Mechanochemical Approach to Gallate BioMOFs: Efficient Synthesis and Cr(VI) Removal from Aqueous and Soil Systems

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Calculation of reaction yields

Fe-Gallate MOF

Assumptions. Product formula: $Fe(C_7O_5H_3)$ (1 Fe: 1 ligand : 1 product). Reagents: gallic acid monohydrate ($C_7H_6O_5 \cdot H_2O$), $FeCl_2 \cdot 4H_2O$, NaOH. Masses reagents used: 0.720 g gallic acid monohydrate, 0.400 g $FeCl_2 \cdot 4H_2O$, 0.240 g NaOH. Isolated product masses after washing and drying (corresponding to different milling times) are given below.

Molar masses (used):

$C_7H_6O_5 \cdot H_2O$ = 188.135 $g \cdot mol^{-1}$; $FeCl_2 \cdot 4H_2O$ = 198.811 $g \cdot mol^{-1}$; $Fe(C_7O_5H_3)$ = 222.941 $g \cdot mol^{-1}$.

Moles of reagents added:

n(gallic acid monohydrate) = 0.720 g ÷ 188.135 $g \cdot mol^{-1}$ = 0.0038270 mol

$n(FeCl_2 \cdot 4H_2O)$ = 0.400 g ÷ 198.811 $g \cdot mol^{-1}$ = 0.0020120 mol (limiting reagent)

n(NaOH) = 0.240 g ÷ 39.997 $g \cdot mol^{-1}$ = 0.0060005 mol

Theoretical mass of product (maximum)

Moles of product (max) = moles of limiting reagent = 0.0020120 mol

Theoretical mass = 0.0020120 mol × 222.941 $g \cdot mol^{-1}$ = 0.44856 g

Table SI 1. Isolated masses and yields (by milling time) for Fe-Gallate MOF

Milling time (min)	**Isolated mass (g)**	**Yield (%) = (mass / 0.44856) × 100**
90	0.414	92.3 %
60	0.411	91.6 %
30	0.310	69.1 %
15	0.285	63.5 %

Mg-Gallate MOF

Assumptions**.** Product formula: $Mg(C_7O_5H_4)$ (1 Mg : 1 ligand : 1 product). Reagents: gallic acid monohydrate ($C_7H_6O_5 \cdot H_2O$), $MgSO_4 \cdot 7H_2O$, NaOH. Masses of reagents used: 0.670 g gallic acid monohydrate, 0.460 g $MgSO_4 \cdot 7H_2O$, 0.223 g NaOH. Isolated product masses after washing and drying (corresponding to different milling times) are given below.

Molar masses (used):

- $C_7H_6O_5 \cdot H_2O$ = 188.135 $g \cdot mol^{-1}$
- $MgSO_4 \cdot 7H_2O$ = 246.471 $g \cdot mol^{-1}$
- $Mg(C_7O_5H_4)$ = 192.409 $g \cdot mol^{-1}$

Moles of reagents added:

- n(gallic acid monohydrate) = 0.670 g ÷ 188.135 $g \cdot mol^{-1}$ = 0.0035613 mol
- $n(MgSO_4 \cdot 7H_2O)$ = 0.460 g ÷ 246.471 $g \cdot mol^{-1}$ = 0.0018663 mol (limiting reagent)
- n(NaOH) = 0.223 g ÷ 39.997 $g \cdot mol^{-1}$ = 0.0055754 mol

Theoretical mass of product (maximum)

Moles of product (max) = moles of limiting reagent = 0.0018663 mol

Theoretical mass = 0.0018663 mol × 192.409 $g \cdot mol^{-1}$ = 0.35910 g

Table SI 2. Isolated masses and yields (by milling time) for Mg-Gallate MOF

Milling time (min)	**Isolated mass (g)**	**Yield (%) = (mass / 0.44856) × 100**
90	0.270	75.2 %
60	0.243	67.7 %
30	0.200	55.7 %
15	0.039	10.9 %

