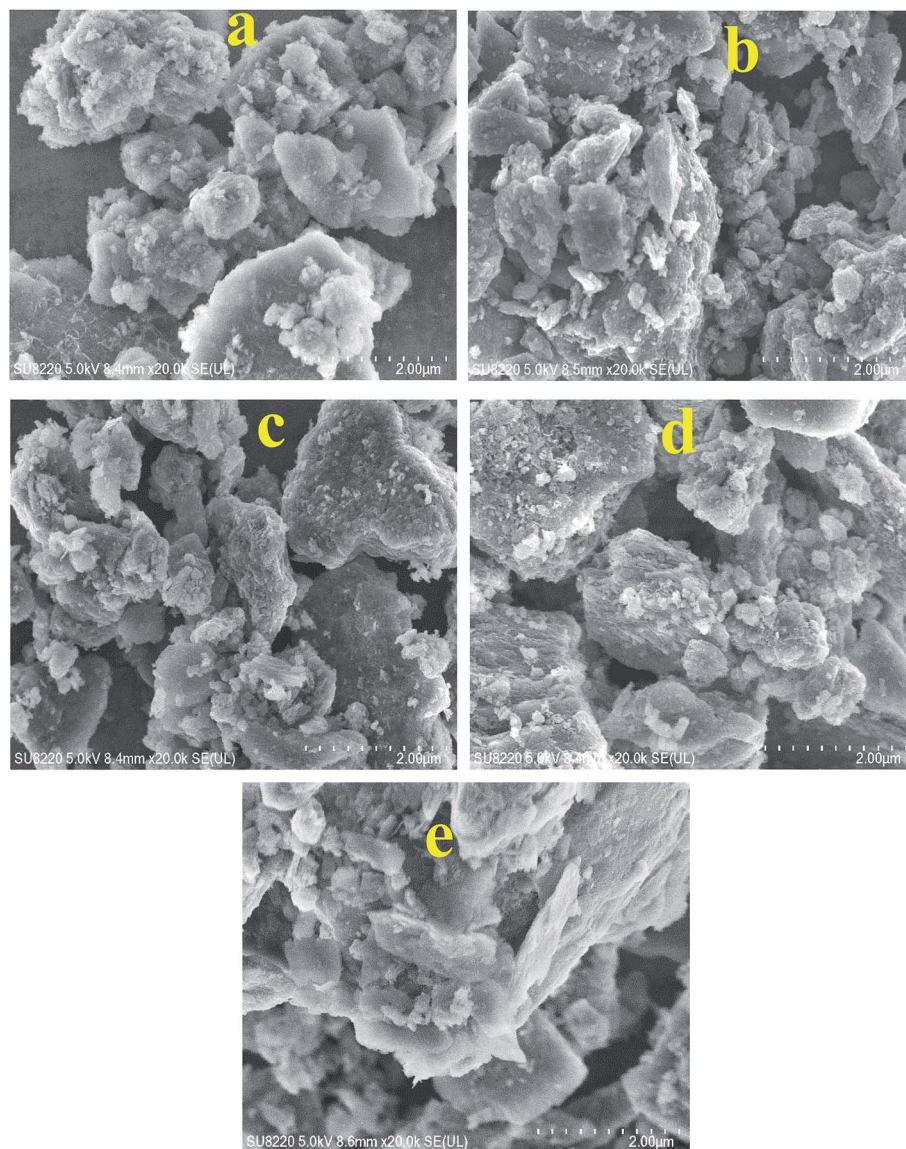


Fig. 2 FESEM images of (a) Al_2O_3 and the fresh catalysts (b) Co-Mo/ Al_2O_3 , (c) Ni-Mo/ Al_2O_3 , (d) Pd-Co-Mo/ Al_2O_3 and (e) Pd-Ni-Mo/ Al_2O_3 .

was obtained from Tian Jin Shifu Chen Chemical Reagent Factory, China. Ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was purchased from Jin Mao Chemical Reagent Co. Ltd, while palladium chloride (PdCl_2) was provided by Sa

En Chemical Technology, Co. Ltd. Shang Hai, China. Five different ILs were purchased from Shanghai Cheng Jie Chemical Co. Ltd. China. Pure H_2 gas was used in all hydrogenation experiments.

Table 1 Surface porosity data for fresh and spent catalysts used in HDS under 1 MPa H_2 pressure, 4 h reaction time and 120 °C temperature coupled with $[(\text{C}_8\text{H}_{17})(\text{C}_4\text{H}_9)_3\text{P}]\text{Br}$

Sample	BET surface area ($\text{m}^2 \text{g}^{-1}$)		Langmuir surface area ($\text{m}^2 \text{g}^{-1}$)		Pore volume ($\text{cm}^3 \text{g}^{-1}$)		Pore diameter (nm)	
	Fresh	Spent	Fresh	Spent	Fresh	Spent	Fresh	Spent
Al_2O_3	200.8	—	291.5	—	0.30	—	6.0	—
Co-Mo/ Al_2O_3	109.6	99.1	156.6	148.5	0.21	0.19	7.7	7.6
Ni-Mo/ Al_2O_3	120.5	91.9	172.5	138.0	0.22	0.17	7.4	7.5
Pd-Co-Mo/ Al_2O_3	115.1	72.5	164.2	109.4	0.22	0.16	8.0	9.0
Pd-Ni-Mo/ Al_2O_3	108.4	79.9	155.0	119.8	0.22	0.17	8.2	8.6



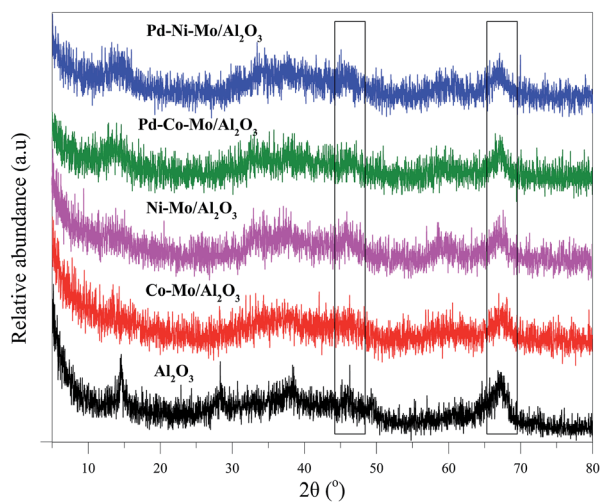
2.2. Experimental

2.2.1. Catalyst preparation. Four types of catalysts were prepared using the incipient impregnation method reported elsewhere.² A known amount of Al_2O_3 support was sequentially impregnated *via* stirring with a known amount of precursor salt solution of Co, Ni, Mo, or Pd, each corresponding to 2, 4, 8, and 0.5 wt%, respectively, at 200 rpm and room temperature for 24 h. The solutions were then dried in an oven at 110 °C for 12 h and subsequently calcined in a muffle furnace at 500 °C for 5 h. The calcined catalysts were then presulfided in a tubular furnace at 500 °C for 6 h using 20% CS_2 solution in cyclohexane in a N_2 flow at a rate of 100 mL min^{-1} and 2 MPa pressure. The presulfided catalysts were stored under N_2 atmosphere.

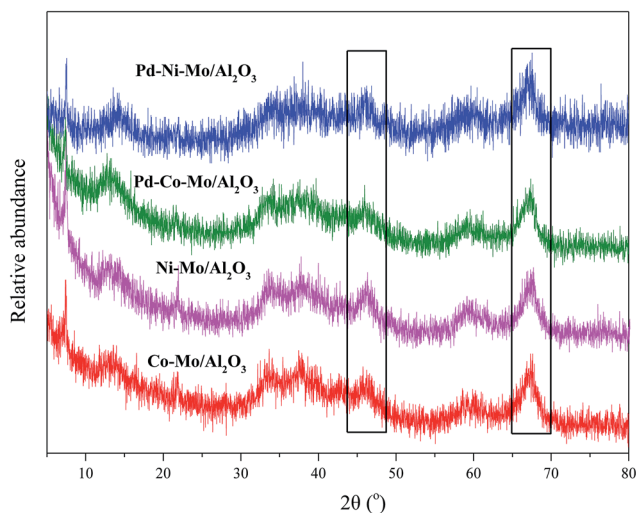
2.2.2. Catalyst characterization. Fresh and spent catalysts were characterized for surface morphology, elemental composition and distribution *via* field emission scanning electron microscopy (FESEM SU-8220N, Hitachi, Japan), ICP-MS

(PerkinElmer NexION™ 350D) and EDX techniques. BET surface area measurements were performed *via* N_2 adsorption method using a Micromeritics Gemini VII surface area and porosity analyzer. Crystal structure and phase characterizations were achieved *via* XRD (Rigaku Smartlab, X-ray diffractometer, Japan) operated at 9 kW with a scan speed of 10° min^{-1} in the 2θ angular range of 5–80°. The surface elemental composition and electronic states of various metals in the catalysts were characterized by XPS (Thermo Electron Corporation, USA).

