

Electronic Supplementary Material

Synthesis of nanofluids composed of deep eutectic solvents and metal-modified MCM-41 particles as multifunctional promoters for fuel oil desulfurization

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I. Preparation of MCM-41

3.6 g of CTAB and 0.6 g of NaOH were dissolved in 50 mL of distilled water, and stirred at 30 °C for 2 h. When the mixed solution became clear, 0.05 mol of TEOS was added dropwise and stirred for another 1 h. after that, the obtained milk-white mixture was transferred to a reactor with PTFE lining and aged at 100 °C for 72 h. Finally, the solid product was collected by filtration, washed with water, dried and calcined in flowing air at 550 °C for 5 h to remove the template.

II. Adsorption desulfurization procedure

designed amount of Cu/Al-MCM-41 was added into 20 ml of model oil. Then, the reaction vessel was placed in the water bath or ice bath at designated temperature with stirring. At specified intervals, the model oil was sampled and its sulfur content was analyzed by gas chromatography with a flame photometric detector (GC-FPD), with the column temperature, 280 °C, injector temperature, 280 °C, and detector temperature,

250 °C.

After reaction, the Cu/Al-MCM-41 was separated from model oil by filtration, and washed by 20 mL of MeCN. Then, the model oil and MeCN were sampled and analyzed by GC-MS with HP-5 chromatographic column (30m×250 µm i.d.×0.25 µm), the temperature was raised from 100 °C to 200 °C at a heating rate of 15 °C/ min, and kept for 10 min.

III. Extraction desulfurization procedure

20 ml of model oil was mixed with equal volume of DES in the reaction vessel to form a bi-phase system and placed in the water bath or ice bath at designated temperature with stirring. At specified intervals, the model oil was sampled and its sulfur content was analyzed by gas chromatography with a flame photometric detector (GC-FPD), with the column temperature, 280 °C, injector temperature, 280 °C, and detector temperature, 250 °C.

After reaction, the DES was separated from model oil by decantation, and mixed with 60 mL of MeCN with stirring for 10 min to extract the reaction product out. Then, the model oil and MeCN were sampled and analyzed by GC-MS with HP-5 chromatographic column (30m×250 µm i.d.×0.25 µm), the temperature was raised from 100 °C to 200 °C at a heating rate of 15 °C/ min, and kept for 10 min.

IV. Combined extraction with adsorption desulfurization procedure

20 ml of model oil was mixed with equal volume of NFs in the reaction vessel to form a bi-phase system and placed in the water bath or ice bath at designated temperature with stirring. At specified intervals, the model oil was sampled and its sulfur content was analyzed by gas chromatography with a flame photometric detector (GC-FPD), with the column temperature, 280 °C, injector temperature, 280 °C, and detector temperature, 250 °C.

After reaction, the NFs was separated from model oil by decantation, and mixed with 60 mL of MeCN with stirring for 10 min to extract the reaction product out. Then, the model oil and MeCN were sampled and analyzed by GC-MS with HP-5 chromatographic column (30m×250 µm i.d.×0.25 µm), the temperature was raised from

100 °C to 200 °C at a heating rate of 15 °C/ min, and kept for 10 min.

V. Combined extraction with oxidative desulfurization procedure

20 ml of model oil was mixed with equal volume of DES in the reaction vessel to form a bi-phase system and placed in the water bath or ice bath at designated temperature. Then, the gaseous oxidant with given flow rate generated by the ozone generator was introduced into the system with stirring. At specified intervals, the model oil in the upper phase was sampled and its sulfur content was analyzed by gas chromatography with a flame photometric detector (GC-FPD), with the column temperature, 280 °C, injector temperature, 280 °C, and detector temperature, 250 °C.

After reaction, the DES was separated from model oil by decantation, and mixed with 60 mL of MeCN with stirring for 10 min to extract the reaction product out. Then, the model oil and MeCN were sampled and analyzed by GC-MS with HP-5 chromatographic column (30m×250 μm i.d.×0.25 μm), the temperature was raised from 100 °C to 200 °C at a heating rate of 15 °C/ min, and kept for 10 min.

VI. Combined adsorption with oxidative desulfurization procedure

designed amount of Cu/Al-MCM-41 was added into 20 ml of model oil. Then, the gaseous oxidant with given flow rate generated by the ozone generator was introduced into the system with stirring. At specified intervals, the model oil in the upper phase was sampled and its sulfur content was analyzed by gas chromatography with a flame photometric detector (GC-FPD), with the column temperature, 280 °C, injector temperature, 280 °C, and detector temperature, 250 °C.

