

STREM Biocompatible MIL-100(Fe) MOF

Porous Iron Trimesate with a Hierarchical Pore Structure

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26-2340 Iron(III) 1,3,5-benzenetricarboxylate hydrate, porous (F-free MIL-100(Fe), KRICT F100) [Iron trimesate] (1257379-83-1)

500mg
2g

[Fe₃O(H₂O)₂(OH){C₆H₃(COO)₃]₂·XH₂O; red solid; SA: 2120 (Langmuir); 1950 (BET); P.Vol. 1.075

Large-pore Iron (III) Carboxylate

As hybrid organic-inorganic structures, porous metal-organic frameworks (MOFs) have interesting coordination structures and topologies, with notable features including well-defined crystalline structures, regular pore structures, and very high porosities and surface areas. Consequently, these advanced functional materials have potential use in gas/liquid storage, gas separation, adsorption chiller, dehumidification, catalysis, drug delivery, magnetic and optical devices, and many other applications.

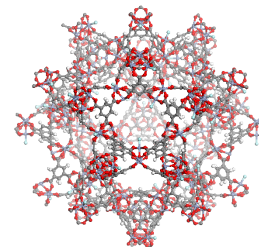
MIL-100(Fe) is a new iron(III) carboxylate that has initially been developed by the collaboration between the CNRS-Institute for Lavoisier (ILV; Prof. G. Férey and Dr. C. Serre) and the Korea Research Institute of Chemical Technology (KRICT; Dr. J.-S. Chang and Dr. Y.K. Hwang). **KRICT F100** is a fluorine-free version of **MIL-100(Fe)** prepared by KRICT with similar physicochemical properties. It would be actually one of the highest porous MOFs that can be produced by the large-scale hydrothermal synthesis. The hierarchically mesoporous crystalline three-dimensional iron(III) trimesate has two sets of mesoporous cages (24 Å and 29 Å) that are accessible through microporous windows (ca. 8.6 Å and ca. 4.7-5.5 Å).

The incorporation of transition metals into the skeleton of MOFs imparts new sorption and catalytic properties to these functional materials. Iron is attractive because it is readily available, inexpensive, environmentally benign, nontoxic, and exhibits interesting redox behavior.

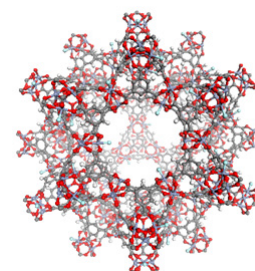
In fact, **KRICT F100** has been shown to be biocompatible and hydrothermally stable in boiling water at 100°C. It has also been found to catalyze several types of Lewis acid catalysis such as Friedel-Crafts acylation, Prins reaction, etc. In addition, this large-pore iron trimesate can be reduced under controlled conditions to generate sites that strongly interact with unsaturated gas molecules and enable selective gas sorption and separation.

Finally, the rapid preparation of **KRICT F100** on a 15kg-scale has been demonstrated using fluorine-free hydrothermal conditions.

Mesoporous Cages in MIL-100(Fe)



Medium cage (24 Å)



Large cage (29 Å)

Color & Form

Hydrated



Dehydrated



Spheres



Washcoated Honeycomb



Slurry Solution



Key Properties of KRICT F100

Chemical formula (hydrated form)	[Fe ₃ O(H ₂ O) ₂ (OH){C ₆ H ₃ (CO ₂) ₃] ₂ · nH ₂ O (n > 12)
Chemical formula (dehydrated form)	[Fe ₃ O(OH){C ₆ H ₃ (CO ₂) ₃] ₂
Purity	>99%
Color	Dark brown (hydrated); Pale brown (dehydrated)
Sensitivity	KRICT F100 is insensitive to air, light, and water, but it is sensitive to heat above 150°C in air
Specific surface area	(after dehydration at 150°C): 2120 m ² /g (Langmuir); 1950 m ² /g (BET)
Pore volume	1.075 cm ³ /g
Gas/liquid uptake	Significantly higher than conventional zeolite beta and commercial iron trimesate; both nonpolar and polar molecules due to the presence of both hydrophilic and hydrophobic sites in the framework.

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Characterization of KRICT F100

KRICT F100 has been characterized using powder X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). It has also been shown to have high hydrothermal and chemical stability.

The terminal water molecules in the as-synthesized MOF are removable upon heating above 100°C under vacuum or a gas stream. The removal of the water molecules from fully saturated **KRICT F100** can be seen in the TGA profile.

Reactivity of KRICT F100

The effectiveness of **MIL-100(Fe)** or **KRICT F100** as a heterogeneous catalyst was demonstrated for the Friedel-Crafts benzylation of benzene by benzyl chloride (BZC) to yield diphenylmethane (DPM). At 70°C, 100% BZC conversion with nearly 100% DPM selectivity was achieved within 5 min over **MIL-100(Fe)**. Solid acid zeolite catalysts were significantly less reactive and slightly less selective for DPM. These results suggest that the unsaturated iron(III) metal sites have potential activity for new catalytic applications.