2.2.3. Measurement of HDS catalytic activity. Catalytic activity tests were performed in a 200 mL stainless steel batch autoclave reactor heated by an electrical furnace (Fig. 1) and connected to a temperature and stirrer console. In a typical experiment, the reactor was charged with 30 mL of 1000 ppm DBT solution in *n*-octane, 0.1 g of presulfided catalyst and a fixed mass of IL. After sealing, the reactor was evacuated of air *via* a vacuum pump for 15 min three times with purges of H_2 at every step at a pressure of 3 MPa. Finally, the reactor was charged with H_2 gas to the desired pressure and then heated to a known temperature at a heating rate of 5 °C min^{-1} . The different reaction parameters, *i.e.* type of catalyst, type of IL, H_2

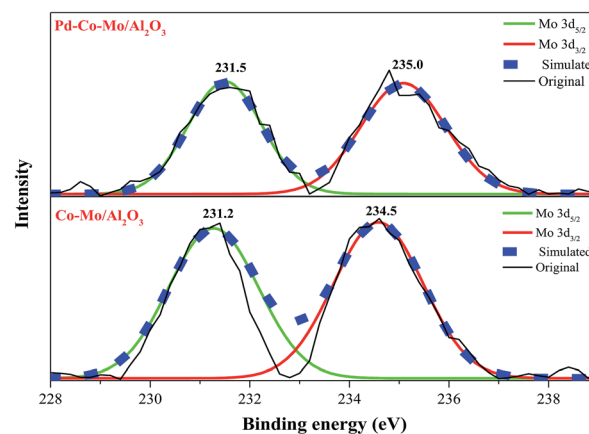


(A)

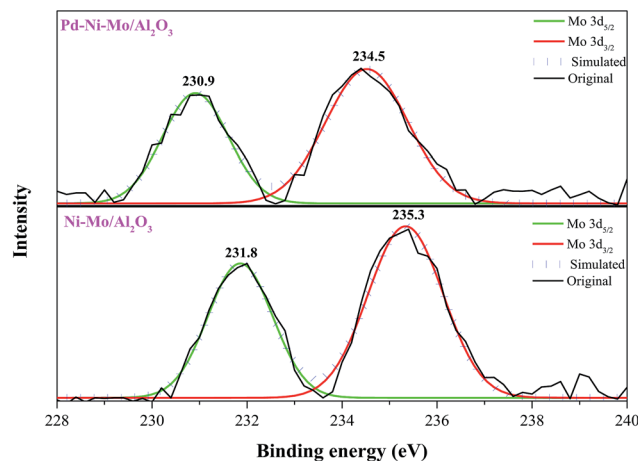


(B)

Fig. 3 XRD patterns of (A) support and fresh catalysts and (B) spent catalysts.



(A)



(B)

Fig. 4 High-resolution XPS spectra of Mo 3d (A) Co-Mo/ Al_2O_3 and Pd-Co-Mo/ Al_2O_3 and (B) Ni-Mo/ Al_2O_3 and Pd-Ni-Mo/ Al_2O_3 catalysts.



pressure, temperature, and oil : IL ratio, were separately optimized.

The catalytic activity in terms of DBT conversion (%) was calculated using eqn (1):

$$\text{DBT conversion (\%)} = \left[\frac{C_o - C_i}{C_o} \right] \times 100 \quad (1)$$

where C_o and C_i are the DBT concentrations before and after the reaction, respectively.

2.2.4. Product analysis. HDS products were quantitatively analyzed *via* HPLC (Agilent 1100 using a Zorbax SB-C18 column with dimensions of 4.6×150 mm) with a UV detector at a wavelength of 320 nm² applying the calibration curve shown in Fig. S1.† Qualitative analyses were performed on a GC-MS chromatograph (Agilent 7890A with a DB-5MS stainless steel column 30 m in length with an inner diameter of 0.25 mm) coupled with a mass spectrometer (MS-5975C). Each GC-MS run utilized 2 μ L of sample and was heated from room temperature to 80 °C in one minute, then increased to 250 °C at a heating rate of 10 °C min⁻¹ till the end of the run.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 2 shows the FESEM images of pure Al₂O₃ and fresh Co-Mo/Al₂O₃, Ni-Mo/Al₂O₃, Pd-Co-Mo/Al₂O₃, and Pd-Ni-Mo/Al₂O₃ catalysts while Fig. S2† summarizes the FESEM images of spent versions of these catalysts. The data in Table 1 and FESEM images in Fig. 2a reveal the highly porous nature of the Al₂O₃ support. Fig. 2b shows that uniformly deposited Mo and Co species led to a decrease in the porosity and surface area and an increase in the particle size compared to those of the pure support (Table 1).^{21–23} The bimetallic Co-Mo/Al₂O₃ and Ni-Mo/

Al₂O₃ catalysts possessed less compact morphology (Fig. 2(b and c)) than those of trimetallic Pd-Co-Mo/Al₂O₃ and Pd-Ni-Mo/Al₂O₃ (Fig. 2(d and e)). The spent catalysts (Fig. S2(a–d)†) (tested in HDS reaction at optimized conditions of 4 h, 1 MPa H₂ pressure at 120 °C using an oil : IL ratio of 10 : 3.3) suffered a significant decrease in porosity, resulting in the appearance of clots with an overall increase in particle size and pore diameter (Table 1).²⁴ This could be due to the deposition of DBT or HDS products, and preferential utilization of micro- and meso-pores during the HDS reaction.²⁵ Compared to the spent Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts in Fig. S2(a and b),† the spent Pd-promoted (Pd-Co-Mo/Al₂O₃ and Pd-Ni-Mo/Al₂O₃) catalysts in Fig. S2(c and d)† exhibited a much more compact and packed morphology, which might be the result of more sulfur species deposited being deposited owing to their much higher DBT conversion than Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ (to be discussed in the following sections).

The ICP-MS results in Table S1† advocate lower concentrations of the impregnated metals in the four types of catalysts than the theoretical values, which could be attributed to the leaching of some metal species during the catalyst synthesis or improper dissolution of the catalysts for ICP analysis, especially for the Pd-based catalysts. The concentration of all metals in the spent catalysts was considerably decreased, which could be attributed to their agglomeration (FESEM images in Fig. S2†) or disposition of HDS products after being tested in the HDS of DBT. The EDX spectrum (Fig. S3(a)†) of the Al₂O₃ support shows abundant Al and O species. Fig. S3(b–e)† confirms the successful impregnation of Co, Ni, Mo and Pd onto the Al₂O₃ support.²⁶ Furthermore, the EDX elemental mappings for the fresh catalysts in Fig. S4A† suggest the uniform distribution of Co, Ni, Mo and Pd over the support surface, which was considerably decreased for the spent catalysts (Fig. S4B†), which

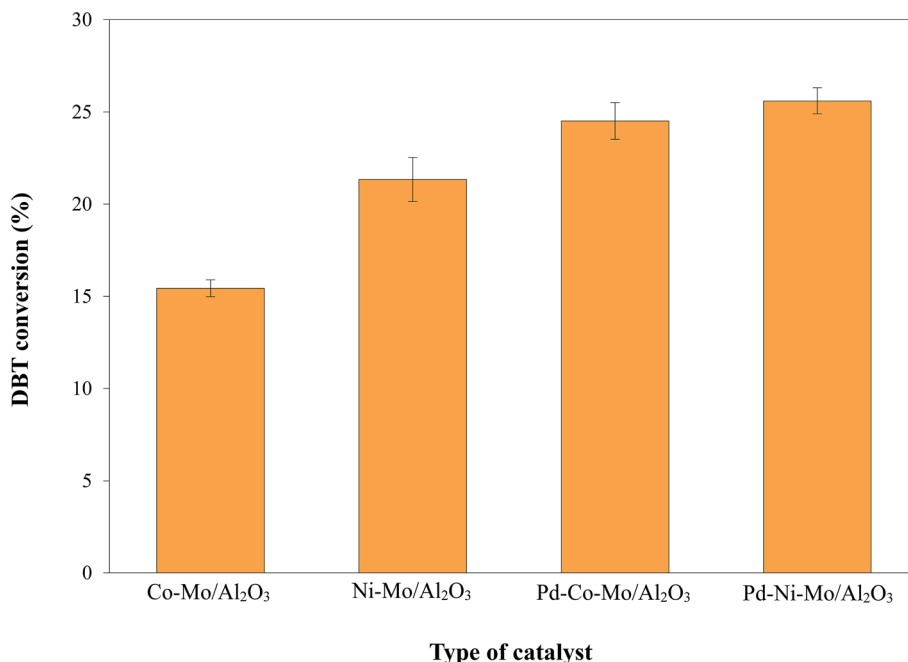


Fig. 5 DBT conversion by 0.1 g of presulfided catalyst at 3 MPa H₂ pressure, 160 °C and 4 h reaction time using 30 mL of 1000 ppm DBT solution.



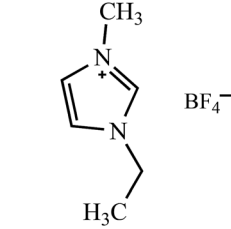
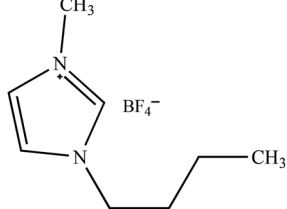
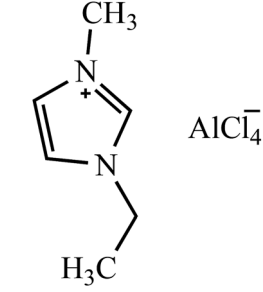
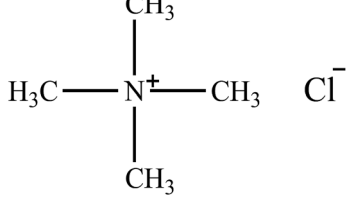
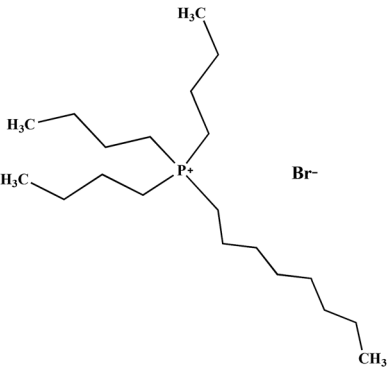
was attributed to the blockage of the surface by DBT molecules in the latter. Moreover, the EDX elemental mapping results further confirmed that Mo had the densest distribution ((Fig. S4A(g–j) and S4B(r–u)†) while Pd had the lowest distribution density (Fig. S4A(e and f) and S4B(p and q)†). Al present in the bulk in the Al₂O₃ support possessed the densest distribution (Fig. S4A(k)†).