Refinements

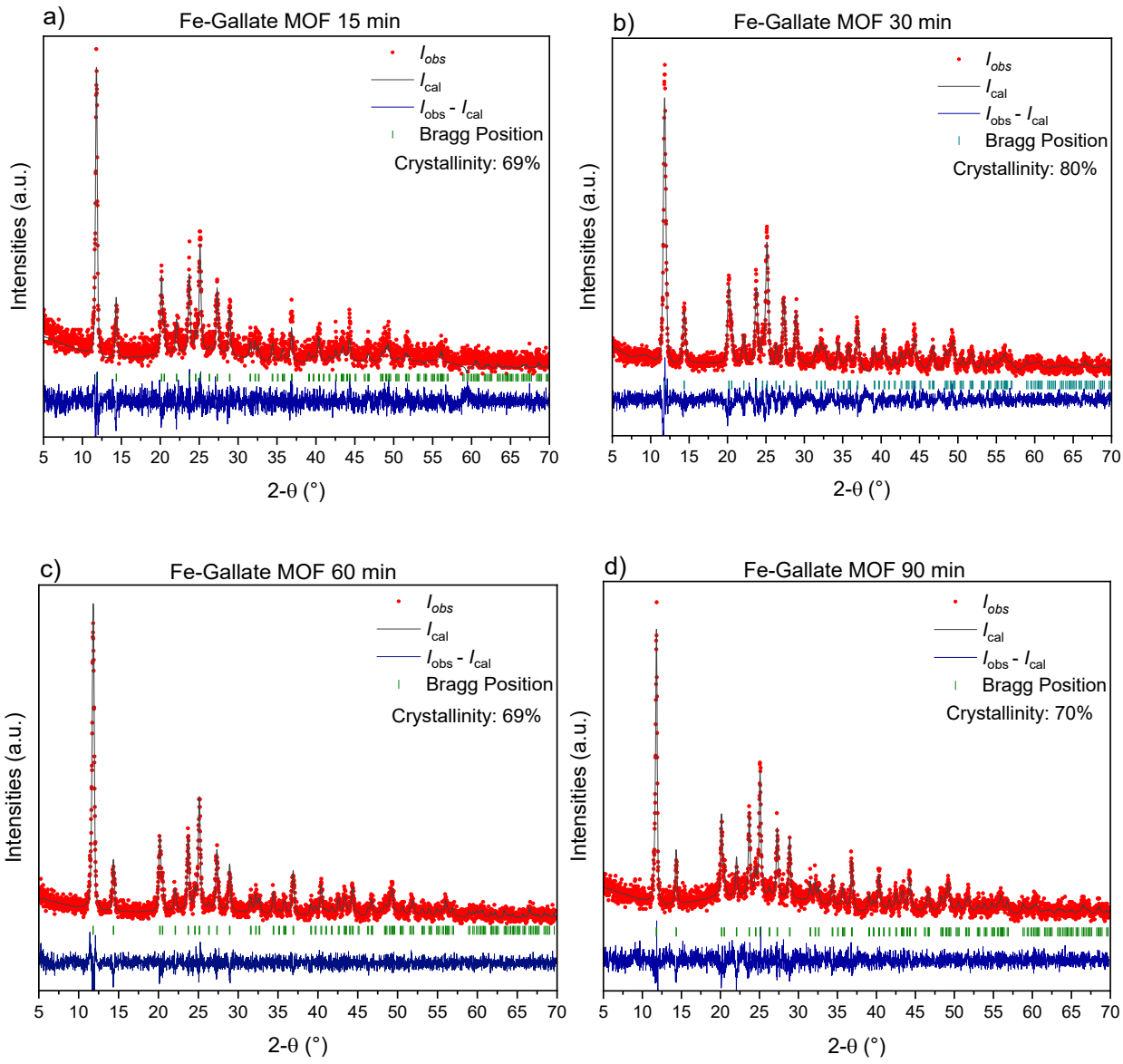

Fig. S1 Refinement for Fe-Gallate MOF at synthesis times of 15 (a) 30 (b), 60 (c), and 90 min (d).