After reaction, the Cu/Al-MCM-41 was separated from model oil by filtration, and washed by 20 mL of MeCN. Then, the model oil and MeCN were sampled and analyzed by GC-MS with HP-5 chromatographic column (30m×250 μm i.d.×0.25 μm), the

temperature was raised from 100 °C to 200 °C at a heating rate of 15 °C/ min, and kept for 10 min.

VII. Supplementary figures

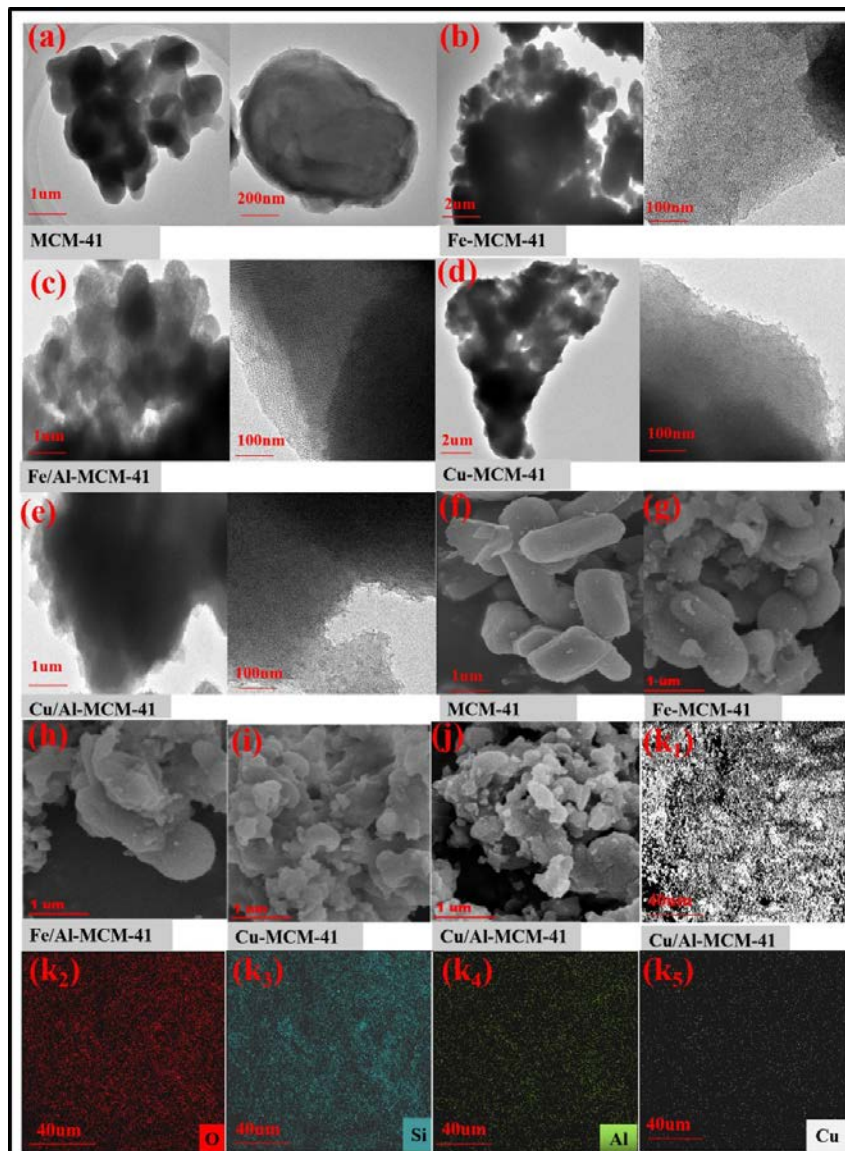


Fig.S1. (a-e) TEM images of different particles, (f-j) SEM images of different particles and (k₁₋₅) element mappings of Cu/Al-MCM-41.