Porosity, specific surface area (SSA) and Langmuir surface area data for the Al₂O₃ support and various catalysts are provided in Table 1. The SSA of the support was considerably decreased upon the impregnation of Co, Ni, Mo and Pd.^{7,27} The hysteresis loop at higher relative pressure ($P/P_o > 0.6$) in Fig. S5† indicates the predominant presence of micropores and mesopores.²⁸ Spent catalysts (tested in HDS reaction for 4 h, 1 MPa H₂ pressure at 120 °C using an oil : IL ratio of 10 : 3.3) exhibited a significantly high decrease in SSA, which could be attributed to the deposition of DBT or HDS products.²⁹ The decrease in the SSA and increase in the pore diameter after the addition of Co or Ni to the Al₂O₃ support and Pd to the Co–Mo/Al₂O₃ or Ni–Mo/Al₂O₃ catalysts could be attributed to the increase in mesoporosity.³⁰ In the case of the spent catalysts (Table 1), the net increase in the pore diameter and decrease in the pore volume could be owing to the preferential utilization of micro- and meso-pores during the HDS reaction, leaving macropores behind with their larger pore diameter.³⁰

The XRD patterns of Al₂O₃ and fresh catalysts compiled in Fig. 3 suggest a high degree of dispersion with a minimum degree of crystallization. Fig. 3A shows strong peaks for Al₂O₃ at 2θ of 47° and 67° (black rectangles),^{31,32} which were weakened by the incorporation of Co, Ni, Mo or Pd, suggesting that the catalysts maintained the proper pore structure required for the HDS reaction. The peaks at 2θ of 33° and 59° were ascribed to MoS₂ species in all catalysts^{33,34} while Ni showed a weak peak at 2θ of 60° in Ni–Mo/Al₂O₃ and Pd–Ni–Mo/Al₂O₃.³⁵ The XRD patterns of the spent catalysts shown in Fig. 3B indicate that there was little change in the bulk structure compared with those of the fresh catalysts (Fig. 3A) suggesting their stable nature under the current HDS reaction conditions.³⁶ However, from the XRD patterns in Fig. 3B, one can see the decrease in the dispersion of metallic species as the peaks become sharper compared to the fresh catalysts (Fig. 3A), which could be due to the deposition of sulfur moieties after the HDS reaction. It can be concluded from Fig. 3(A and B) that with low metal loading, specifically of Pd, and a highly amorphous nature with a high degree of dispersion of the catalyst (Fig. S4A and S4B†), the XRD data provided little information about the exact composition and crystallinity of the individual species^{18,33}. Furthermore, the low metal loading of Pd (0.5 wt%) was below the detection limit of the XRD instrument and hence no clear peak appeared for Pd in the Pd–Co–Mo/Al₂O₃ or Pd–Ni–Mo/Al₂O₃ catalysts.

The full survey XPS spectra of the four types of fresh catalysts are shown in Fig. S6(I),† confirming the presence of Co, Mo, Ni and Al. In Fig. S6(I),† the presence of a large amount of C 1s could be owing to the presence of organic compounds or the C left from cyclohexane in the presulfidation step.³⁷ The Co–Mo/Al₂O₃ catalyst in Fig. 4A exhibited two prominent peaks at

Table 2 Molecular and structural formulae of ILs tested in catalytic HDS of DBT

Molecular formula	Structural formula
[EMIM]BF ₄	
[BMIM]BF ₄	
[EMIM]AlCl ₄	
[(CH ₃) ₄ N]Cl	
[(n-C ₈ H ₁₇)(C ₄ H ₉) ₃ P]Br	

binding energies (BE) of 231.2 eV and 234.5 eV ascribed to Mo 3d_{5/2} and Mo 3d_{3/2} as MoS₃ phase, respectively.^{38,39} Elemental Mo (at 227.5 or 230.6 eV)³⁹ was not detected in any of the samples, indicating the complete sulfidation of Mo species. The shift towards higher BE of Mo 3d_{5/2} (231.5 eV) and Mo 3d_{3/2} (235.0 eV) (Fig. 4A) for Pd–Co–Mo/Al₂O₃ compared to those in Co–Mo/Al₂O₃ could be attributed to the stronger interaction of



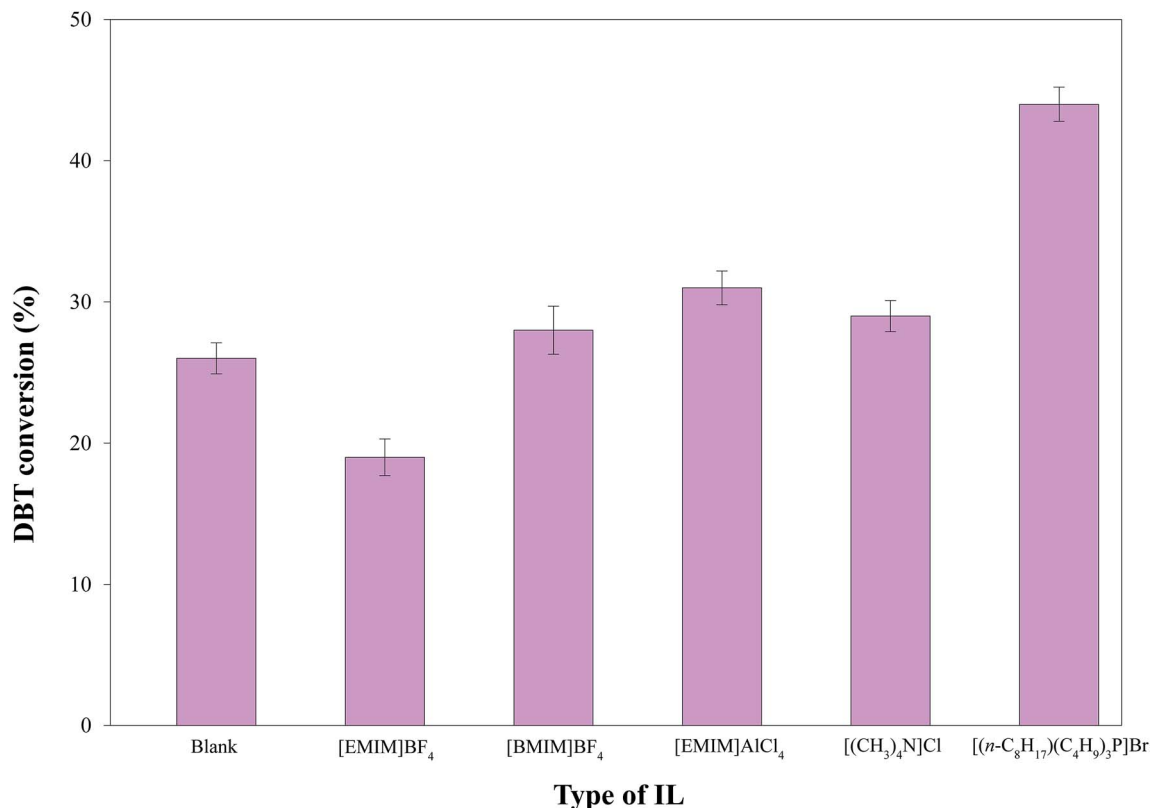


Fig. 6 Comparison of DBT conversion by Pd–Ni–Mo/Al₂O₃ (0.1 g) combined with 4 g of each IL at 160 °C, 3 MPa H₂ pressure, and 4 h reaction time with 30 mL of 1000 ppm DBT solution.

Mo with Pd in the former. On the contrary, the lower BE for Mo 3d_{5/2} and 3d_{3/2} (230.9 and 234.5, respectively) in Pd–Ni–Mo/Al₂O₃ than those for the same two states in Ni–Mo/Al₂O₃ (231.8 and 235.3, respectively) in (Fig. 4B) was indicative of a weaker interaction between Mo and Pd species in Pd–Ni–Mo/Al₂O₃, leading to better dispersion of the active phase, which can play an active role in enhancing the catalytic activity towards DBT conversion. The degree of interaction of Pd with Mo in the Pd–Co–Mo/Al₂O₃ and Pd–Ni–Mo/Al₂O₃ catalysts could be justified by a charge compensation model in which Mo loses d-electrons and gains sp-electrons while Pd gains d-electrons and loses sp electrons.⁴⁰ The weaker interaction of Pd with Ni in the Pd–Ni–Mo/Al₂O₃ catalyst (lower BE in Fig. 4B) could be attributed to stronger Ni–Mo interaction owing to the 3d⁸4s⁰ configuration than that in the Pd–Co–Mo/Al₂O₃ catalyst (with 3d⁷4s⁰ configuration).⁴¹ In brief, XPS analysis indirectly confirmed the extremely low loading of Pd (0.5 wt%) in Pd–Co–Mo/Al₂O₃ and Pd–Ni–Mo/Al₂O₃ catalysts, which was not achieved by XRD analysis. A similar trend can be observed in Fig. S6(II and III)[†] showcasing the S 2p_{3/2} and S 2p_{1/2} states in various catalysts.⁴¹

3.2. Catalytic HDS activity tests

HDS catalytic activity tests of the presulfided catalysts were performed in a 200 mL batch autoclave reactor (Fig. 1) as detailed in Section 2.2.3. Different reaction parameters were independently optimized, as discussed below.

3.2.1. HDS activity of different catalysts and effect of Pd incorporation. Four types of sulfide phase catalysts *i.e.* Co–M/Al₂O₃, Ni–Mo/Al₂O₃, Pd–Co–Mo/Al₂O₃ and Pd–Ni–Mo/Al₂O₃ (each 0.1 g) were separately tested for HDS activity in the absence of IL at 160 °C, 4 h reaction time, 3 MPa H₂ pressure, and 200 rpm stirring speed utilizing 30 mL of a 1000 ppm DBT model solution. The results in Fig. 5 indicate that the Ni-based catalysts exhibited higher catalytic activity than the Co-based catalysts, which is attributed to the higher reduction potential of Ni with 3d⁸4s⁰ configuration (higher affinity towards the electron-rich sulfur center in DBT) than that of Co with 3d⁷4s⁰ configuration. Furthermore, the lower adsorption strength over the Al₂O₃ support of Ni compared to Co allows the Ni to remain on the surface without forming aluminate ions⁴² and ultimately facilitates higher chances of DBT hydrogenation. The enhanced activity of the Pd-promoted catalysts was obviously due to the extra Pd active phase,⁴³ better dispersion of Co, Ni and Mo species by the incorporation of Pd, and hindrance of sintering and clotting.⁴⁴ From Fig. 5, the HDS activity order of the various catalysts was found to be: Pd–Ni–Mo/Al₂O₃ > Pd–Co–Mo/Al₂O₃ > Ni–Mo/Al₂O₃ > Co–Mo/Al₂O₃.

