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Immobilized Multifunctional Ionic Liquids for Highly Efficient Oxidative Desulfurization of Model Fuel

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Oxidative desulfurization is a promising mild conditions method to produce clean fuels with ultra-low sulfur content. Herein, we present for the first time multifunctional ionic liquid catalysts immobilized on mesoporous SBA-15 for highly efficient oxidation of dibenzothiophene. A combination of two catalytic active sites (phosphomolybdic acid fragment and carboxylic group) allows us to achieve complete oxidation of the most intractable dibenzothiophene to the corresponding sulfone in 5 min at 80°C and H₂O₂:S = 6:1 (molar). The structure of both support and catalysts was investigated by low-temperature nitrogen adsorption/desorption, Fourier-transform infrared spectroscopy, X-ray fluorescence analysis, CHN analysis, and transmission electron microscopy techniques. Nicotinic acid fragments, connected with support via a covalent bond, are also connected with phosphomolybdic acid anion with ion bond, which prevents active sites from leaching and allows to retain catalysts activity at least 10 reaction runs with preliminary regeneration, making them promising systems for clean fuel production.

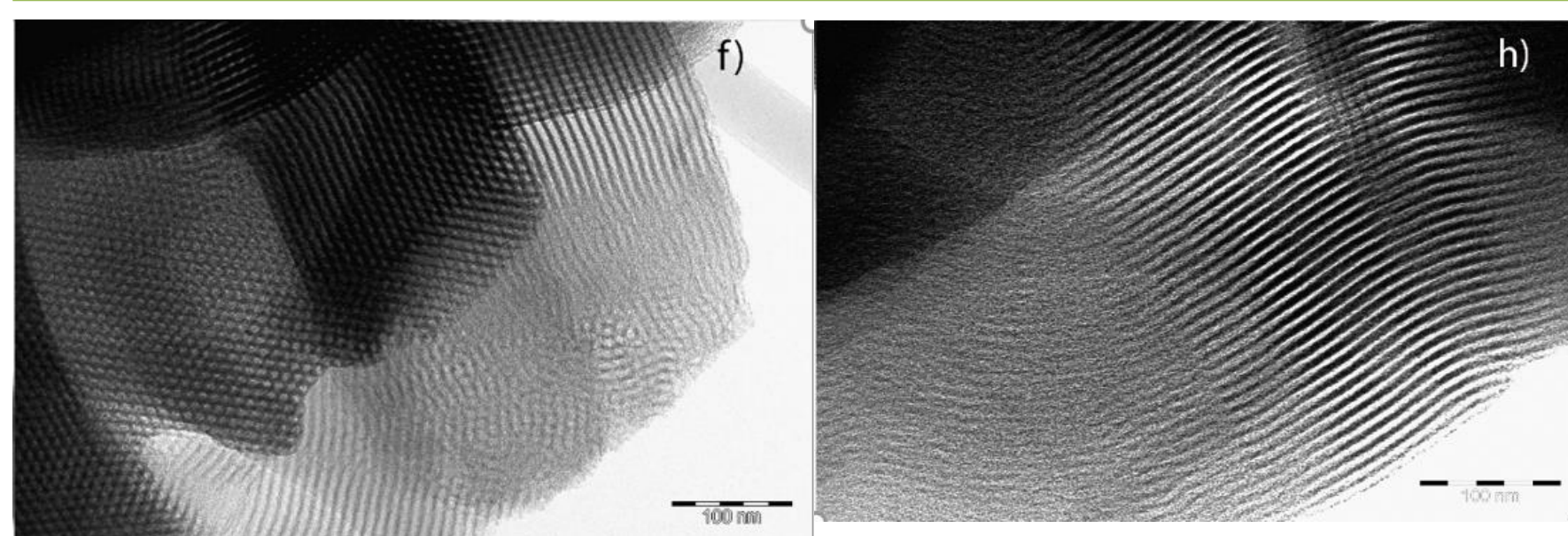
Problems:

- The constantly increasing amount of sulfur-containing compounds in the produced crude oil
- The absence of low capital-cost processes to remove sulfur