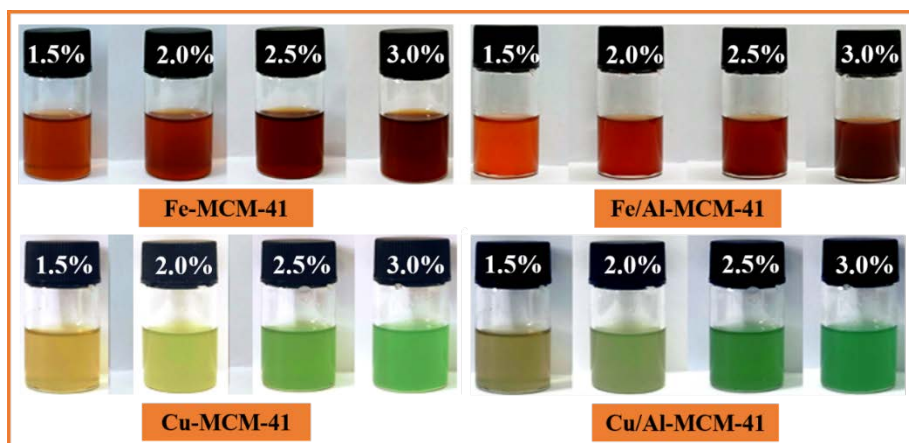
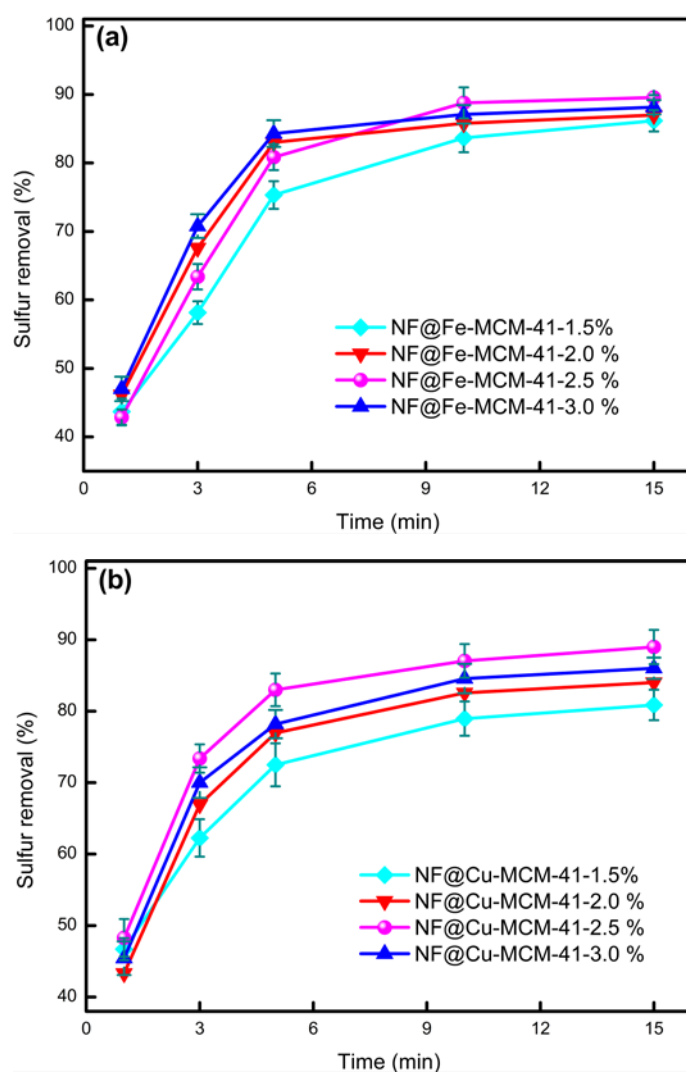


Fig.S2. NF systems with different particles after standing for 24 h.



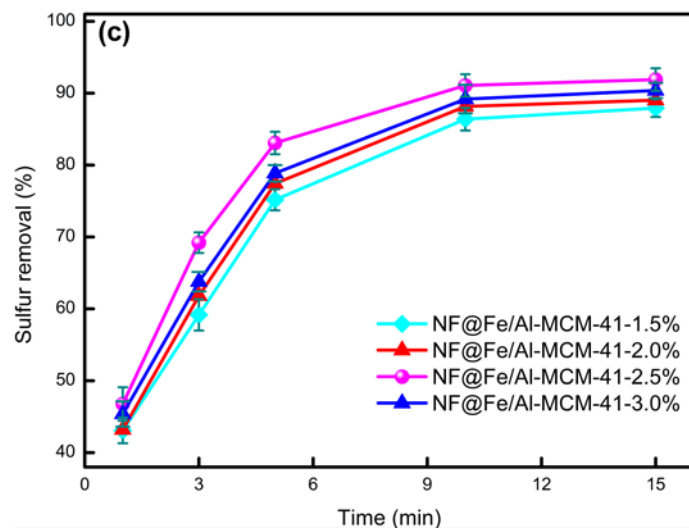


Fig.S3. The effects of different weight percent of added particles on sulfur removal.