3.2.2. Process and mechanism of HDS by the solid catalyst–IL coupled system. The selected ILs (4 g; Table 2) coupled with 0.1 g of Pd–Ni–Mo/Al₂O₃ catalyst in the HDS of 30 mL of 1000 ppm DBT solution at 160 °C temperature, 3 MPa H₂ pressure, 200 rpm stirring speed and 4 h reaction time were separately tested. The results in Fig. 6 indicate that [BMIM]BF₄,



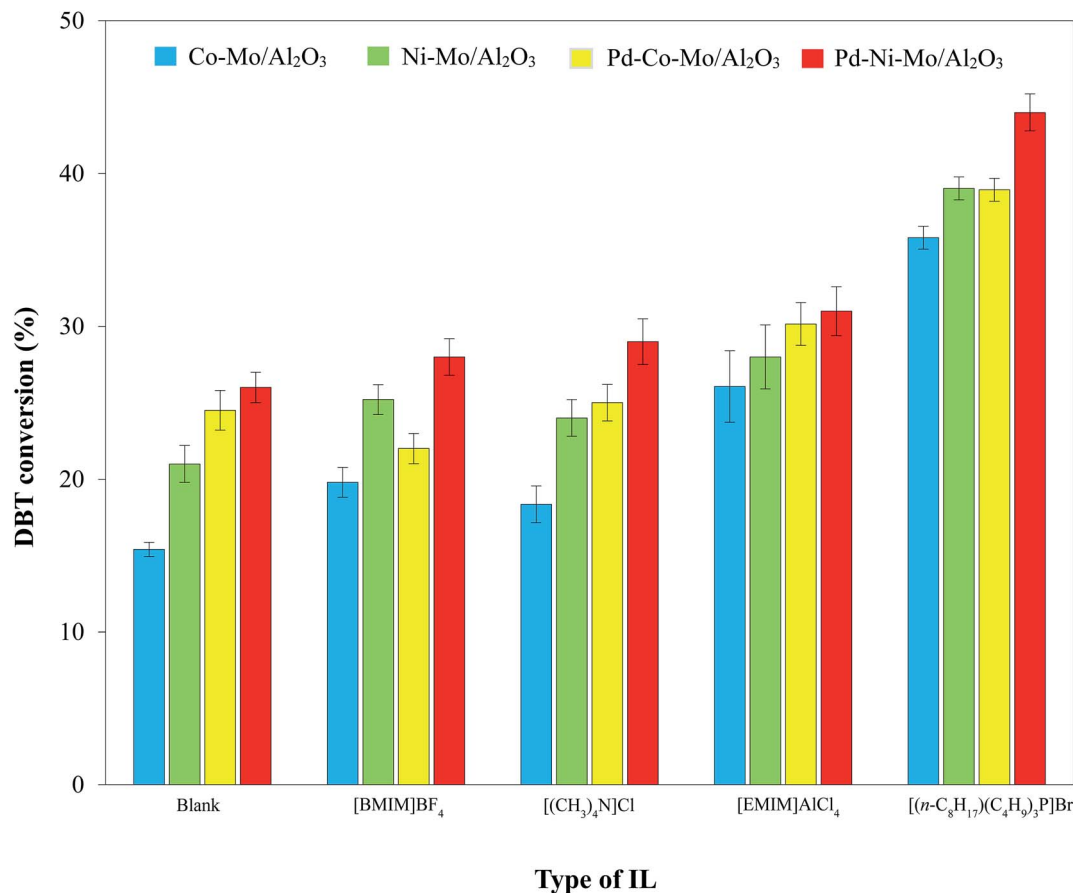


Fig. 7 Comparison of DBT conversion by different catalysts (0.1 g) combined with 4 g of each IL at 160 °C, 3 MPa H₂ pressure and 4 h reaction time using 30 mL of 1000 ppm DBT solution.

[EMIM]AlCl₄, [(CH₃)₄N]Cl, and [(n-C₈H₁₇)(C₄H₉)₃P]Br coupled with the solid catalyst exhibited higher HDS activity than blank catalysts, which could be attributed to certain electronic factors. The nature and structure of the anions and cations of ILs play crucial roles in their desulfurization efficiency.⁴⁵ For example, in [BMIM]BF₄ and [EMIM]BF₄, the higher desulfurization efficiency of the former could be attributed to the longer cation chain.⁴⁵ The higher HDS of DBT by the coupled application of ILs with the solid catalyst was owing to the synergistic effect of extraction by the ILs^{18,46–48} and hydrogenation by the solid catalyst. The extraction of DBT by IL is owing to the insertion of sulfur from DBT (with conjugation between the lone pair on S and the π electrons of the aromatic ring) into the dynamic structure of the IL.⁴⁹ [EMIM]AlCl₄ produces AlCl₄[−] and Al₂Cl₇[−] ions in the solution phase, which drastically enhances its extractive efficiency towards DBT.⁴⁶ Similarly, [(CH₃)₄N]Cl possesses outstanding extraction ability⁴⁵ and hence led to enhanced DBT conversion coupled with the solid catalyst. The highest DBT conversion by [(n-C₈H₁₇)(C₄H₉)₃P]Br coupled with Pd-Ni-Mo/Al₂O₃ in Fig. 6 and 7 was accredited to its superior extraction ability, higher thermal stability, higher solubility of polarizable delocalized bonds of DBT and van der Waals forces than the other tested ILs.⁵⁰ Similarly, the higher conversion by quaternary cation-based ILs, *i.e.* [(CH₃)₄N]Cl and [(n-C₈H₁₇)(C₄H₉)₃P]Br, could also be attributed to their cation-

anion interaction being looser than those of the other ILs, while the longer cation chain of [(n-C₈H₁₇)(C₄H₉)₃P]Br compared to [(CH₃)₄N]Cl resulted in higher desulfurization efficiency of the former.⁴⁵ In addition, the higher DBT conversion by [(n-C₈H₁₇)(C₄H₉)₃P]Br could also be owing to the looser bond between phosphonium and its anion than that of ammonium with the corresponding anion and the higher thermal stability of the former than the latter. Under identical experimental conditions, the other three types of catalyst, *i.e.*, Co-Mo/Al₂O₃, Ni-Mo/Al₂O₃ and Pd-Co-Mo/Al₂O₃, followed a similar activity trend (Fig. 7) to that in Fig. 6. [(n-C₈H₁₇)(C₄H₉)₃P]Br was selected for subsequent experiments owing to its maximum DBT conversion efficiency coupled with the solid catalyst.

Table 3 Catalytic/extractive performance in terms of DBT conversion by 4 g of [(n-C₈H₁₇)(C₄H₉)₃P]Br coupled with HDS reaction (in the absence of a solid catalyst) at 160 °C, 4 h reaction time, 200 rpm and 3 MPa H₂ pressure

Type of experiment	Type of IL	H ₂ pressure (MPa)	DBT conversion (%)
Extraction	[(n-C ₈ H ₁₇)(C ₄ H ₉) ₃ P]Br	—	13
Extraction with HDS	[(n-C ₈ H ₁₇)(C ₄ H ₉) ₃ P]Br	3	22



The catalytic role of ILs coupled with solid catalysts was further analyzed by performing experiments in the same autoclave reactor without the addition of Pd–Ni–Mo/Al₂O₃ over 4 g of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br IL with 200 rpm stirring speed and 160 °C temperature for 4 h using 30 mL of 1000 ppm DBT solution. After the reaction, the concentration of DBT in the oil phase (separated by decantation) was analyzed by HPLC. The results in Table 3 suggest that DBT extraction by

mere [(*n*-C₈H₁₇)(C₄H₉)₃P]Br (13%) was enhanced by combining it with HDS (22%). From these results, one can conclude that [(*n*-C₈H₁₇)(C₄H₉)₃P]Br along with extraction also played a catalytic role to a certain extent in combination with HDS. This synergistic effect was further enhanced by the introduction of the Pd–Ni–Mo/Al₂O₃ catalyst to the reaction medium (Fig. 6 and 7), enhancing the DBT conversion from 26% to 44% (Fig. 6).

