Porous materials for catalysis and sustainability

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Abstract: Emerging applications of zeolites, mesoporous silica, MOFs, COPs, and the carbons derived from these porous materials for heterogeneous catalysis and adsorption (CO_2 capture and rare earth elements (REEs) separation) are summarized with their new syntheses and organic-functionalization.

Keywords: Porous materials, heterogeneous catalysis, adsorption.

1. Introduction

Heterogeneous catalysis and adsorption for sustainability are strongly influenced by the porous materials used. In this lecture, recent progress made on the synthesis, modification, and applications of zeolite SSZ-13, mesoporous silica KCC-1, metal-organic frameworks (MOFs), covalent-organic polymers (COPs), and the zeolite/MOF-derived carbons (Fig.1) will be presented with emphasis on their organic-functionalization and metallic nanoparticles (NPs) supported for catalysis.

2. Experimental

1) SSZ-13 was hydrothermally prepared using USY as a precursor using benzyltrimethylammonium hydroxide as a structure-directing agent, and its selective catalytic reduction (SCR) activity was studied. 2) KCC-1 was prepared in reverse micelles and tested for Nd^{3+} separation and compared with KIT-6. 3) ML-101, UiO-66, MIL-125, ZIF-8 and their functionalized forms were synthesized and applied for various catalysis and adsorption. 4) COPs were synthesized via the Friedel-Crafts or Schiff base reactions and tested for CO_2 adsorption and cycloaddition reactions after organic-functionalization. Pd/Co NPs were immobilized and tested for C-C coupling reactions. 5) ZIF-8/ZIF-67 were immobilized on cellulose and after carbonization tested for oxygen reduction reaction (ORR).

3. Results and discussion

Highly stable SSZ-13 in large scale was prepared via inter-zeolite conversion from USY using an economical template, and Cu-SSZ-13 for thermal stability in SCR reaction using urea as the NOx reducing agent is monitored. Adjustable Si/Al ratio could be achieved by Na^+ control in the synthesis gel. Interestingly, Fe-SSZ-13 showed some activity in the direct conversion of CH_4 to methanol. When applied for Nd^{3+} adsorption in aqueous phase, functionalized KCC-1 exhibited a comparable performance against KIT-6 or mesoporous silica foams (MSF). Power plant ashes could also be recycled to make a high quality MSF for environmental applications. MOFs with excellent textural properties, high metal loading (and open metal sites, sometimes), and diverse post-synthesis organic functionalization available led to interesting catalysis for various liquid phase reactions: acid-base and redox reactions. It is unlikely that MOFs will replace existing catalysts for mature processes. Several gas phase reactions with industrial implications were also reported by the carbonized MOFs. An efficient and economic synthesis scheme was developed for the preparation of COPs (amorphous) with the high surface area and high stability through Friedel-Crafts reaction. The obtained networks were post-synthetically functionalized with ethylenediamine and tested for CO_2 adsorption and cycloaddition reactions. Metal NPs immobilized on COPs can be effective for various C-C coupling reactions. Crystalline COPs with high stability and good textural properties was prepared via Schiff base reactions, which are potentially useful for adsorption and catalysis. Carbonized ZIF-8/ZIF-67 on cellulose exhibited an ORR performance close to the commercial Pt/C. Fig 2 shows the representative applications in catalysis and adsorption discussed above.