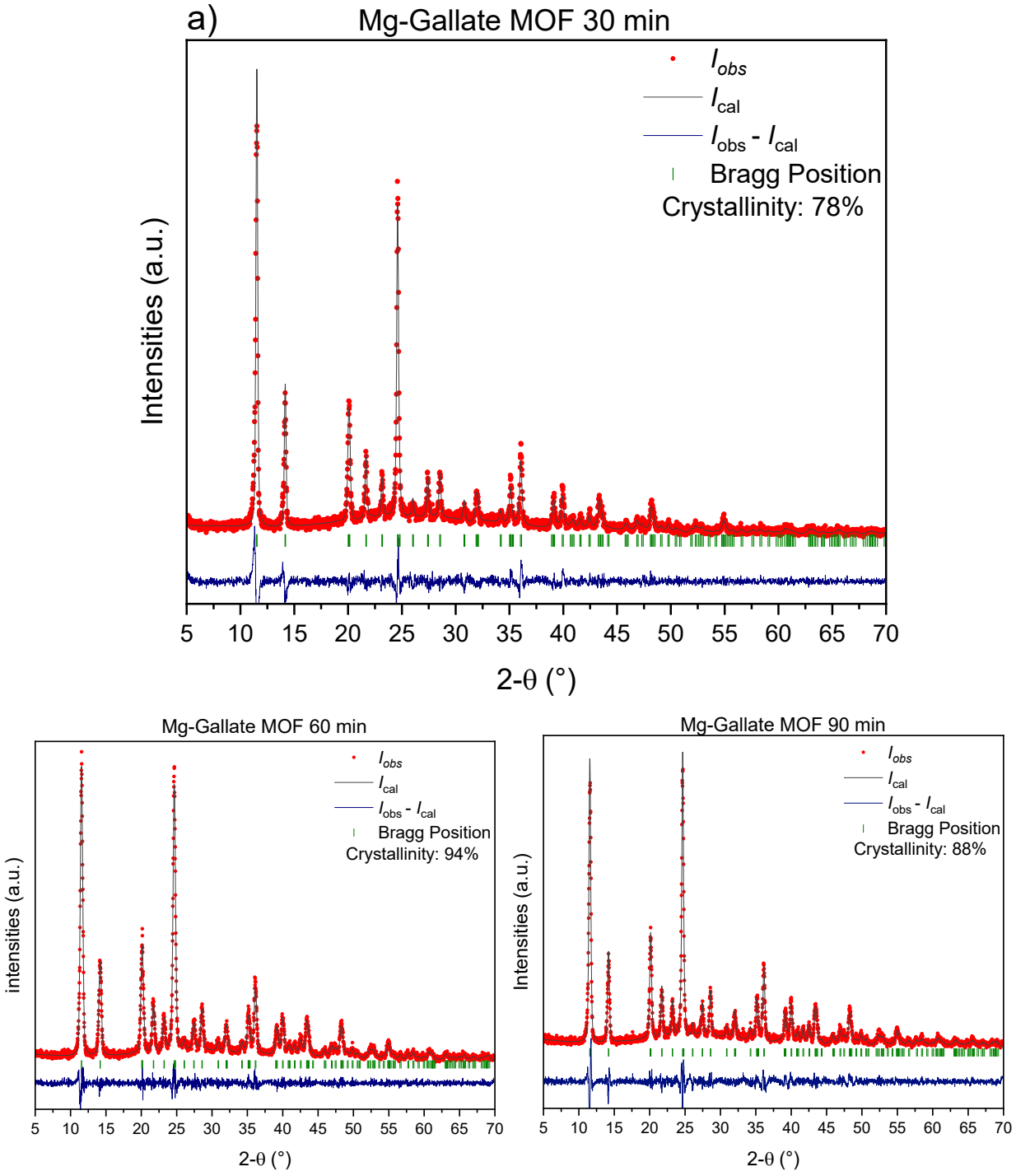

Fig. S2 Refinement for Mg-Gallate MOF at synthesis times of 30 (a), 60 (b), and 90 min (c).

Table SI 3. Unit cell and refinement parameters obtained from the Rietveld method for Fe-Gallate and Mg-Gallate materials were obtained for each mechanochemical reaction time. Rietveld refinement was performed based on crystallographic data obtained from model reference structures (CCDC Code 1260549 and 1899504).

Fe-Gallate MOF					**Mg-Gallate MOF**		
	15 min	30 min	60 min	90 min	30 min	60 min	90 min
Cell Parameters – Space Group *P*3$_1$21 (152)							
a (Å)	8.659(6)	8.651(5)	8.658(6)	8.673(5)	8.868(3)	8.849(3)	8.848(3)
b (Å)	8.659(6)	8.651(5)	8.658(6)	8.673(5)	8.868(3)	8.849(3)	8.848(3)
c (Å)	10.877(17)	10.88(11)	10.86(12)	10.88(11)	10.772(8)	10.765(9)	10.764(8)
$\alpha = \beta = 0°$ $\gamma = 120°$							
Rietveld R-factors for Pattern	R_p = 17.15 R_{wp}=21.85	R_p = 18.1 R_{wp}=23.1	R_p =18.1 R_{wp}=23.1	R_p = 16.1 R_{wp}=20.5	R_p =12.7 R_{wp}=16.9	R_p=12.86 R_{wp}=16.4	R_p=13.75 R_{wp}=17.26
χ^2	1.68	1.96	1.73	1.60	2.29	2.73	2.63