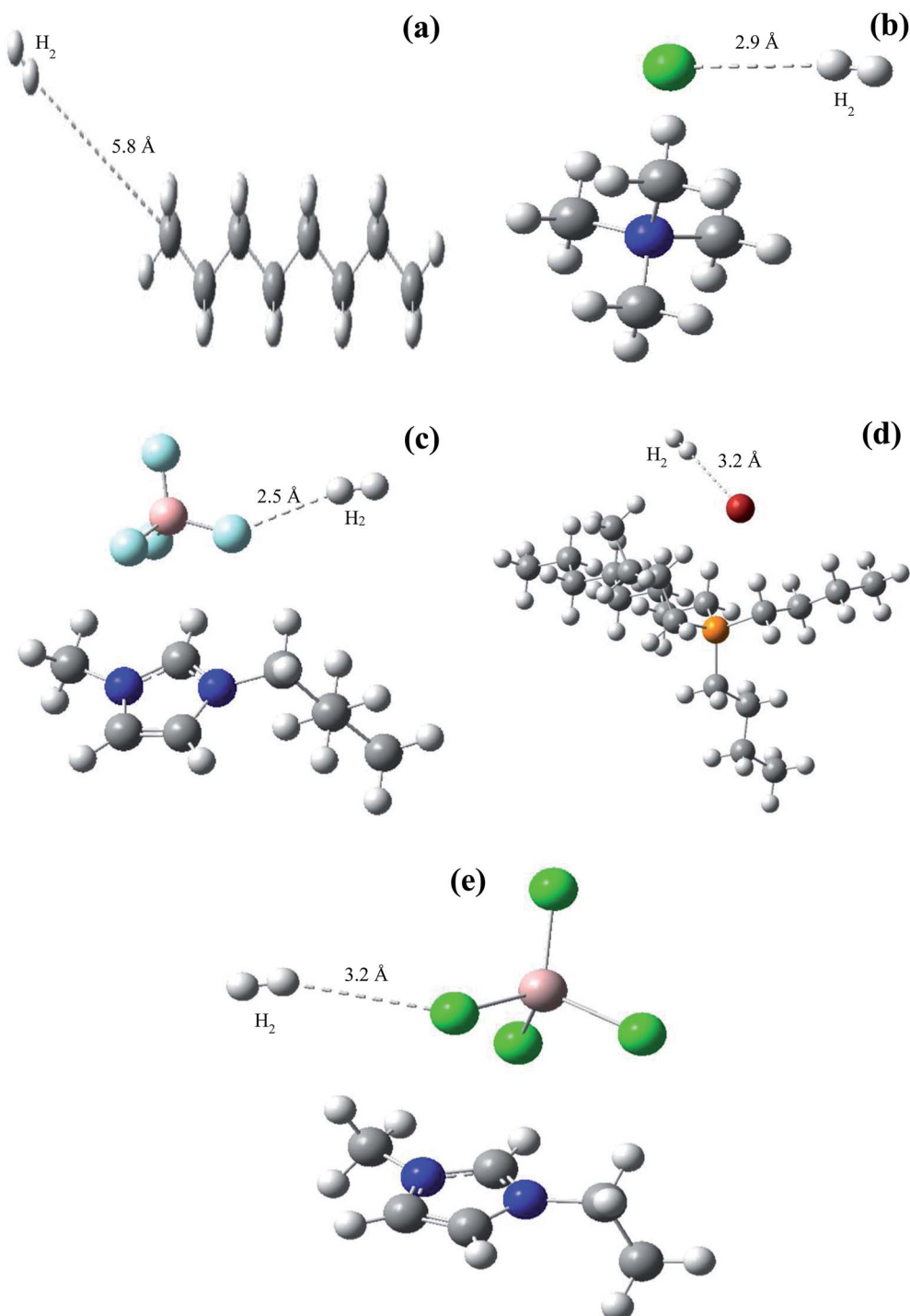


Fig. 8 DFT simulation indicating interaction of H₂ with (a) *n*-octane, (b) [(CH₃)₄N]Cl, (c) [BMIM]BF₄, (d) [(*n*-C₈H₁₇)(C₄H₉)₃P]Br and (e) [EMIM]AlCl₄ in terms of binding energy and relative distance between atoms.

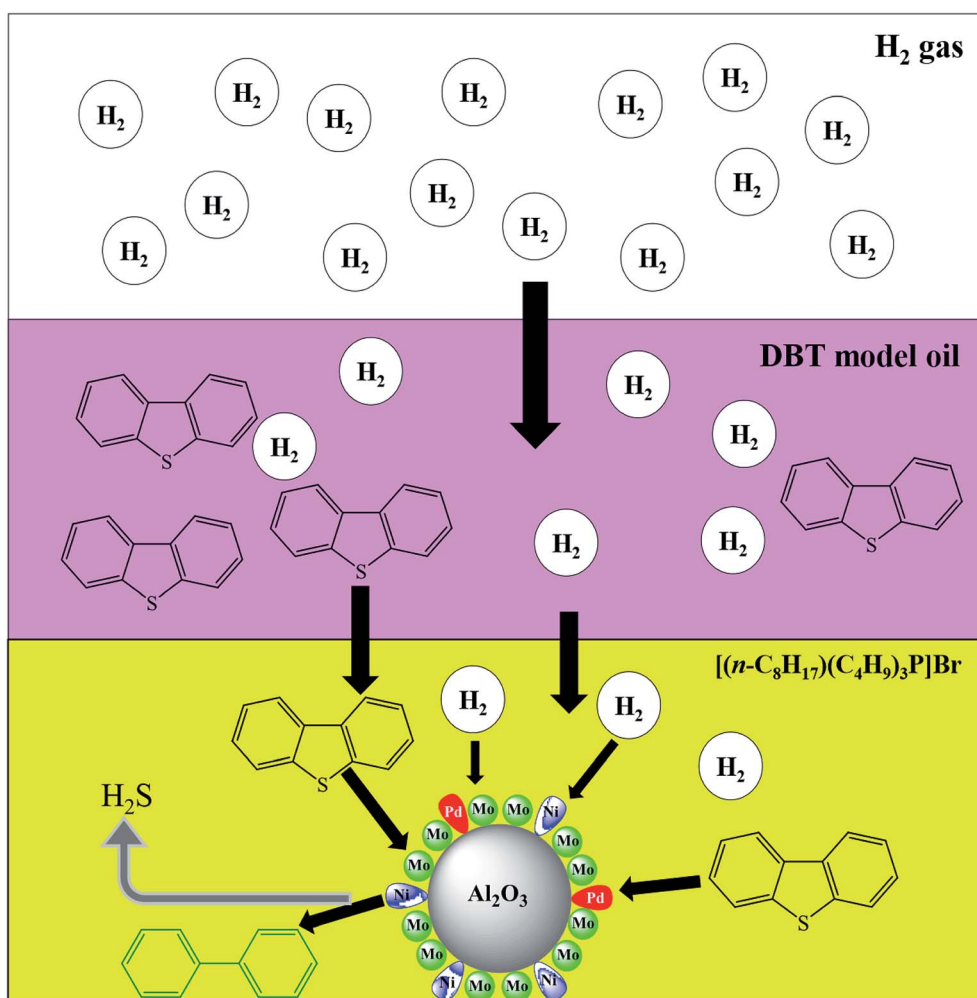


Table 4 DFT simulation data in terms of binding energy of H₂ interaction with *n*-octane and different types of IL

Sample	Binding energy (uncorrected) kJ mol ⁻¹	BSSE correction factor	Binding energy (corrected) kJ mol ⁻¹
<i>n</i> -Octane	0.029	0.004	0.033
[(CH ₃) ₄ N]Cl	-3.77	0.321	-3.449
[BMIM]BF ₄	-2.64	0.378	-2.262
[(<i>n</i> -C ₈ H ₁₇)(C ₄ H ₉) ₃ P]Br	-2.75	0.091	-2.659
[EMIM]AlCl ₄	-1.19	0.366	-0.824

The effect of the ILs-solid catalyst coupled system on HDS was further validated *via* DFT simulation using Gaussian 3 software (Fig. 8) and the resulting BE are provided in Table 4. The geometries of the reacting species were optimized at the B3LYP/6-311+g(d,p) level, both with and without BSSE corrections, while the geometry parameters of each IL with H₂ are shown in Table S2.† The relative distance between H₂ and the terminal C atom of *n*-octane (Fig. 8a) was much larger (5.8 Å) than that between H₂ and the anionic center of the ILs (Fig. 8b–e and Table 4), suggesting a stronger interaction between the latter pair. Furthermore, the BE between H₂ and ILs in Table 4

were much smaller than those between H₂ and *n*-octane, confirming the higher solubility of H₂ in IL than in *n*-octane. This can facilitate easier mass transfer of H₂ through the IL and hence better chances of activated H atom generation⁵¹ which can, in turn, enhance the HDS activity. Better H₂ solubility in ILs is envisaged in Fig. 9. A heterogeneous catalytic process, *e.g.*, HDS, is controlled by the adsorption of H₂ gas onto the surface of the solid catalyst. As illustrated in Fig. 9, H₂ gas introduced into the reactor faces and penetrates through the barrier of the oil phase (DBT solution) followed by the film between the oil phase and the solid catalyst and finally reaches and spreads

Fig. 9 HDS of DBT process demonstrating transport of H₂ through oil and IL phase reaching the solid catalyst surface.

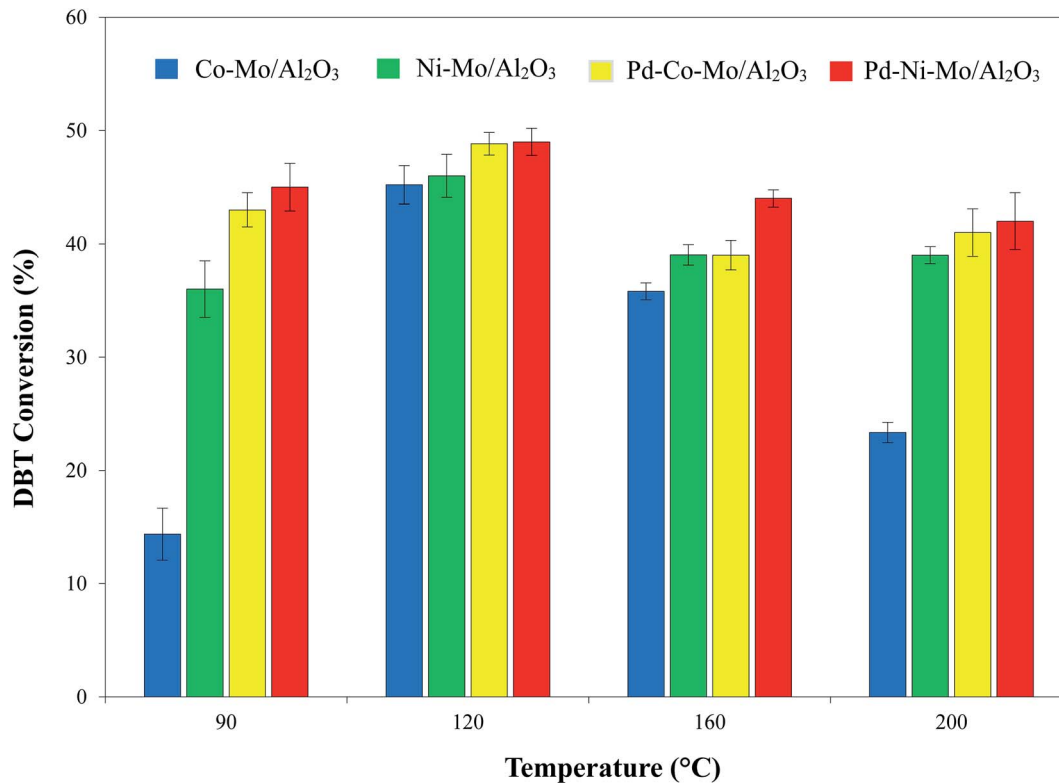


Fig. 10 Effect of reaction temperature on DBT conversion utilizing 0.1 g of each catalyst at 3 MPa H₂ pressure, 4 h reaction time, 200 rpm stirring speed, 30 mL of 1000 ppm DBT solution and 4 g of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br.