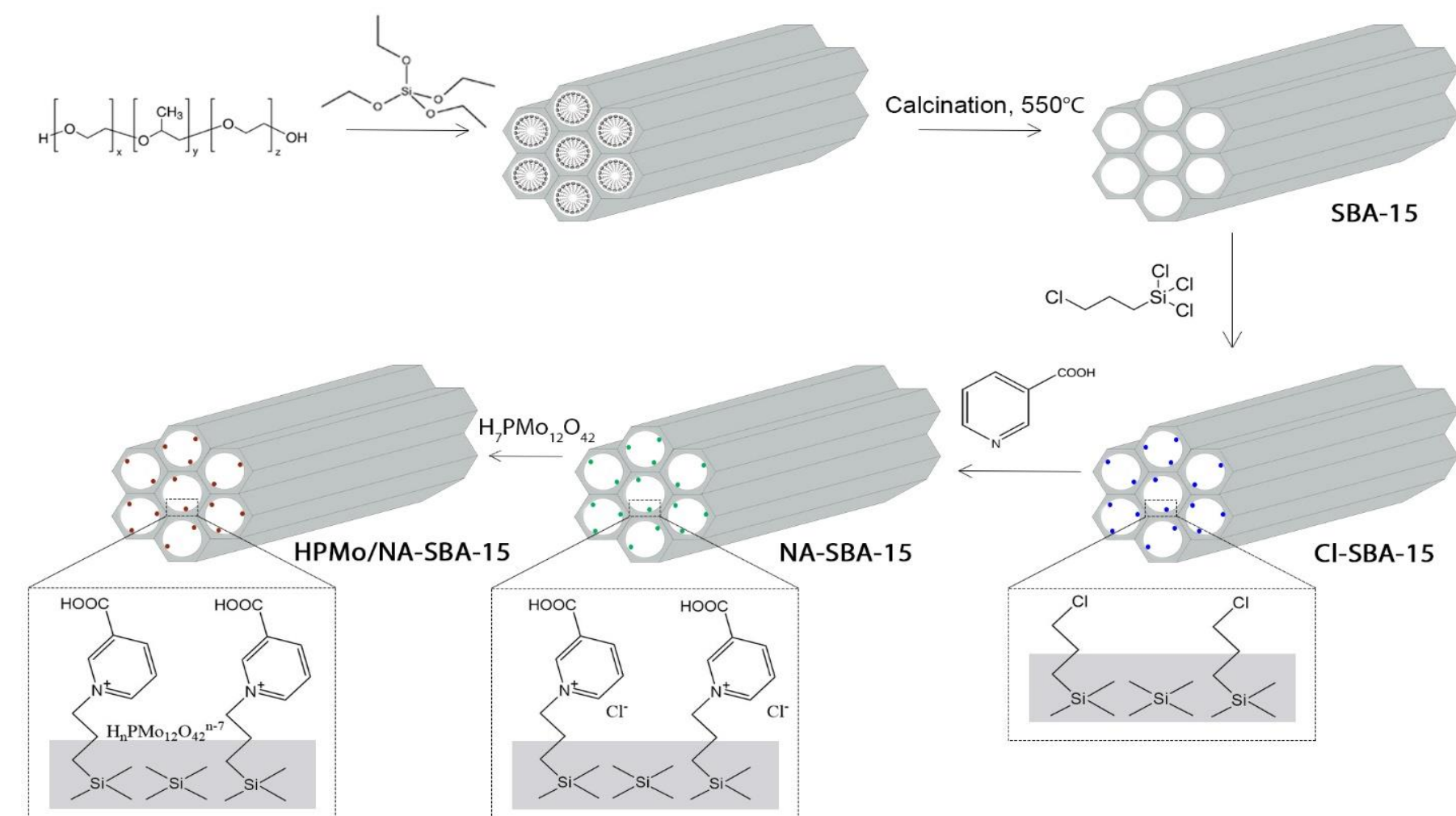
