

Continuous Liquid Phase Epitaxial Growth of Moisture-tolerant Metal-Organic Framework Thin Films: Crystallinity Enhancing and Assessment of Selective Sorption Properties

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Aiming for integration of functionalized metal-organic framework (MOF) materials in micro systems and devices, the deposition of MOFs thin films on substrates has increasingly been investigated and the obtained results indicate the potential in various applications such as chemical sensors, separation membranes and chromatographic capillary columns.^[1] Stepwise liquid phase epitaxial growth (LPE) is one of promising methods to fabricate precise-controlled MOF thin films even at low temperature when coupled with the controlled secondary building units approach (CSA). Integrating into practical uses, not only the selections of MOFs with high stabilities but also the preparative methods need to be considered to achieve such desired performances. Herein, thin films of the moisture-tolerant MOFs, $[\text{Zn}_4\text{O}(\text{L})_3]_n$ (L= dialkyl-substituent carboxypyrazolate derivatives), are successfully fabricated in the well-controlled manner on the self-assembled monolayer (SAM) modified gold substrates by using the continuous, automated step-by-step CSA-LPE method. The crystallinity of the homostructured surface mounted MOFs (SURMOFs) are significantly improved. Thank to the advantages of the heteroepitaxial growth, the low crystallinity of some SURMOF constructed with more sophisticated linker (**B**) can be overcome by fabricating as shell layers on top of the highly crystalline, lattice-matching SURMOF core layers (**A**) resulting in the heterostructured **B@A** SURMOFs.^[2] Proposing a model for separating and selective sensing devices, the selective adsorption properties of the heterostructured films are examined by the single- as well as the multi-component adsorptions based on quartz crystal microbalance. An acceptable total adsorption capacity, an excellent size selectivity of different alcohol adsorptions and a high degree of moisture-tolerance of the heteroepitaxial MOF films are observed.^[2,3]

Keywords Metal-Organic frameworks; Thin films; Stepwise deposition; Separation; Sensing

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Preparation of BaZr_{1-x}Y_xO₃-Based Proton Conducting Electrolyte Using TEA-Metal Precursor by The Sol-Gel Method

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A simple and rapid method, triethanolamine (TEA) sol-gel, for preparing barium zirconate (BaZrO₃, BZ) and yttrium-doped barium zirconate (BaZr_{1-x}Y_xO₃, BZY) with 0.1 < x < 0.2 is reported. Appropriate amount of Y(NO₃)₃ was introduced to 1:1 mole ratio of Ba(NO₃)₂ and ZrO(NO₃)₂ in excess TEA. The as-prepared ceramic powders were characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). The evolution of the crystalline phase is studied as a function of the calcination temperature (1000 °C, 1100 °C, 1200 °C, and 1300 °C in static air). As increasing calcination temperature, the impurity phase, BaCO₃, decreases. The XRD pattern of the powder calcined at 1300 °C displayed pure cubic perovskite phase of barium zirconate. EDX mappings showed homogeneous distribution of Ba²⁺, Zr²⁺ and Y³⁺ in the doped samples. In addition, the total conductivity in different doping concentration of yttrium in BaZrO₃ has been systematically studied and the highest total conductivity was obtained for 15% Y-doped BaZrO₃ with the lowest activation energy in proton transportation of 0.34 eV. The electrical properties of the as-prepared BZ and BZY showed potential application for electrolyte membrane in solid oxide fuel cell.

Keywords Barium zirconate; Yttrium-doped barium zirconate; Triethanolamine (TEA) sol-gel; Electrolyte membrane; Solid oxide fuel cell.

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Preparation of Crystalline Nanoseeds to Induce Formation of Zeolite Beta Structure

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Crystalline nanoseeds were successfully synthesized using mesoporous SBA-15 as silica source, aluminium isopropoxide as aluminium source, and tetraethylammonium hydroxide as organic template. The TEAOH/SiO₂/H₂O mole ratio of 0.40/1/7.5 was used. The starting mixture was sonicated thoroughly prior to crystallization in an autoclave under autogenous pressure at 135°C for 48 hours. The product was characterized by XRD, N₂ adsorption and SEM techniques. The XRD results presented complete phase transformation from SBA-15 to crystalline seeds. The SEM image showed uniform shape and size of nanoseeds with the average size of approximately 160 nm. Nitrogen adsorption data showed the characteristic behavior of microporous nanoseeds having specific surface area of 702 m²/g. A small amount of calcined crystalline nanoseeds was used successfully as a structure directing agent in the synthesis of highly thermal zeolite beta. It was found that the structure of zeolite beta was formed under hydrothermal conditions. In the absence of the crystalline nanoseeds, the structure of zeolite beta was difficult to form.