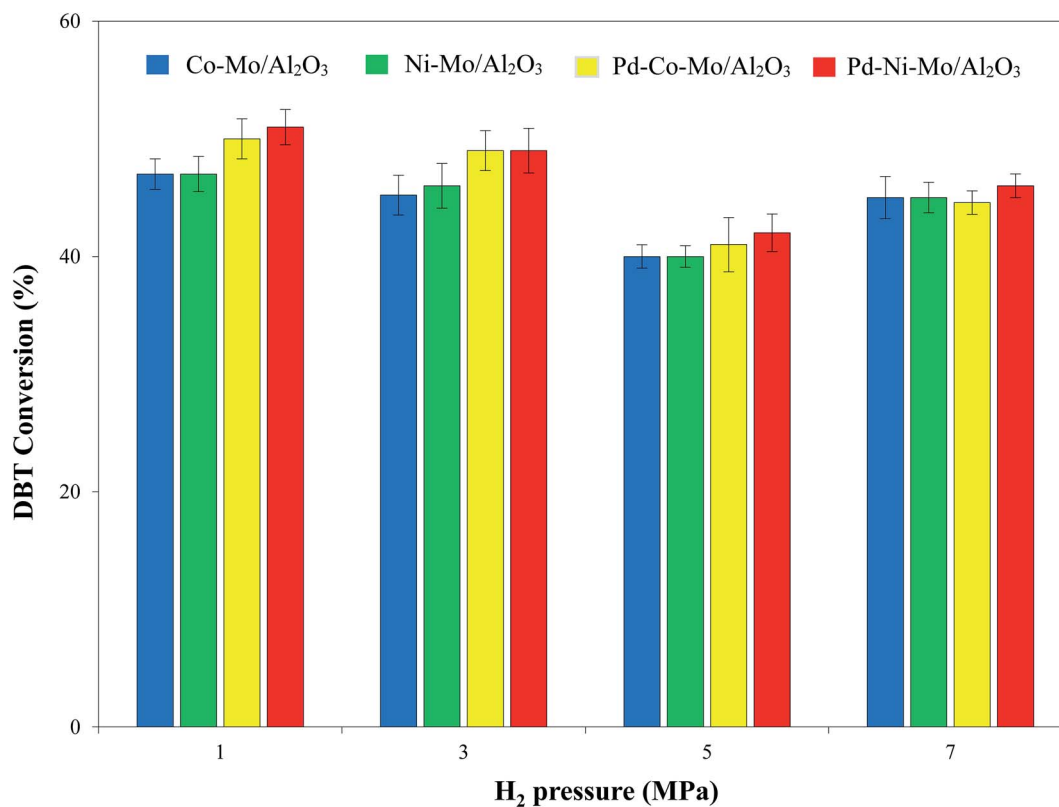


Fig. 11 Effect of H₂ pressure on the HDS activity of different catalysts (0.1 g each) in the presence of 4 g of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br at 120 °C and 4 h reaction time and 30 mL of 1000 ppm DBT solution.



over the surface of the Pd–Ni–Mo/Al₂O₃ catalyst. Over the catalyst surface, H₂ is activated into H atoms and then performs the HDS reaction of DBT. In this scenario, the solubility of H₂ in the liquid phase is the major activity-controlling factor.⁵¹ The DFT results in Fig. 8 show the much higher solubility of H₂ in all of the four ILs than in the DBT model oil, which is conducive to better H₂ transport through the reaction mixture in the presence of IL, allowing the H₂ to reach and then be activated on the surface of the Pd–Ni–Mo/Al₂O₃, ultimately performing the HDS reaction. Thus, one can conclude that ILs concomitantly act as DBT extractants as well as enhancing the solubility of H₂, which augmented the HDS activity of the solid catalyst and hence recorded better activity than that of the blank catalysts.

3.2.3. Effect of reaction temperature on the HDS activity.

The effect of mild reaction temperatures (90–200 °C) on the catalytic HDS of DBT coupled with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br IL (4 g) shown in Fig. 10 indicates the higher activity of the IL-coupled system than of the blank catalysts owing to the synergistic effect of the catalytic desulfurization reaction (by H₂) and extraction (by IL).⁴⁸ Increasing the temperature from 90 to 120 °C leads to a decrease in the viscosity of the IL, facilitating better H₂ solubility,⁵² and can also provide the activation energy for the reaction, thus leading to a corresponding increase in DBT conversion. However, temperatures beyond 120 °C may lead to reverse migration of DBT to the solution media according to Van't Hoff law, hence decreasing the DBT conversion.⁵⁰ Apart from this, increasing the temperature beyond 120 °C may lead to the dissociation of the IL,⁴⁸ hence diminishing the synergistic effect of the IL coupled with the solid catalyst, and a decrease in DBT conversion is observed. Another reason could be the decreased solubility of H₂ in the IL or *n*-octane beyond 120 °C.⁵³ At the optimized 120 °C, a maximum DBT conversion of 50% was recorded for Pd–Ni–Mo/Al₂O₃ coupled with 4 g of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br.

3.2.4. Effect of hydrogen pressure on the HDS activity.

Fig. 11 shows a relatively mild effect of H₂ pressure in the range of 1–7 MPa on the HDS activity of the four types of catalysts coupled with 4 g of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br at 120 °C with a 4 h reaction time. A higher partial pressure of a gas can lead to its better solubility in liquid medium⁵⁴ and hence provides better chances of H₂-catalytic active site interactions. However, at the same time, HDS of DBT results in bulk production of H₂S, which can poison the catalyst and hence inhibit the HDS process at higher pressures.^{55–57} The closed autoclave type reactor in this study did not allow the escape of produced H₂S from the reaction system. An increase in H₂ pressure (1 MPa onward) consequently leads to a corresponding increase in H₂S partial pressure, which retarded the HDS process,⁵⁶ as shown in Fig. 11. Another reason for the decline in DBT conversion could be the high solubility of H₂S in ILs at higher pressure decreasing the extraction efficiency of the IL.⁵⁸ A DBT conversion of 51% by the Pd–Ni–Mo/Al₂O₃ catalyst at 1 MPa H₂ pressure and 120 °C coupled with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br is superior to an earlier report in terms of catalyst cost, operating pressure and temperature.¹⁸ Based on these results, 1 MPa pressure was selected for onward experiments.

3.2.5. Effect of the amount of IL on the HDS activity of the solid catalyst.

The effect of the amount of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br (3–10 g) using 30 mL of 1000 ppm DBT solution was tested using the optimized reaction conditions. The results compiled in Fig. 12 suggest a corresponding increase in DBT conversion with increasing IL content. A higher IL content provides more sulfur extraction sites and increased H₂ solubility (DFT results in Fig. 8) and hence the maximum DBT conversion (70%) was recorded by the Pd–Ni–Mo/Al₂O₃ catalyst with an oil : IL ratio of 10 : 3.3. These results suggest a 4.5-fold increase in the HDS activity *versus* blank Co–Mo/Al₂O₃ and 2.5-fold *versus* blank Pd–Ni–Mo/Al₂O₃ after coupling with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br. Furthermore, at 3-fold milder operating conditions than those for the classical HDS process,^{59,60} a DBT conversion of 70% with a low-cost (0.5 wt%) Pd-loaded Pd–Ni–Mo/Al₂O₃ catalyst coupled with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br credits this approach with great promise for industrial applications.

3.2.6. Recycling of IL.

The uncontrolled release of used ILs to the ecosystem can concomitantly damage the environment⁶¹ and increases process costs.⁶² Thus, [(*n*-C₈H₁₇)(C₄H₉)₃P]Br was separated and recycled from the HDS products using vacuum distillation and was tested for four consecutive cycles coupled with Pd–Ni–Mo/Al₂O₃ using the optimized conditions. Fig. 13 shows that [(*n*-C₈H₁₇)(C₄H₉)₃P]Br remained highly stable for four consecutive cycles with net DBT conversions from the first to the last cycle of 70, 68, 68 and 67%, respectively. The Fourier transform infrared (FT-IR) spectra (after four cycles, obtained *via* Nicolet iS50 FT-IR spectrometer) and the ¹H NMR (ASCEND-600, Bruker) spectra of the fresh and recycled ILs shown in Fig. S7† revealed minimal changes in the structures of the fresh and recycled ILs. This indicates the highly stable nature of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br under the current experimental conditions, which could further help in controlling process costs and facilitating the industrial applicability of the proposed process for fuel oil desulfurization.