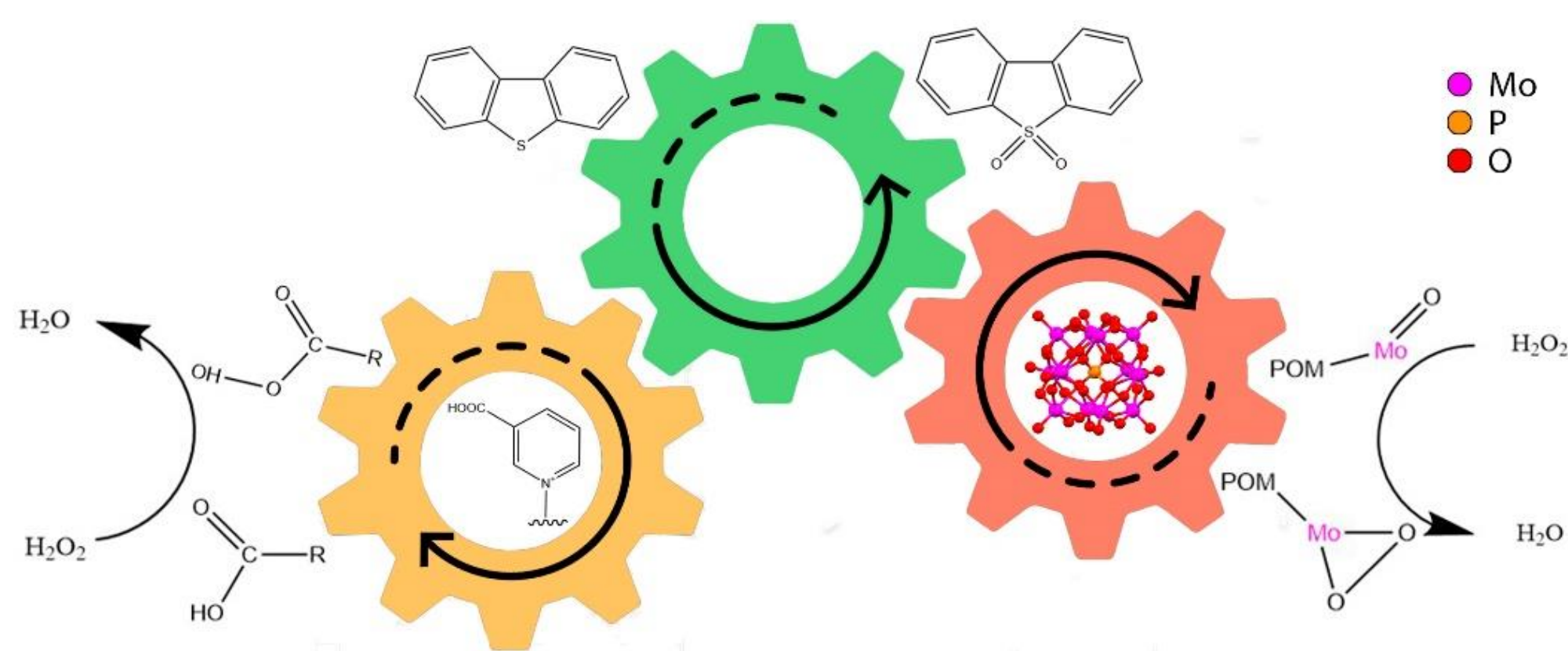
Solution:

- The oxidative desulfurization method using heterogeneous immobilized multifunctional ionic liquid as catalyst

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (Å)
SBA-15	720	0.70	48
Cl-SBA-15	646	0.61	45
NA-SBA-15	627	0.58	41
HPMo/NA-SBA-15	549	0.55	38
HPMo/SBA-15	693	0.70	43



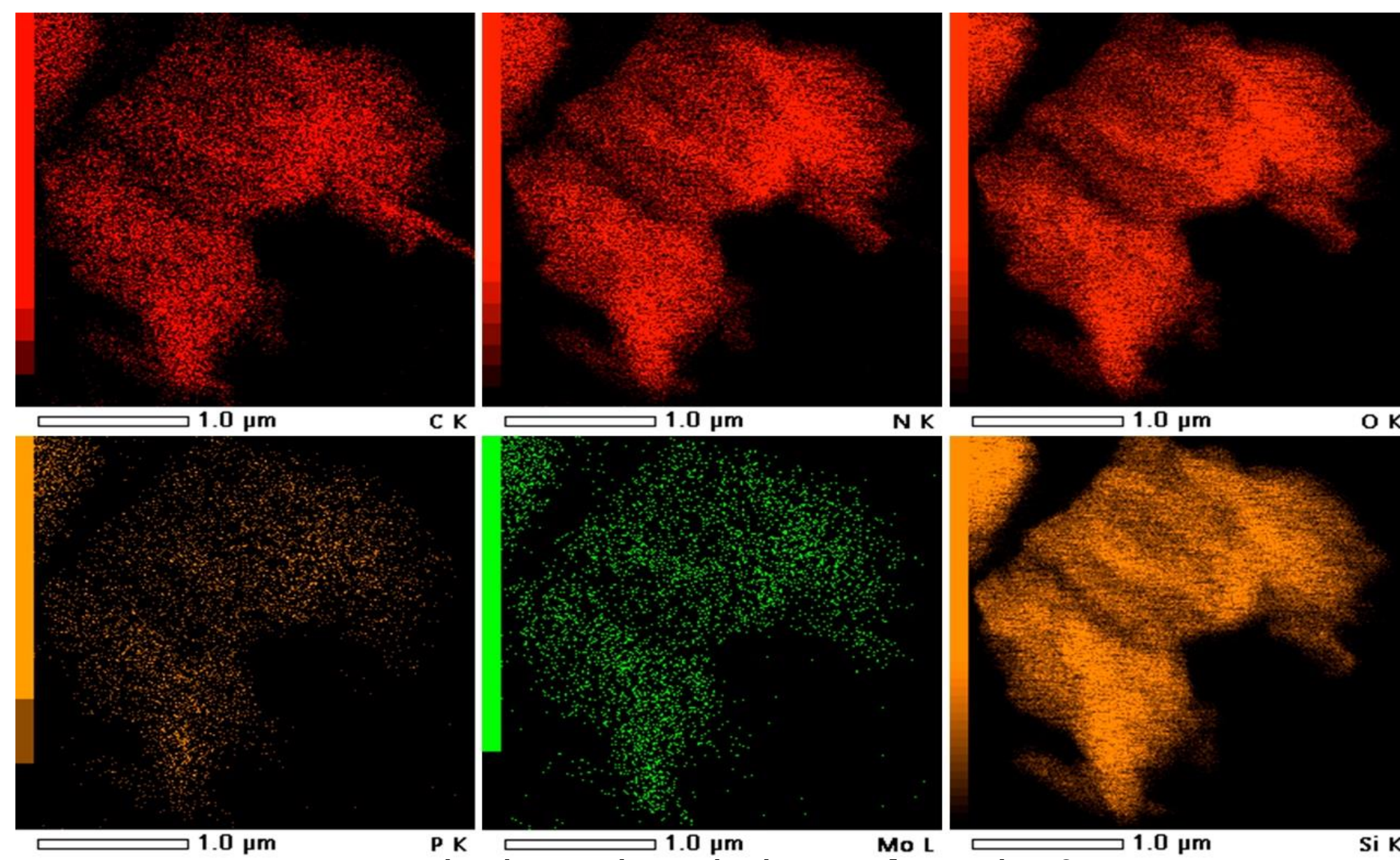
TEM images of HPMo/NA-SBA-15



Synthesis of immobilized multifunctional ionic liquids

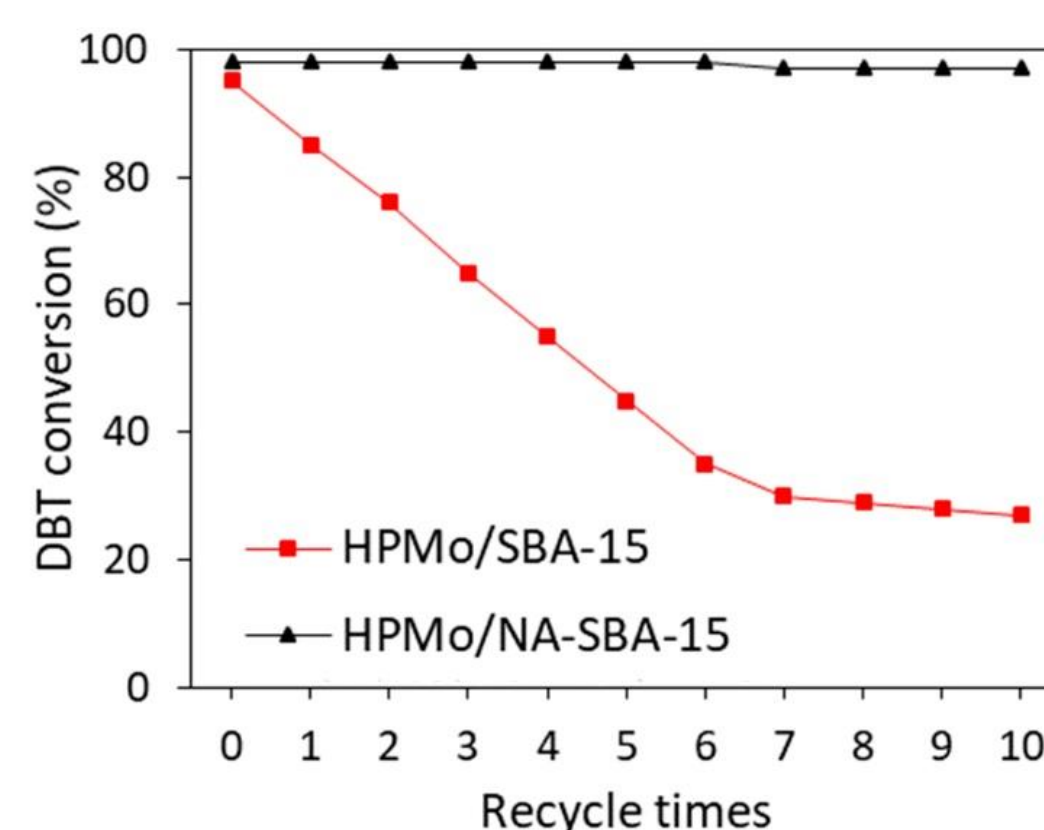
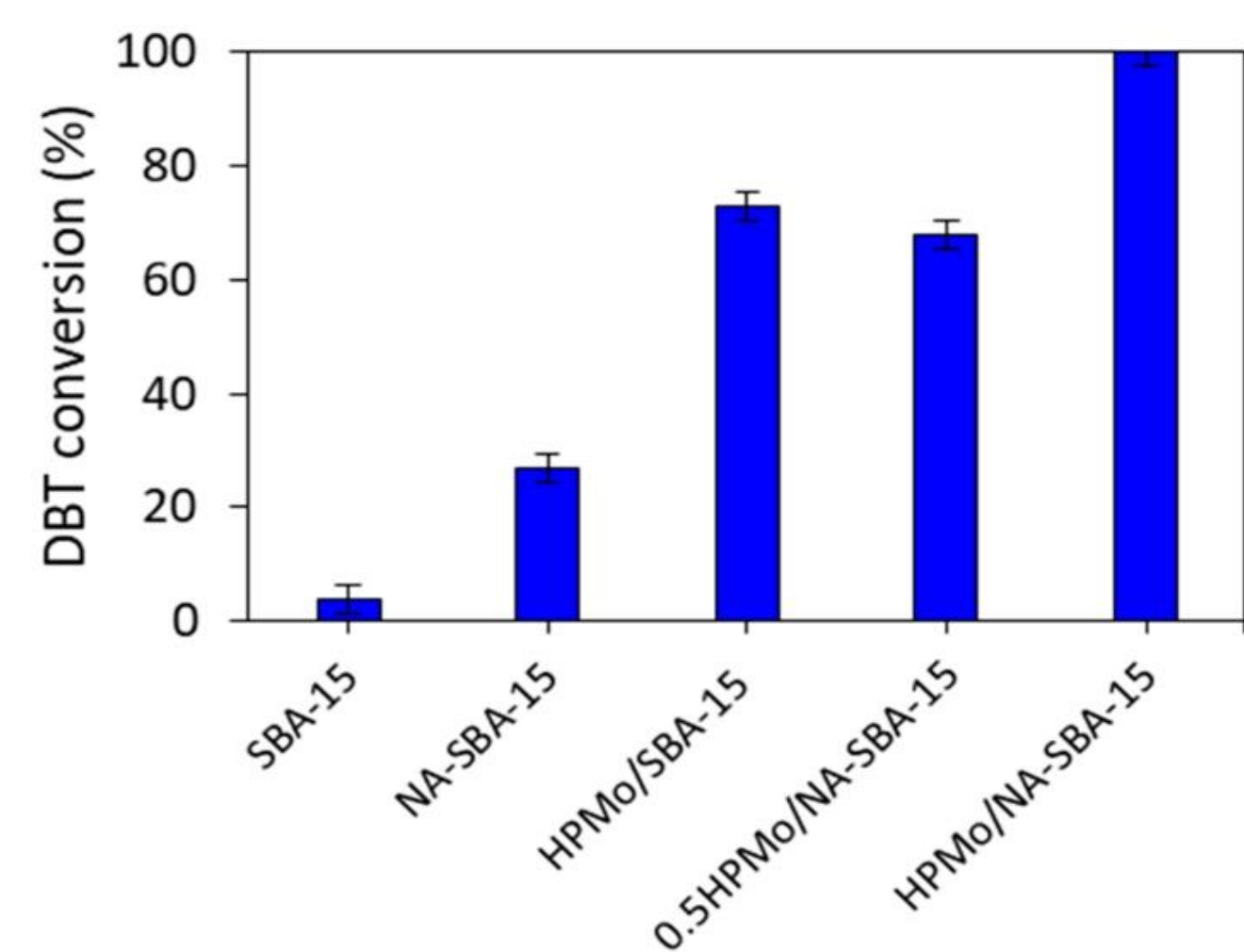
Elemental analysis of the obtained catalysts

