Active-site-accessible porous metal-organic framework composed of triangular building units: preparation, catalytic activity and magnetic property

Shengqun Su\textsuperscript{ab}, Yibo Zhang\textsuperscript{ab}, Min Zhu\textsuperscript{ab}, Xuezhi Song\textsuperscript{ab}, Song Wang\textsuperscript{ab}, Shuna Zhao\textsuperscript{ab}, Shuyan Song\textsuperscript{a}, Xiangguang Yang\textsuperscript{a}, Hongjie Zhang\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. Tel.: +86 431 85262127; fax: +86 431 85698041. E-mail address: hongjie@ciac.jl.cn (H.-J. Zhang).

\textsuperscript{b} Graduate School of the Chinese Academy of Sciences, Beijing, 100039, P. R. China.

Experimental Section

Materials: 1H-pyrazole-4-carboxylic acid (H\textsubscript{2}L) was synthesized as reported in the literature,\textsuperscript{1} and the other reagents were purchased from commercial sources and used as received.

\‡ Synthesis of 1: A mixture of H\textsubscript{2}L (0.0336 g, 0.3 mmol), Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (0.0483 g, 0.2 mmol) was dissolved into 2.0 ml N, N-Dimethylformamide (DMF), 1.5 ml H\textsubscript{2}O and 2.0 ml CH\textsubscript{3}CH\textsubscript{2}OH in a 15 ml Teflon-lined reactor and heated at a constant rate of 2 °C/min to 80 °C, kept at that temperature for 3 days, and cooled to room temperature at a constant rate of 0.1 °C/min. The resulting dark-blue block crystals were obtained (0.0362 g, yield: 76%). Elemental analysis (%) calcd for 1: C 26.65, H 4.19, N 11.65; found: C 26.77, H 4.15, N 11.71. When the CH\textsubscript{3}OH was used instead of CH\textsubscript{3}CH\textsubscript{2}OH, the dark-blue block crystals were also obtained. The PXRD result shows it has the same framework as the compound 1. In addition, compound 1 can be dissolved in the aqueous ammonia, and the blue solution could evaporate at room temperature to produce blue crystalline solid, which is the reported compound NH\textsubscript{4}[Cu\textsubscript{3}(\mu\textsubscript{3}-OH)(\mu\textsubscript{3}-4-carboxypyrazolato)\textsubscript{3}] (see the reference 12 in the text).

Ion exchange

The typical procedure makes use of 50 mg of the compound 1 which is suspended in 5 mL of a 0.1 M aqueous solution of the corresponding inorganic salt: NaNO\textsubscript{3} and Gd(NO\textsubscript{3})\textsubscript{3}. After seven days, the exchanged solids were subsequently filtered, washed with distilled water and later on suspended during 4 hours in distilled water in order to remove the eventual adsorbed ion pairs. Afterwards, the materials were filtered again and washed with distilled water. The effect of ion exchange on the materials was examined by means of Atomic absorption. The results are indicative that Na\textsuperscript{+} gives rise to exchange of 58% H\textsubscript{3}O cation only. In the case of ion with higher charge (Gd\textsuperscript{3+}) complete ion exchange takes place. The results are in agreement with the ion exchange behavior of compound NH\textsubscript{4}[Cu\textsubscript{3}(\mu\textsubscript{3}-OH)(\mu\textsubscript{3}-4-carboxypyrazolato)\textsubscript{3}] (see the reference 12 in the text).

In addition, the magnetic susceptibilities of compound 1 exchanged with Gd\textsuperscript{3+} was measured at 0.1 T field in the temperature rang 2-300 K. As shown in Fig. S6, the \(\chi_M T\) value is 3.52 cm\textsuperscript{3} mol\textsuperscript{-1} K at 300K, which is close to the spin-only value of 3.75 cm\textsuperscript{3} mol\textsuperscript{-1} K calculated for three high-spin Cu(II) ions and one-third of Gd\textsuperscript{3+} (\(g = 2\)). Thermal dependence of the \(\chi_M T\) curves for this compound and compound 1 are similar, just with different value.
N₂ adsorption-desorption isotherms were measured at 77 K on an automatic volumetric adsorption equipment (ASAP2020, Micromeritics). Before the measurements, the samples (150 mg) were outgassed at 120 °C for 8h.

Catalysis Experiment: The catalytic oxidation of CO oxidation was conducted under atmospheric pressure in a quartz-tube fixed-bed reactor (i.d. 8 mm). The sample was activated in vacuum at 120 °C for 6h before the reaction. The mass of the catalyst sample was 0.06 g and it was well mixed with quartz sand. A gas mixture of 1% CO-6% O₂-93% Ar was passed through the catalyst bed at a flow rate of 30 ml/min, which gave a space velocity (SV) of 30000 ml h⁻¹ (g cat)⁻¹. The effluent gases were analyzed by an online gas chromatograph (Shimadzu GC-8A) equipped with a TCD detector. CO conversion was calculated from the measured CO concentration using the formula CO conversion = [(CO_in – CO_out)/CO_in], where CO_in and CO_out were the inlet and outlet CO concentrations, respectively.

Powder X-Ray diffraction data were collected on a Bruker D8-ADVANCE diffractometer equipped with Cu Kα at a scan speed of 5° min⁻¹. IR spectra were obtained from KBr pellets on a Perkin-Elmer 580B IR spectrometer in the 400-4000 cm⁻¹ region (SI). Elemental analyses (C, H, N) were performed with a VarioEL analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 40 to 700°C under nitrogen.

Temperature-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-7 magnetometer with an applied field of 1000 Oe. The diamagnetic corrections for the compounds were estimated using Pascal’s constants, and magnetic data were corrected for diamagnetic contributions of the sample holder. The experimental data were fitted to the expression derived from the Hamiltonian \( H = -J(S_1S_2 + S_2S_3 + S_1S_3) \), which corresponds to a regular triangular array of spins corrected with a \( zJ' \) intertrimer coupling parameter in order to fit the low temperature data. The best-fit parameters obtained with this model are, \( J = -154.37 \text{ cm}^{-1} \), \( zJ' = -9.14 \text{ cm}^{-1} \), \( g = 2.16 \). The negative coupling constant \( J \) and \( zJ' \) confirms the existence of a strong antiferromagnetic exchange within 1, which is consistent with the structural characteristics and previously reported data.

Fig. S1 TGA curves of 1.
Fig. S2 PXRD patterns for 1: (a) simulated, (b) as-synthesized, (c) after nitrogen sorption, and (d) after catalytic reaction.

Fig. S3 Nitrogen sorption isotherm at 77 K.

Fig. S4 Thermal dependence of the $\chi_M T$ curves for 1. Continuous lines correspond to the best least-squares fit.
Fig. S5 IR spectra of 1.

Fig. S6 Thermal dependence of the $\chi_M T$ curves for 1 exchanged with Gd$^{3+}$.

Reference