4. Product analysis and proposed reaction mechanism

Qualitative analyses of the reaction products were performed *via* GC-MS and the chromatograms (pre- and post-HDS reaction) are presented in Fig. S8(a and b).† The DBT peak at the retention time of 14 min was recorded in both the samples.⁸ In the post reaction GC-MS chromatogram in Fig. S8b† (performed over Pd–Ni–Mo/Al₂O₃ catalyst at optimized conditions using 10 g of [(*n*-C₈H₁₇)(C₄H₉)₃P]Br), a new peak for biphenyl (BP) was observed at 9.2 min. This evidenced the preferential direct desulfurization (DDS) pathway for the HDS of DBT.^{8,20} This is because at the low temperature of 120 °C, hydrogenation of the benzene ring is not feasible and hence C–S scission occurs preferentially *via* the DDS pathway. In the first step, H₂ attacks the C–S bond, resulting in biphenyl-2-thiol, which is immediately hydrogenated to an unstable hydrogenated BP thiol intermediate, and which upon extraction of H₂S leads to BP. No cyclohexylbenzene (CHB) was found in the product stream (Fig. S8(b)),† which could be due to insufficient catalytic active



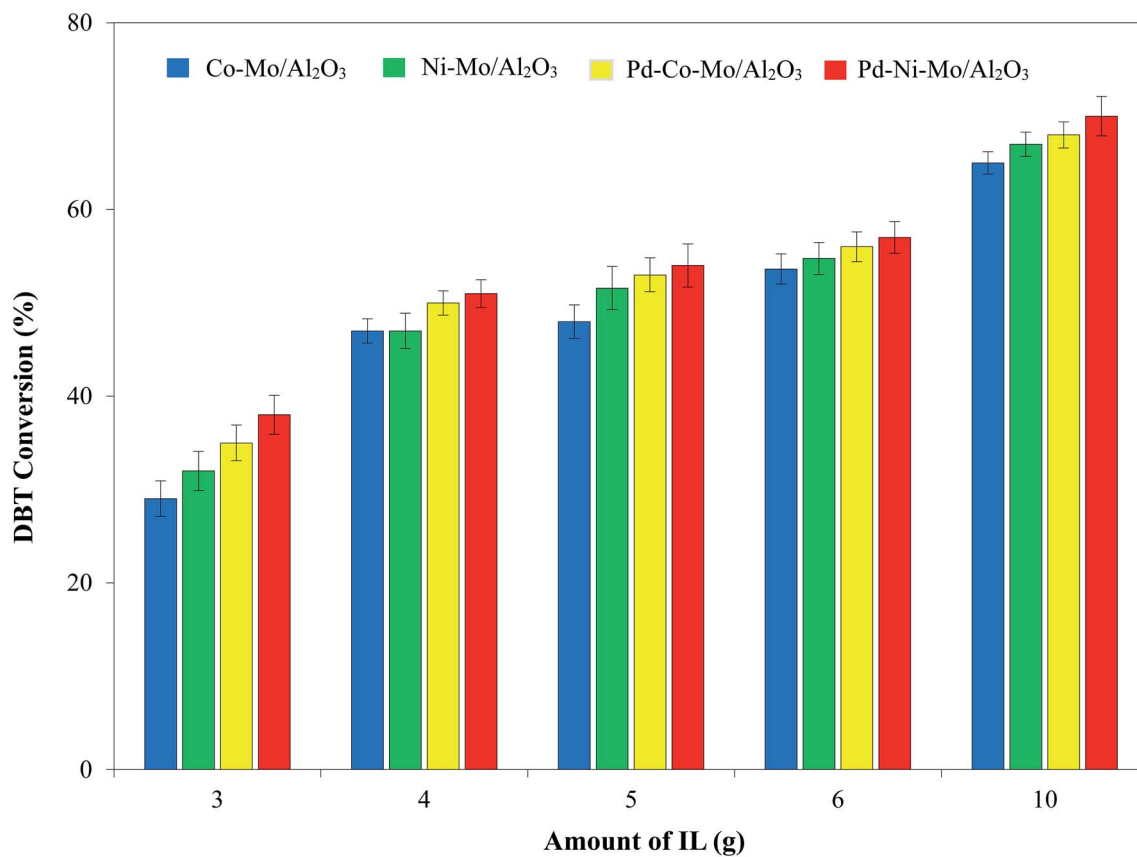


Fig. 12 Effect of amount of IL on DBT conversion using 30 mL of 1000 ppm DBT solution, 1 MPa H₂ pressure, 120 °C reaction temperature, 200 rpm stirring speed and 4 h reaction time.

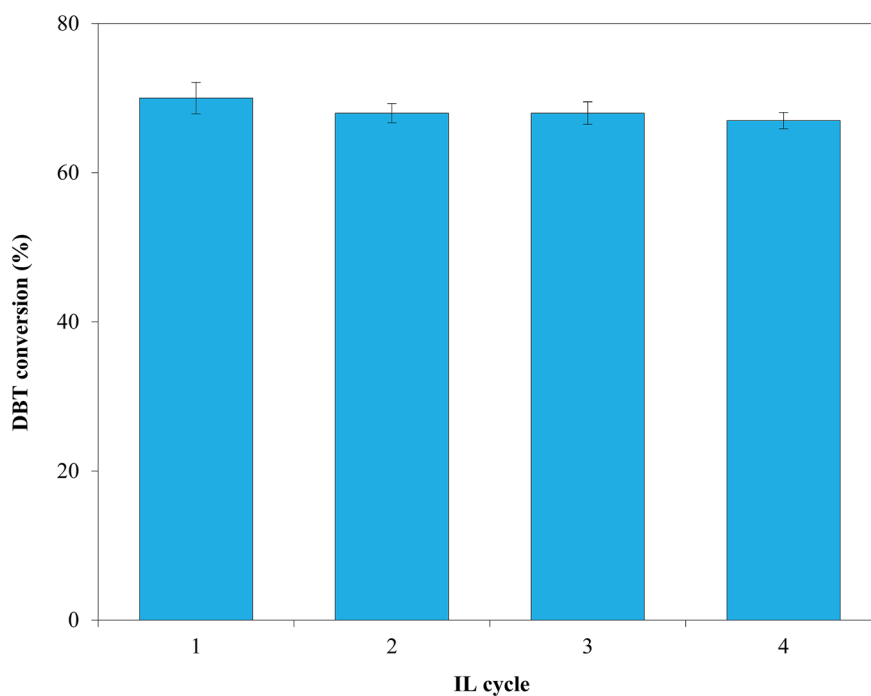
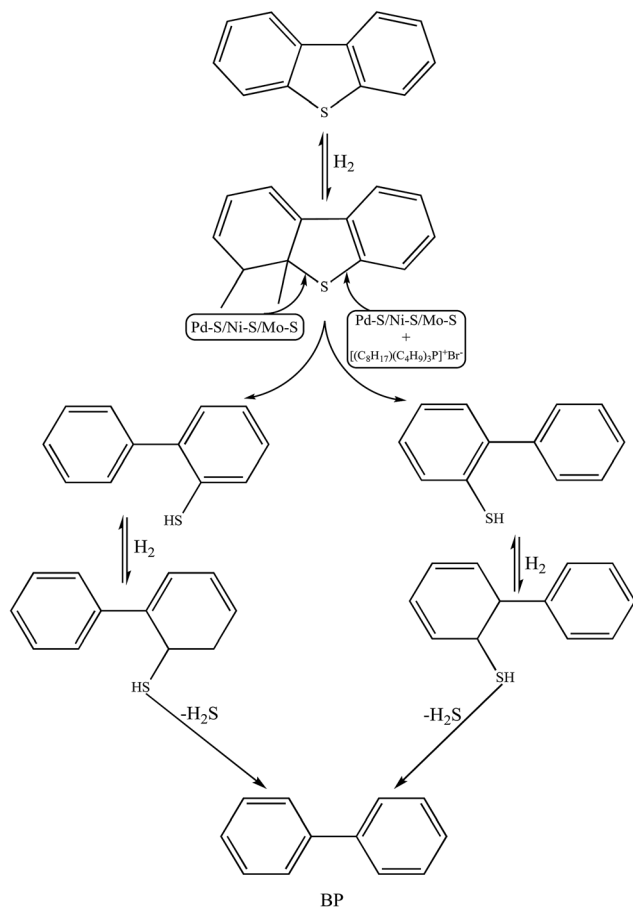


Fig. 13 Effect of four consecutive recycles on DBT conversion using 10 g of [(*n*-C₈H₁₇)(C₃H₇)₃P]Br coupled with 0.1 g of Pd-Ni-Mo/Al₂O₃ catalyst at 1 MPa H₂ pressure, 120 °C temperature, 4 h reaction time, 200 rpm stirring speed and 30 mL of 1000 ppm DBT solution.





Scheme 1 Proposed reaction mechanism for HDS reaction by blank Pd–Ni–Mo/Al₂O₃ and Pd–Ni–Mo/Al₂O₃ coupled with IL.

sites (having already been used up in the first hydrogenation step of DBT into BP) or engagement of IL with DBT. Another reason could be the mild operating conditions since catalytic hydrogenation of BP into CHB usually occurs at 300 °C and 6.6 MPa H₂ pressure.⁶³ The reaction mechanism presented in Scheme 1 proposes that the strongly electrophilic Pd active phase in Pd–Ni–Mo/Al₂O₃ readily attacks the electron-rich sulfur center of DBT *via* the DDS pathway, which was further augmented by the synergistic effect of the IL (as DBT extractant)⁶⁴ and hence an enhanced DBT conversion (70%) was observed with the coupled application of Pd–Ni–Mo/Al₂O₃ with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br compared to that for the blank catalyst. From the GC–MS results, it was concluded that the IL merely changed the activity of the HDS process rather than altering the selectivity and chemistry of the HDS reaction.

5. Conclusions

This study reported the integrated application of selected ILs with low Pd (0.5 wt%) loaded Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃ catalysts in the HDS of DBT under mild operating conditions. The coupled application of ILs synergistically increased the HDS activity of the solid catalysts by about four-fold folds at three times milder operating conditions compared to the

conventional HDS process. At genial operating conditions of 1 MPa H₂ pressure, 120 °C temperature, oil : IL ratio of 10 : 3.3 and 4 h reaction time, 70% DBT conversion was achieved over Pd–Ni–Mo/Al₂O₃ coupled with [(*n*-C₈H₁₇)(C₄H₉)₃P]Br. Textural characterization revealed that Pd incorporation decreased the surface area while increasing the pore diameter of the pristine catalysts. DFT simulations validated that enhanced HDS activity of the solid catalysts coupled with ILs was owing to the synergistic effect of extraction by IL and hydrogenation by the solid catalyst. The IL could be recycled four times with minimal loss of HDS activity. GC–MS results confirmed that the HDS reaction under the current setup followed the DDS pathway. The present approach with its cost-effectiveness (0.5 wt% Pd loading), extremely mild operating conditions with good catalytic activity, and simplified mechanization could be deemed as an alternative approach for the HDS of fuel oils on an industrial level.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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References

- H. Hori, K. Ogi, Y. Fujita, Y. Yasuda, E. Nagashima, Y. Matsuki and K. Nomiya, *Fuel Process. Technol.*, 2018, **179**, 175–183.
- Y. Muhammad, A. Shoukat, A. U. Rahman, H. U. Rashid and W. Ahmad, *Chin. J. Chem. Eng.*, 2018, **26**(3), 593–600.
- S. Bhatia and D. K. Sharma, *Biochem. Eng. J.*, 2010, **50**, 104–109.
- E. Kianpour, S. Azizian, M. Yarie, M. A. Zolfigol and M. Bayat, *Chem. Eng. J.*, 2016, **295**, 500–508.
- M. J. B. Souza, A. M. Garrido Pedrosa, J. A. Cecilia, A. M. Gil-Mora and E. Rodríguez-Castellón, *Catal. Commun.*, 2015, **69**, 217–222.
- U. T. Turaga and C. Song, *Catal. Today*, 2003, **86**, 129–140.
- R. Singh, D. Kunzru and S. Sivakumar, *Catal. Sci. Technol.*, 2016, **6**, 5949–5960.
- Y. Muhammad, Y. Lu, C. Shen and C. Li, *Energy Convers. Manage.*, 2011, **52**, 1364–1370.
- W. Shi, L. Zhang, Z. Ni, S. Xia and X. Xiao, *RSC Adv.*, 2014, **4**, 58315–58324.
- H. Ziaei-Azad and N. Semagina, *Appl. Catal., B*, 2016, **191**, 138–146.
- Y. Muhammad and C. Li, *Fuel Process. Technol.*, 2011, **92**, 624–630.