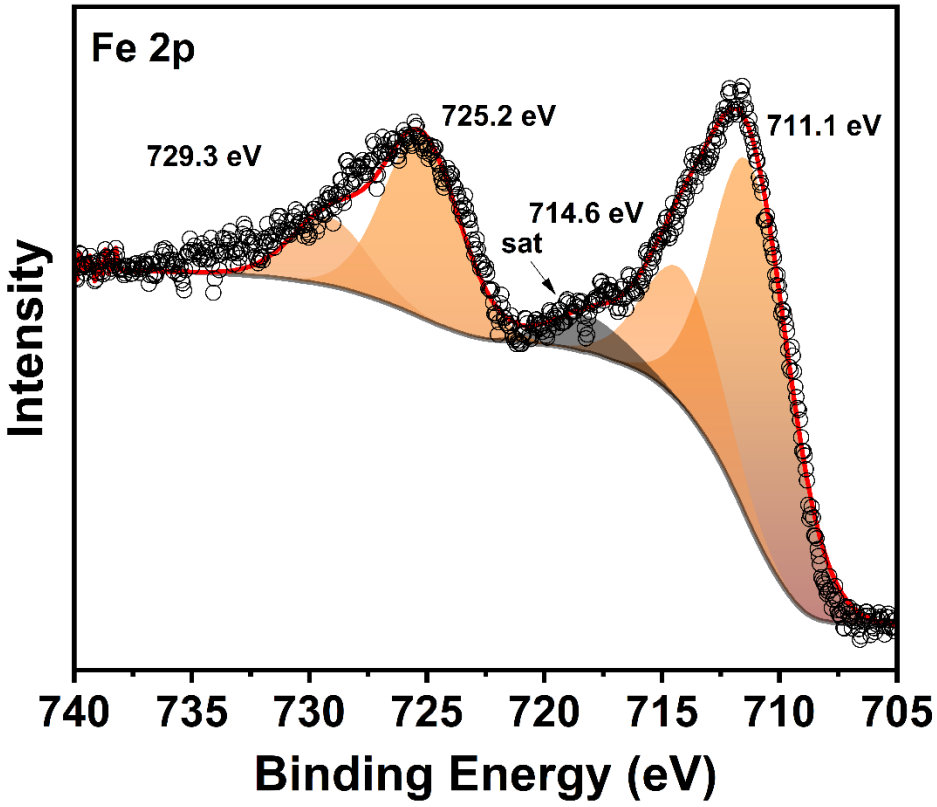

Fig. S3 High Resolution XPS spectrum of Fe-Gallate MOF in the Fe 2p region.

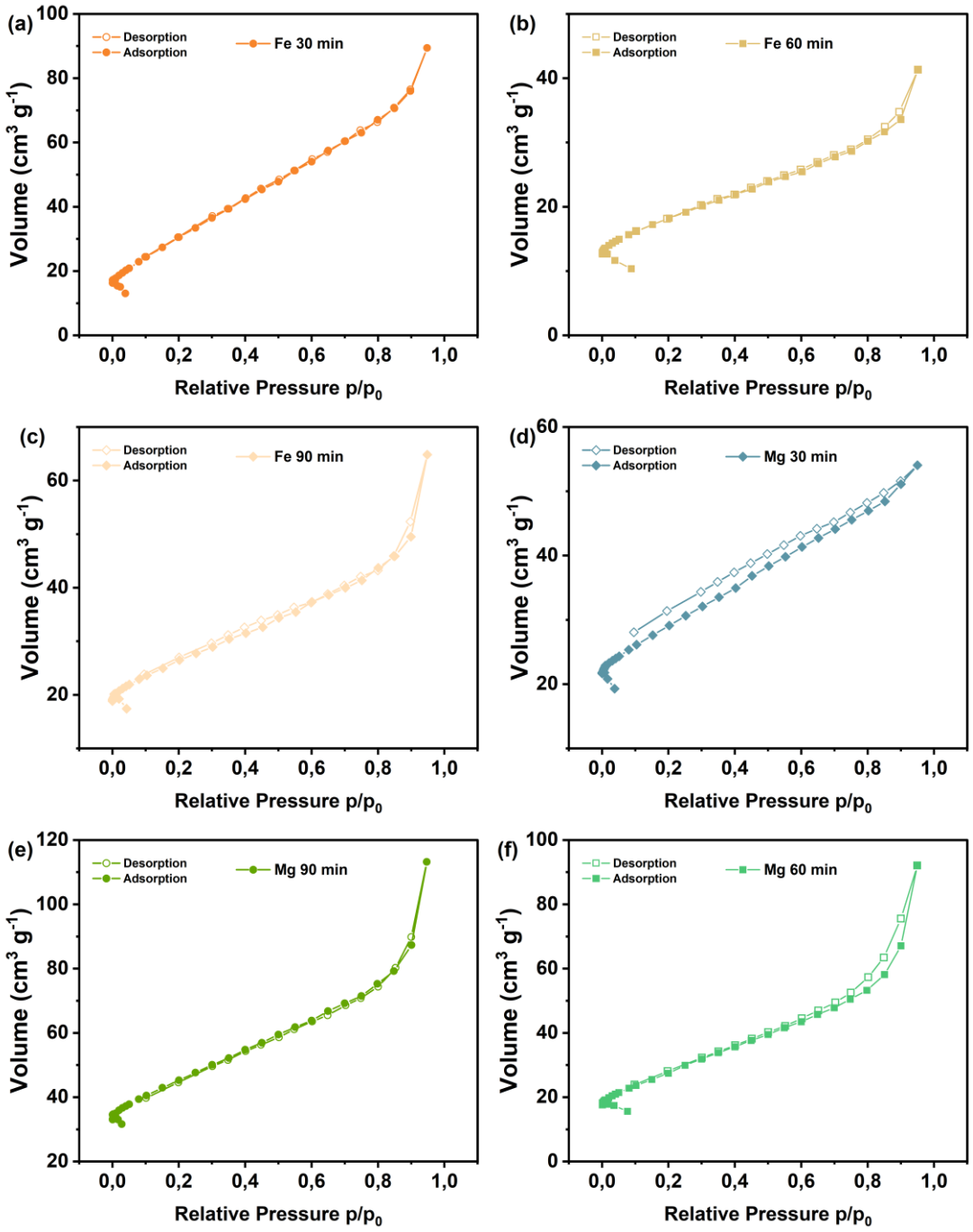

Fig. S4 N_2 adsorption-desorption isotherms of (a – c) Fe-Gallate MOF, and (d – f) Mg-Gallate MOF at synthesis times of 30, 60, and 90 min.