Keywords Nanoseeds; Formation; Zeolite beta

Spin Crossover in Iron(II) Imidazolylmethylene-aryl amine Complexes: Tuning of the Spin Transition Temperature

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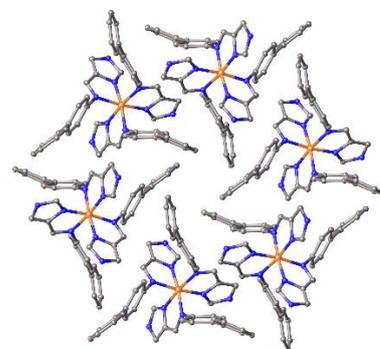
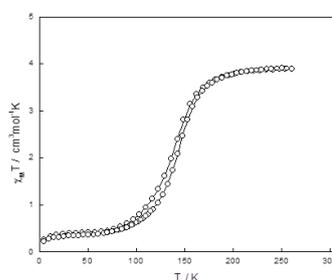
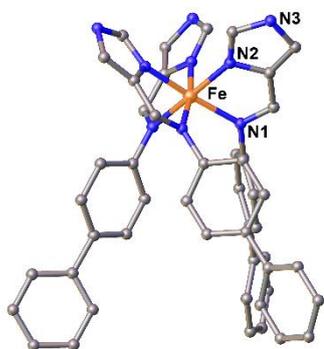
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The new ligands imidazol-2-ylmethylene-aryl amine {2-ima^{Ar}; Ar = biphenyl (Bp), fluorenyl (Fl), anthracenyl (An)} and imidazol-4-ylmethylene-aryl amine (4-ima^{Ar}; Ar = Bp, Fl, An) have been prepared by reaction of the aryl amine with imidazole-2-carboxaldehyde or imidazole-4-carboxaldehyde. Related substituted ima^{Ar} ligands N-methyl-imidazol-2-ylmethylene-aryl amine (1-Me-2-ima^{Ar}; Ar = Bp, Fl) and 5-methyl-imidazol-4-ylmethylene-aryl amine (5-Me-4-ima^{Ar}; Ar = Bp, Fl). Reaction of the ligands with [Fe(H₂O)₆][Y]₂ (Y = BF₄, ClO₄) in MeOH or EtOH yields the complexes, [Fe(X-ima^{Ar})₃][Y]₂·sol or [Fe(Me-X-ima^{Ar})₃][Y]₂·sol (Ar = Bp, Fl; Y = BF₄, ClO₄; sol = MeOH or EtOH). X-ray crystallographic studies reveal strong C-H···π and hydrogen bonding interactions leading to high cooperativity. SQUID magnetic susceptibility studies show that spin crossover varies from gradual to abrupt with the spin transition occurring at temperatures from *ca.* 150 to 400 K.



Keywords Spin crossover; iron(II) complexes; Imidazolyl diimine ligands; Molecular magnetism

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Enhance the catalytic activities in nanocatalysis by ferrocene moieties

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Magnetic iron-oxide nanoparticles stabilized by imine or amine ligands containing ferrocene moieties were synthesized and characterized by FTIR, XRD, AAS, TEM, vibrating sample magnetometer (VSM) and Mössbauer spectroscopy. The oxidation of benzyl alcohol was carried out in the presence of the synthesized magnetic nanoparticles with or without ferrocene moieties as nanocatalysts and H_2O_2 as oxidant. The synergistic activities between magnetic nanoparticles and ferrocene moieties in the stabilizing ligands were observed in this nanocatalysis. It turned out that the conversions of benzyl alcohol and the selectivities of benzaldehyde in the nanocatalytic systems with magnetic iron-oxide nanoparticles stabilizing by ligands containing ferrocene moieties were enhanced more significantly than the ferrocene-free nanocatalytic systems. The nanocatalysis was proposed to be proceeded via first adsorption of benzyl alcohol on the surface of nanoparticles and then Fenton-typed reactions operating at both magnetic iron-oxide nanoparticles and ferrocene moieties. Ferrocene moieties play an important role in the nanocatalysis for the enhanced selectivity of benzaldehyde by their synergistic interactions to magnetic iron-oxide nanoparticles. Accordingly, the enhanced catalytic activity of nanocatalysts can be achieved by tuning the structure of stabilizing ligands surrounding to nanoparticles.

Bimetallic Aluminum Complexes Supported by Methylene Bridged Bis(phenoxy-imine) Ligands for the ROP of *rac*-lactide

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A series of bimetallic aluminum complexes bearing methylene bridged bis(phenoxy-imine) ligands (**1-3**) have been successfully synthesized and characterized by NMR spectroscopy. The complexes were obtained in good yields by the reaction between the corresponding ligand and 2 equivalents of trimethyl aluminum (TMA) in toluene at 90 °C. All bimetallic aluminum complexes were not only found to be an efficient initiator for the ring-opening polymerization of *rac*-lactide, but the polymerizations also proceeded in a controlled manner. Kinetic studies revealed that all polymerizations were the first-order reaction in monomer. The plots between molecular weight *versus* conversion exhibited a good linear relationship which is indicative of living polymerizations. In addition, the imino substituents on the ligand framework and the *ortho* phenoxy substituents have an significant impact on the catalytic activities and the stereoselectivities of catalysts.

Keywords *Rac*-lactide; Ring-opening polymerization; Bimetallic aluminum complexes; Polylactide