- 12 O. Y. Gutiérrez and T. Klimova, *J. Catal.*, 2011, **281**, 50–62.
- 13 K. Sakanishi, T. Nagamatsu, I. Mochida and D. D. Whitehurst, *J. Mol. Catal. A: Chem.*, 2000, **155**, 101–109.
- 14 H. Gao, S. Zeng, X. Liu, Y. Nie, X. Zhang and S. Zhang, *RSC Adv.*, 2015, **5**, 30234–30238.
- 15 Z. Li, J. Xu, D. Li and C. Li, *RSC Adv.*, 2015, **5**, 15892–15897.
- 16 A. Arce, M. Francisco and A. Soto, *J. Chem. Thermodyn.*, 2010, **42**, 712–718.
- 17 P. J. Dyson, D. J. Ellis, T. Welton and D. G. Parker, *Chem. Commun.*, 1999, 25–26.
- 18 F. Dai, Y. Muhammad, X. Gong, C. Li, Z. Li and S. Zhang, *Fuel*, 2014, **134**, 74–80.
- 19 R. Navarro, B. Pawelec, J. L. G. Fierro, P. T. Vasudevan, J. F. Cambra, M. B. Gomez and P. L. Arias, *Fuel Process. Technol.*, 1999, **61**, 73–88.
- 20 R. H. Bowker, M. C. Smith, B. A. Carrillo and M. E. Bussell, *Top. Catal.*, 2012, **55**, 999–1009.
- 21 M. Yaseen, M. Shakirullah, I. Ahmad, A. U. Rahman, F. U. Rahman, M. Usman and R. Razzaq, *J. Fuel Chem. Technol.*, 2012, **40**, 714–720.
- 22 A. A. Lemonidou, L. Nalbandian and I. A. Vasalos, *Catal. Today*, 2000, **61**, 333–341.
- 23 J. A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón and A. Jiménez-López, *J. Catal.*, 2009, **263**, 4–15.
- 24 D. Ferdous, A. K. Dalai and J. Adjaye, *Appl. Catal., A*, 2004, **260**, 153–162.
- 25 M. S. Rana, E. M. R. Capitaine, C. Leyva and J. Ancheyta, *Fuel*, 2007, **86**, 1254–1262.
- 26 Y. Huang, Z. Zhou, Y. Qi, X. Li, Z. Cheng and W. Yuan, *Chem. Eng. J.*, 2011, **172**, 444–451.
- 27 A. M. Venezia, V. L. Parola, B. Pawelec and J. L. G. Fierro, *Appl. Catal., A*, 2004, **264**, 43–51.
- 28 M. Zhu, Y. Muhammad, P. Hu, B. Wang, Y. Wu, X. Sun, Z. Tong and Z. Zhao, *Appl. Catal., B*, 2018, **232**, 182–193.
- 29 S. K. Maity, E. Blanco, J. Ancheyta, F. Alonso and H. Fukuyama, *Fuel*, 2012, **100**, 17–23.
- 30 M. Rezaei, S. M. Alavi, S. Sahebdehfar, P. Bai, X. Liu and Z.-F. Yan, *Appl. Catal., B*, 2008, **77**, 346–354.
- 31 K. Djebaili, Z. Mekhalif, A. Boumaza and A. Djelloul, *J. Spectrosc.*, 2015, **2015**, 16.
- 32 K. Zhou, X. Sun, Y. Muhammad, P. Hu, Y. Li, Z. Tong and Z. Zhao, *Appl. Catal., A*, 2018, **555**, 138–147.
- 33 F.-L. Pua, C. H. Chia, S. Zakari, T. K. Liew, M. A. Yarmo and N. M. Huang, *Sains Malays.*, 2010, **39**, 243–248.
- 34 K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi and H. Zhang, *Nano Lett.*, 2012, **12**, 1538–1544.
- 35 M. L. Toebes, J. H. Bitter, A. J. van Dillen and K. P. de Jong, *Catal. Today*, 2002, **76**, 33–42.
- 36 S. J. Sawhill, D. C. Phillips and M. E. Bussell, *J. Catal.*, 2003, **215**, 208–219.
- 37 J. Iranmahboob, S. D. Gardner, H. Toghiani and D. O. Hill, *J. Colloid Interface Sci.*, 2004, **270**, 123–126.
- 38 A. Sarkar, A. V. Murugan and A. Manthiram, *J. Phys. Chem. C*, 2008, **112**, 12037–12043.
- 39 H. W. Wang, P. Skeldon and G. E. Thompson, *Surf. Coat. Technol.*, 1997, **91**, 200–207.
- 40 C. W. Yi, K. Luo, T. Wei and D. W. Goodman, *J. Phys. Chem. B*, 2005, **109**, 18535–18540.
- 41 K. K. Sarda, A. Bhandari, K. K. Pant and S. Jain, *Fuel*, 2012, **93**, 86–91.
- 42 R. Palcheva, L. Kaluža, A. Spojakina, K. Jirátová and G. Tyuliev, *Chin. J. Catal.*, 2012, **33**, 952–961.
- 43 A. Aguirre-Gutiérrez, J. A. M. de la Fuente, J. A. de los Reyes, P. del Angel and A. Vargas, *J. Mol. Catal. A: Chem.*, 2011, **346**, 12–19.
- 44 Z. Ma, S. H. Overbury and S. Dai, *J. Mol. Catal. A: Chem.*, 2007, **273**, 186–197.
- 45 S. Zhang, Q. Zhang and Z. C. Zhang, *Ind. Eng. Chem. Res.*, 2004, **43**, 614–622.
- 46 H. Li, Y. Chang, W. Zhu, W. Jiang, M. Zhang, J. Xia, S. Yin and H. Li, *J. Phys. Chem. B*, 2015, **119**, 5995–6009.
- 47 F.-t. Li, R.-h. Liu, W. Jin-hua, D.-s. Zhao, Z.-m. Sun and Y. Liu, *Green Chem.*, 2009, **11**, 883–888.
- 48 W. Jiang, W. Zhu, H. Li, J. Xiong, S. Xun, Z. Zhao and Q. Wang, *RSC Adv.*, 2013, **3**, 2355–2361.
- 49 C. Song, *Catal. Today*, 2003, **86**, 211–263.
- 50 O. U. Ahmed, F. S. Mjalli, A. M. Gujarathi, T. Al-Wahaibi, Y. Al-Wahaibi and I. M. AlNashef, *Fluid Phase Equilib.*, 2015, **401**, 102–109.
- 51 H. Yao, G. Wang, C. Zuo, C. Li, E. Wang and S. Zhang, *Green Chem.*, 2017, **19**, 1692–1700.
- 52 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2003, 70–71, DOI: 10.1039/B210714G.
- 53 J. Jacquemin, P. Husson, V. Majer and M. F. Costa Gomes, *J. Solution Chem.*, 2007, **36**, 967–979.
- 54 R. Luo, X. Zhou, W. Zhang, Z. Liang, J. Jiang and H. Ji, *Green Chem.*, 2014, **16**, 4179–4189.
- 55 M. S. Rana, J. Ancheyta, P. Rayo and S. K. Maity, *Fuel*, 2007, **86**, 1263–1269.
- 56 V. Rabarihoela-Rakotovo, S. Brunet, G. Perot and F. Diehl, *Appl. Catal., A*, 2006, **306**, 34–44.
- 57 M. S. Rana, A. Al-Barood, R. Brouesli, A. W. Al-Hendi and N. Mustafa, *Fuel Process. Technol.*, 2018, **177**, 170–178.
- 58 Y. J. Heintz, L. Sehabiague, B. I. Morsi, K. L. Jones, D. R. Luebke and H. W. Pennline, *Energy Fuels*, 2009, **23**, 4822–4830.
- 59 R. Huirache-Acuña, T. A. Zepeda, E. M. Rivera-Muñoz, R. Nava, C. V. Loricera and B. Pawelec, *Fuel*, 2015, **149**, 149–161.
- 60 S. J. Danforth, D. R. Liyanage, A. Hitihami-Mudiyanselage, B. Ilic, S. L. Brock and M. E. Bussell, *Surf. Sci.*, 2016, **648**, 126–135.
- 61 T. P. Thuy Pham, C.-W. Cho and Y.-S. Yun, *Water Res.*, 2010, **44**, 352–372.
- 62 M. Smiglak, J. Pringle, X. Lu, L. Han, S. Zhang, H. Gao, D. MacFarlane and R. Rogers, *Chem. Commun.*, 2014, **50**, 9228–9250.
- 63 M. Koussathana, D. Vamvouka, H. Economou and X. Verykios, *Appl. Catal.*, 1991, **77**, 283–301.
- 64 H. Gao, C. Guo, J. Xing, J. Zhao and H. Liu, *Green Chem.*, 2010, **12**, 1220–1224.