Sample	Calculated values, % mass.			Found amount, % mass.	
	Mo	Cl	Mo values	Cl values	
NA-SBA-15	-	3.0	-	2.90	
HPMo/NA-SBA-15	4.0	-	3.78	0.17	
HPMo/SBA-15	7	-	6.90	-	
HPMo/NA-SBA-15 (after 10 cycles of regeneration)	4.0	-	3.71	0.15	
HPMo/SBA-15 (after 10 cycles of regeneration)	7	-	2.95	-	

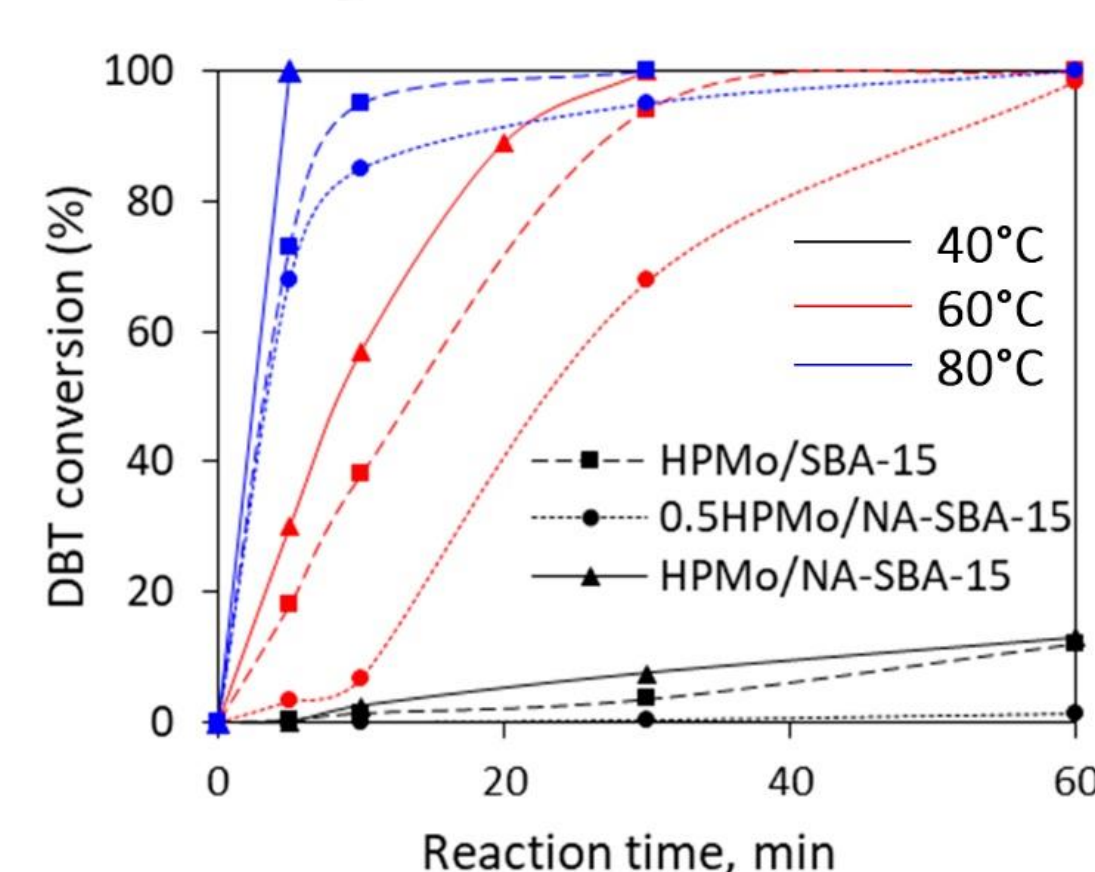


The elemental mapping images of HPMo/NA-SBA-15

Effect of catalyst nature on DBT conversion. Oxidation conditions: 5 min, 6:1 H₂O₂:S (molar ratio), 80°C, catalyst dosage = 0.018 g/5 mL, the concentration of the DBT solution = 500 ppm



Effect of regeneration of the catalysts on DBT conversion



Effect of temperature and reaction time on DBT conversion

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Conclusions:

1. Immobilized multifunctional ionic liquids were synthesized for the first time
2. The obtained catalysts were characterized by nitrogen adsorption/desorption, TEM, XRF.
3. The activity of catalysts in the oxidation reactions of organosulfur compounds was investigated