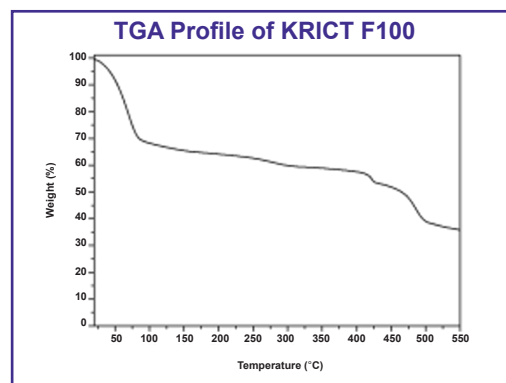
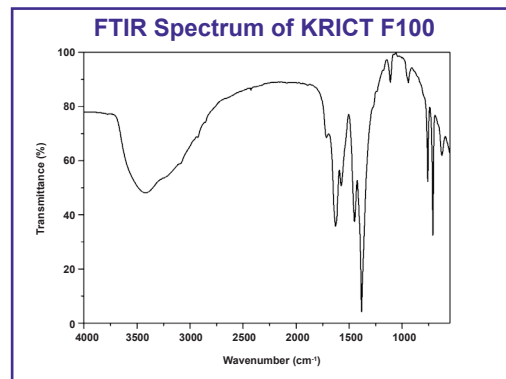
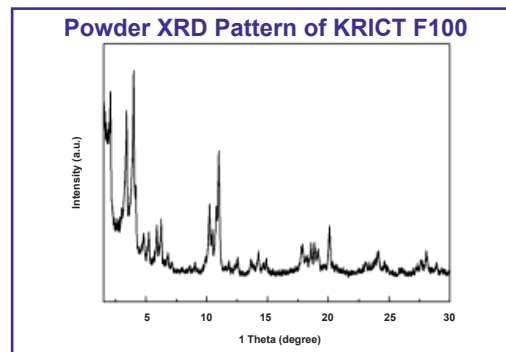
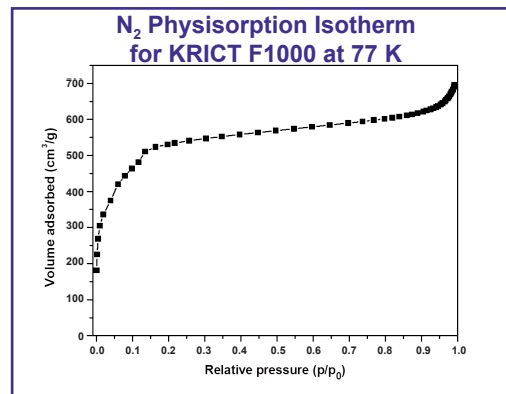
Removal of the terminal water molecules from **KRICT F100** leads initially to the generation of a large number of coordinatively unsaturated Fe(III) sites that act as Lewis acid sites in the pores. After activation, the reduced framework iron sites in octahedral iron trimers strongly interact with unsaturated gas molecules, such as CO and propylene, and also exhibit improved preferential sorption properties for unsaturated gases, such as propylene over propane. Thus, **KRICT F100** and its derivatives have the potential to serve as environmentally friendly gas adsorbents with preferential gas sorption properties.

Activation: **KRICT F100** is generally activated by heating at 150°C for 6 h under a vacuum or nitrogen flow.

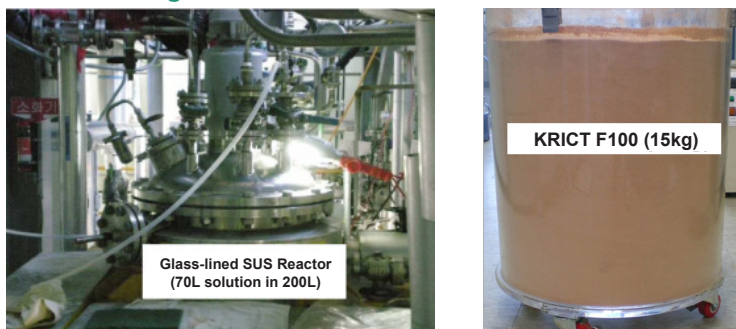
Large-scale Preparation of KRICT F100

The highly productive rapid (>1700 kg/m³-day), large-scale (15 kg) synthesis of **KRICT F100** via hydrothermal reactions in the absence of HF has been achieved using a highly concentrated reactant mixture. The HF-free route is both less time-consuming and less expensive, and the **KRICT F100** obtained using this method has similar physicochemical properties as **MIL-100(Fe)** and is the highest surface area MOF produced at this scale with such a high space-time yield. **KRICT F100** can also be formed into spheres, pellets, monoliths or washcoated honeycombs for ease of handling on a large scale.

Storage conditions: No special storage conditions are required. It is recommended, however, that **KRICT F100** be placed in a desiccator prior to use.



Large-scale Manufacture of KRICT F100



References:

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3. Y.-K. Seo, et al., "Large Scale Fluorine-Free Synthesis of Hierarchically Porous Iron(III) Trimesate MIL-100(Fe) with a Zeolite MTN Topology," *Micropor. Mesopor. Mater.*, 157, 137-145 (2012).
4. Y.-K. Seo, et al., "Energy-Efficient Dehumidification over Hierarchically Porous Metal-Organic Frameworks as Advanced Water Adsorbents," *Adv. Mater.*, 24, 806-810 (2012).
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