Analysis of residues obtained after thermal decomposition

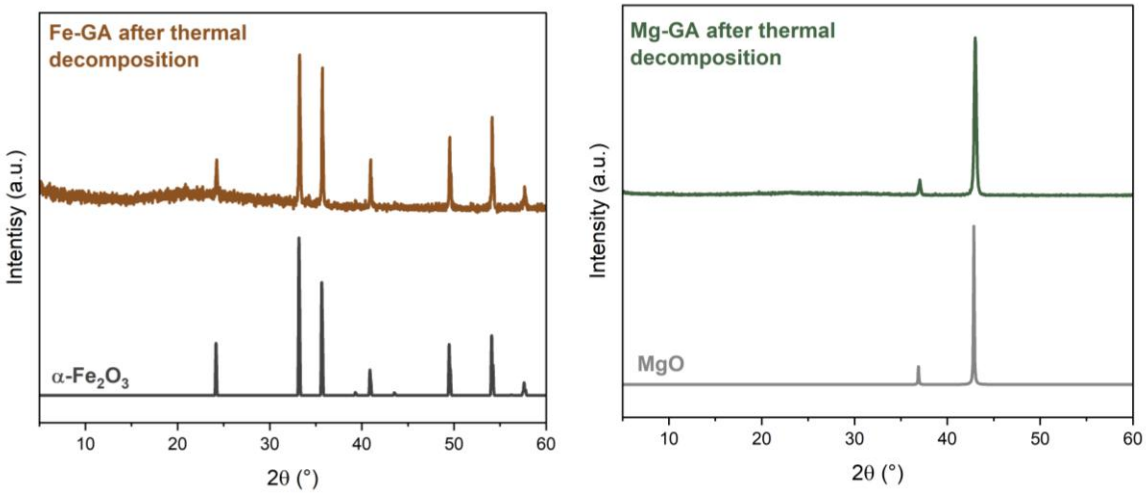

Fig. S5 XRD pattern obtained after thermal decomposition of Fe-GA (a) and Mg-GA (b)

Kinetic Adsorption

To compare the adsorption process of Fe-Gallate and Mg-Gallate MOF, four adsorption kinetics models were analysed: pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich kinetic models, shown respectively in equations 1-4.[1–3] All the plots are shown in Figure S6, while the correlation coefficients as well the kinetics constants and Qe values are shown **Table SI 4**.

Pseudo-First Order (Lagergren Model)

The pseudo-first-order kinetics is applicable if the plot $ln(q_e - q_t)$ against time (t) shows a linear relationship, in which the slope indicates the k_1, and the interception the $ln(q_e)$. The model suggests a phenomenon of adsorption based on physical interaction.

$$ln(q_e - q_t) = ln\, q_e - k_1 t \qquad (1)$$

q_e = quantity absorbed in the equilibrium (mg/g)

q_t = quantity absorbed in a giving time t

k_1 = velocity constant of a pseudo-first order system

Pseudo-Second Order (Ho and Mckay Model)

The pseudo-second order kinetics is applicable if the plot $\frac{t}{q_t}$ against time (t) shows a linear relationship, in which the slope indicates the $\frac{1}{q_e}$, and the interception $\frac{1}{k_2 q_e^2}$. The model suggests a phenomenon of adsorption based on chemical interaction.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

k_2 = velocity constant of a pseudo-second order system

Elovich Model

The Elovich kinetics is applicable if the plot q_t against $ln(t)$ show a linear relationship, in which the slope indicates $\frac{1}{\beta}$ and the interception $\frac{1}{\beta} ln(\alpha\beta)$. The model suggests a phenomenon of adsorption based on chemical adsorption, strongly influenced by the morphology of the material, with heterogeneous active sites, which can occur both on the surface and within the pores.