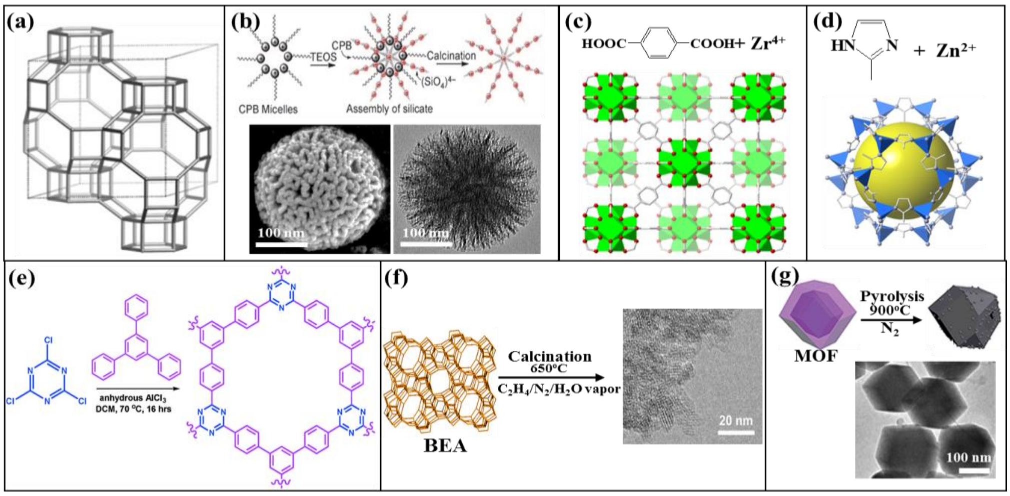

Figure 1. Emerging porous materials of interest: (a) SSZ-13; (b) KCC-1; (c) UiO-66; (d) ZIF-8; (e) MCTP-1; (f) Zeolite-derived carbon; and (g) MOF-derived carbon.

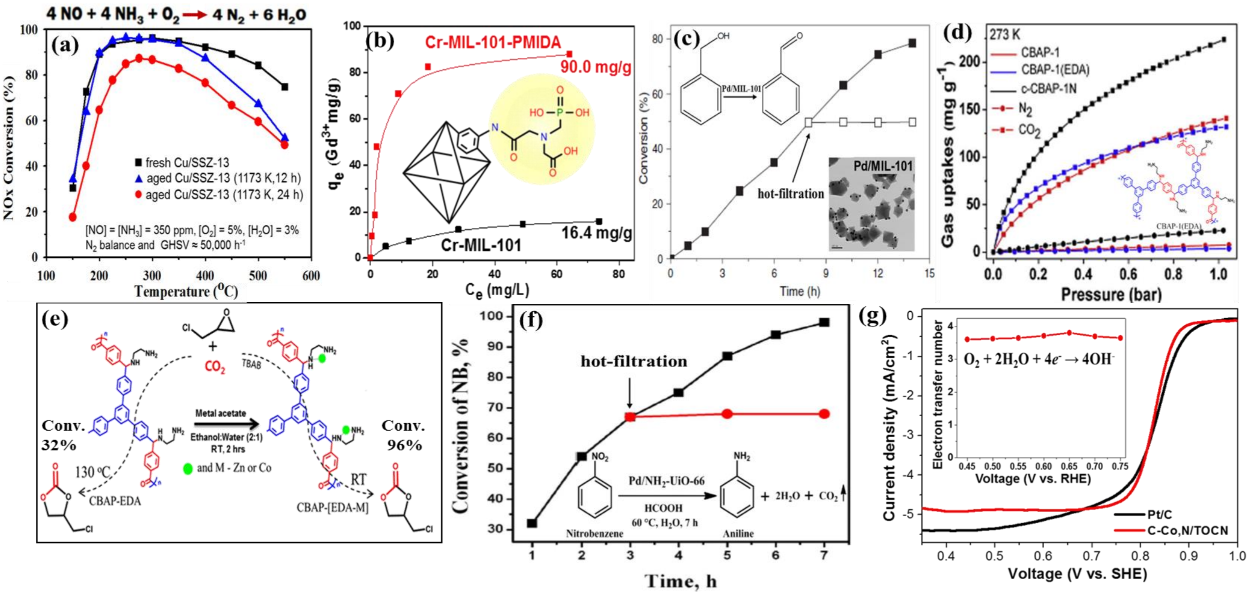

Figure 2. (a) SCR; (b) REEs adsorption; (c) Oxidation reaction; (d) CO_2 adsorption; (e) CO_2 cycloaddition reaction; (f) Transfer hydrogenation; and (g) Oxygen reduction reaction.

4. Conclusions

Small pore zeolites are emerging important in SCR and potentially promising for C1 chemistry. Inter-zeolite conversion can be an effective synthesis tool. KCC-1 has limitations for synthesis scale-up and stability, and comparable performances seem possible with KIT-6 or mesoporous silica foams. MOFs can offer novel catalysis for new catalytic applications and more hydrothermally stable kinds are being produced. COPs offer opportunities to develop multi-functional catalysts for chemical intermediates synthesis. Tandem reactions can be effectively carried out using MOFs and COPs. Pyrolysis of MOFs and COPs can lead to useful catalysts and energy storage materials.

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