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t) \quad (3)$$

q_t = quantity absorbed in a giving time t

α = initial adsorption ratio (mg/g.min)

β = related to the activation energy and complexity of the surface

Intraparticle diffusion (Weber-Morris)

The Weber-Morris kinetics is applicable if the plot q_t against $t^{1/2}$ show a linear relationship, in which the slope indicates k_{id} and the interception C. The model suggests a phenomenon of adsorption in multiple steps, in which the intraparticle diffusion may be the limiting factor.

$$q_t = k_{id} t^{1/2} + C \quad (4)$$

q_t = quantity absorbed in a giving time t

k_{id} = constant of the intraparticle diffusion ratio (mg/g.min$^{1/2}$)

C = constant related with the limitant layer width

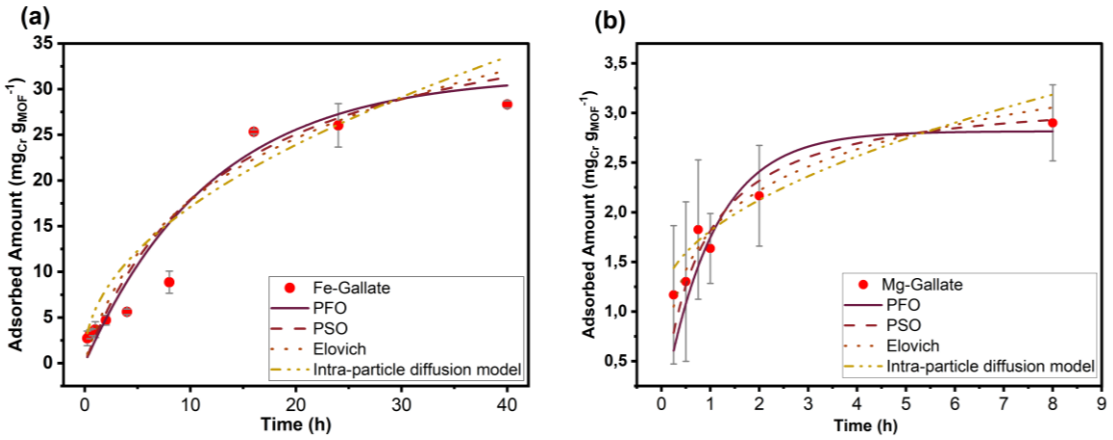

Fig. S6 Fitting of Cr adsorption kinetics by Fe-Gallate (a) and Mg-Gallate MOF (b). Pseudo-first (PFO) and Pseudo-second order (PSO); Intra-particle diffusion or Weber-Moris model and Elovich model.

Table SI 4: Values obtained for Fe-Gallate and Mg-Gallate MOF by pseudo-first, pseudo-second-order, Weber-Moris and Elovich kinetics for Chromium adsorption

Fe-Gallate MOF			**Mg-Gallate MOF**		
Pseudo-First Order			**Pseudo-First Order**		
Qe = 31.52	K_1 = 0.0834	R^2 = 0.9441	Qe = 2.8150	K_1 = 0.9682	R^2 = 0.8446
Pseudo-Second Order			**Pseudo-Second Order**		
Qe = 41.67	K_2 = 0.0018	R^2 = 0.9970	Qe = 3.2130	K_2 = 0.4028	R^2 = 0.9705
Elovich			**Elovich**		
α ≈4.1270	β = 0.0844	R^2 = 0.9972	α ≈11.1270	β = 1.6320	R^2 = 0.9751
Weber-Moris			**Weber-Moris**		
K_{id} = 5.1930	C = 0.6832	R^2 = 0.9871	K_{id} = 0.7510	C = 1,0617	R^2 = 0.9690

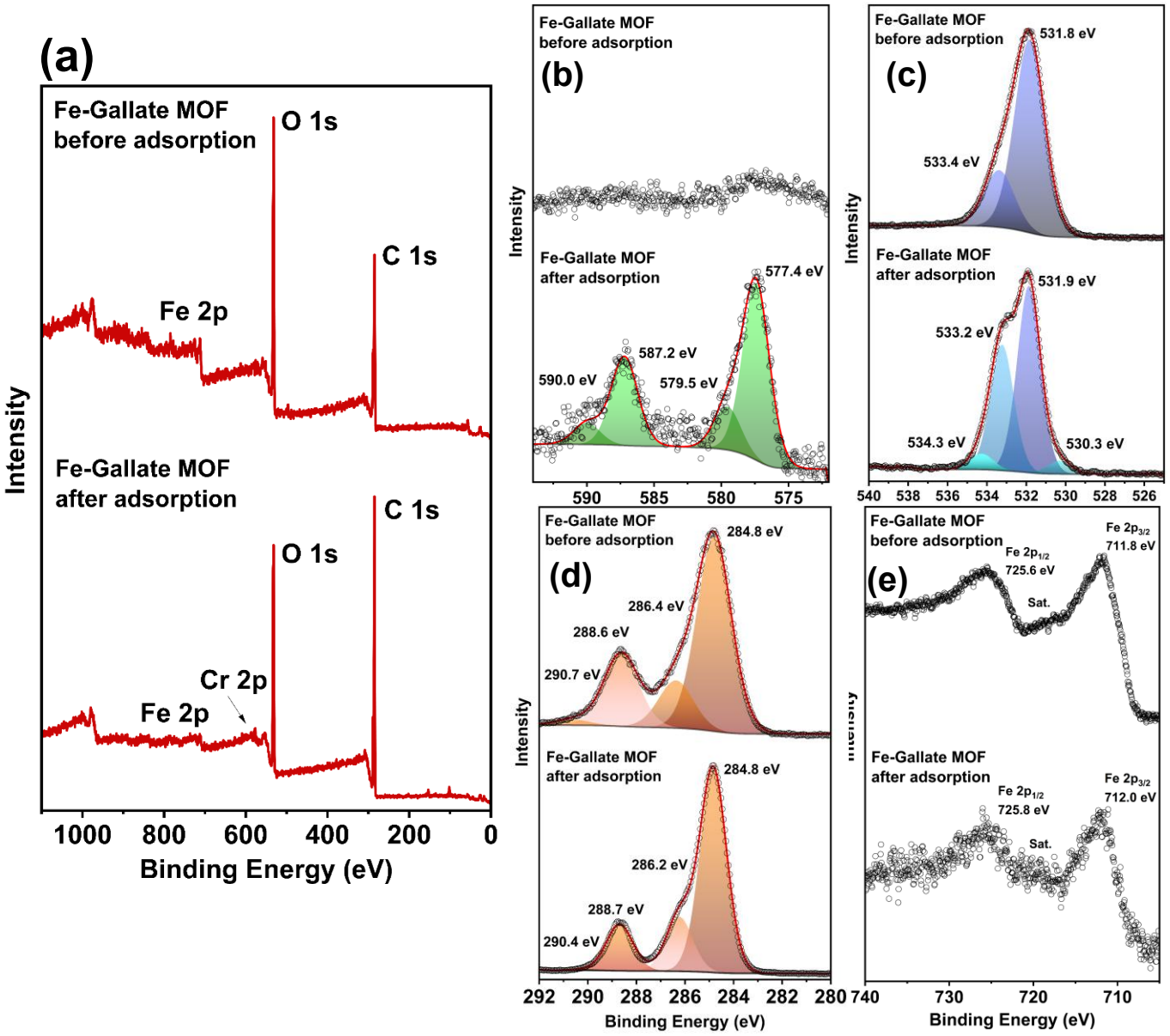

Fig S7 XPS spectra of Fe-Gallate MOF before and after the Cr adsorption

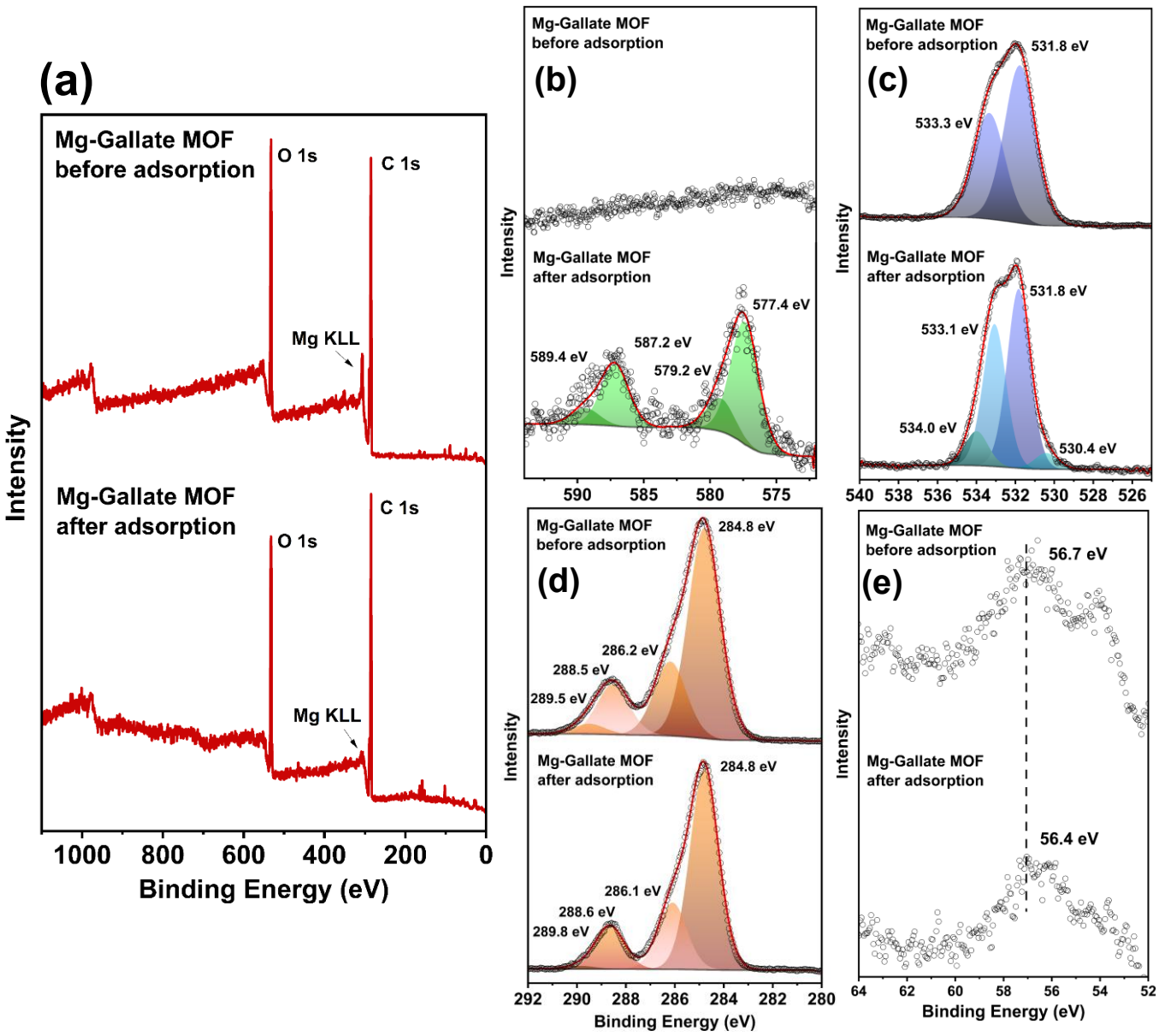

Fig S8 XPS spectra of Mg-Gallate MOF before and after the Cr adsorption

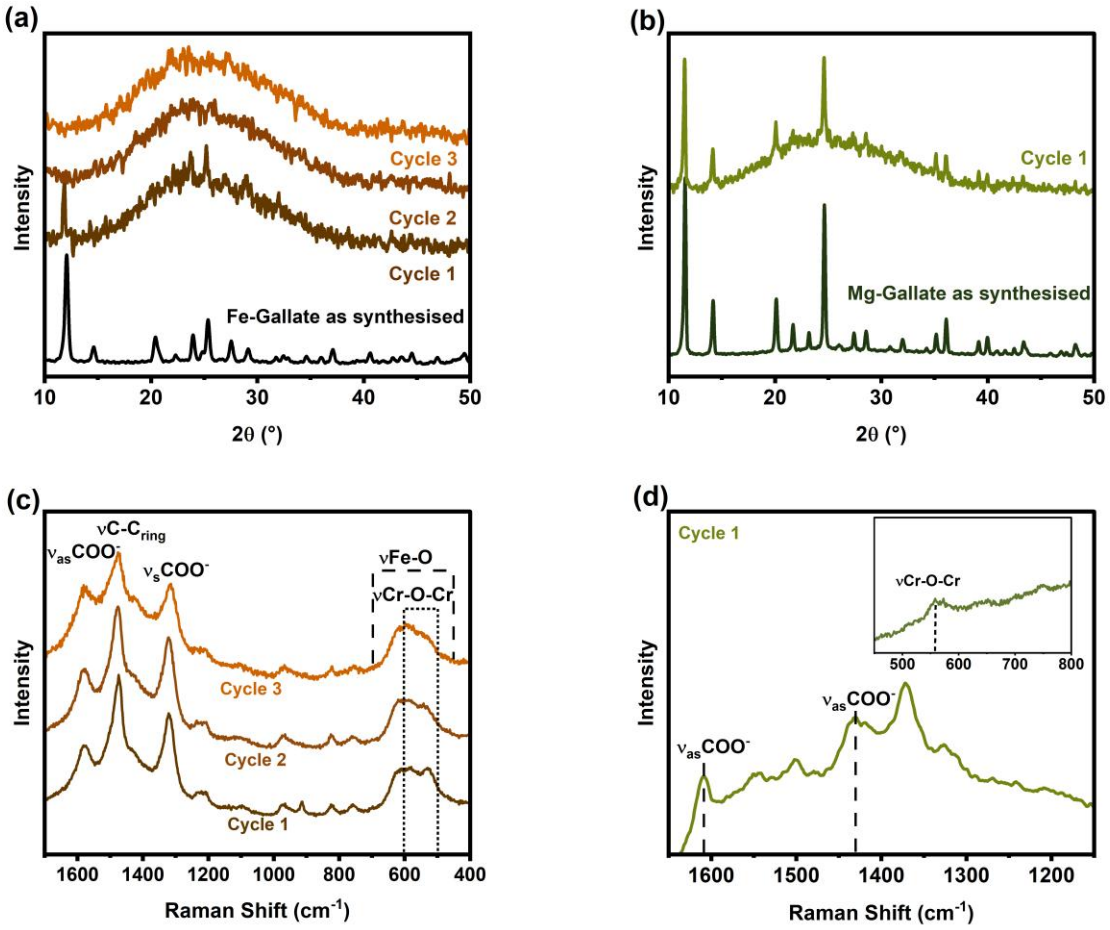

Fig. S9 Characterization of samples after three cycles of Cr adsorption (a) PXRD pattern and (c) Raman spectra of Fe-Gallate from 1700 to 400 cm^{-1} (b) PXRD pattern and (d) Raman spectra of Mg-Gallate from 1700 to 400 cm^{-1}.

References

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