Supporting information

Sustainable recovery of molybdenum, cobalt, and bismuth from hazardous spent selective oxidation catalysts via efficient hydrometallurgical process

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2. Materials and methods

2.1. Materials

The spent selective oxidation catalyst utilized in this study was sourced from a plant located in Jiangsu province, China. A sieving process was used to separate the spent catalyst, which contains some porcelain rings. The macro-porous weakly basic anion exchange resin D314 was purchased from Hangzhou Zhengguang Chemical Company, China. Prior to usage, the resin underwent treatment with sodium hydroxide (NaOH) and hydrochloric acid (HCl) separately to ensure optimal performance. All chemical reagents utilized in this study, including sulfuric acid (H_2SO_4), HCl, NaOH, oxalic acid ($C_2H_2O_4$), potassium chloride (KCl), and magnesium chloride ($MgCl_2$), were of analytical grade. De-ionized water served as both dilution and washing water throughout the experimental procedures.

2.2. Recovery of metals from spent catalyst

2.2.1 Alkaline leaching of Mo

Alkali-leaching experiments were performed in four-neck round-bottom flask, adhering to the following parameters: alkali-catalyst ratio of 0.35:1, temperature set at 80.0 °C, liquid-to-solid ratio of 4:1, and duration of 120 min [1]. Post-leaching, solid and liquid phases were separated through vacuum filtration. Residue was washed with de-ionized water until reaching neutral pH and then dried at 105 °C for 12 h to prepare for recovery of Co, Bi, Fe, and residual Mo. Leaching solution and wash water were analyzed separately to determine metal ion concentrations for calculating leaching efficiency, with leaching solution specifically used for Mo precipitation.

2.2.2 Purification and precipitation of Mo

The alkaline-leached solution was processed to remove impurities such as alumina, silicon, and

phosphorus by adjusting the pH to 8.0-9.0 with $MgCl_2$, followed by filtration [2]. The clarified solution was then treated with HCl to precipitate H_2MoO_4 at pH 1.0 and a temperature of 95.0 °C. After filtration, the precipitate was air-dried at 65.0 °C. Mo enrichment from the mother liquor was achieved using ion exchange with D314 resin [3]. Enrichment trials were conducted in a glass column ($\varphi20\times600$ cm) containing 60.0 mL of wet-packed resin. Following desorption, the Mo - enriched solution was further processed to produce H_2MoO_4.

2.2.3 Hot acid leaching

Hot acid leaching experiments were performed using 2000 mL four-neck round-bottom flask equipped with heating mantles. Each experiment processed 100 g of alkaline leaching residue. Optimal leaching conditions for H_2SO_4 were identified through orthogonal tests that varied H_2SO_4 concentration (3.0 to 5.0 $mol\cdot L^{-1}$), temperature (70 to 110 °C), solid-liquid ratio (1:4 to 1:6), and leaching duration (2.0 to 6.0 h). The leached solution was then filtered to separate solution rich in Co, Fe, Mo, and Bi from Bi-rich residue. The residue was extensively washed with de-ionized water and dried at 105.0 °C for 12 h, meeting the quality standards for Bi concentrate used in Bi metallurgy [4]. Metal ion concentrations in the leaching solution and wash water were analyzed to calculate leaching efficiency.

2.2.4 Pre-neutralization leaching

The highly acidic primary hot acid leaching solution was used for pre-neutralization by adding alkaline-leaching residue. After filtration, the residue underwent a second hot acid leaching, while the filtrate was reserved for additional metal recovery processes.

2.2.5 Precipitation of Fe

In the leaching solution containing Co, Fe, Mo, and Bi, the purification phase entailed strategic co-

precipitation of Bi and Mo using the jarosite method. This method required maintaining pH between 1.8 and 2.0 at an elevated temperature of 95.0 °C [5]. Following precipitation and subsequent filtration, the process produced two distinct products: Co-enriched purified solution and solid form of potassium jarosite $[KFe_3(SO_4)_2(OH)_6]$, within which Mo and Bi were co-precipitated.

2.2.6 Precipitation of Co

Co precipitation was meticulously executed by titrating $C_2H_2O_4$ solution, with concentration 1.2-fold above the stoichiometric requirement, into the system. Simultaneously, 3.0 M NaOH solution was employed to precisely adjust and maintain pH levels. This reaction proceeded at controlled temperature of 50.0 °C for duration of 2.0 hours, with constant stirring speed set at 200 r·min^{-1} to ensure homogeneity. Following the reaction, the mixture was allowed to cool, followed by filtration. Resultant precipitate was then subjected to series of thorough washings using both de-ionized water and ethanol, serving to eliminate any residual impurities. Finally, clean precipitate was air-dried at temperature of 65.0 °C [6], achieving desired purity and consistency.

2.3. Characterization

Solid phase was first characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) before undergoing alkali fusion and dissolution into aqueous phase for quantitative metal analysis. Metal concentrations in aqueous phase were accurately measured using inductively coupled plasma optical emission spectrometry (ICP-OES), following suitable dilution.
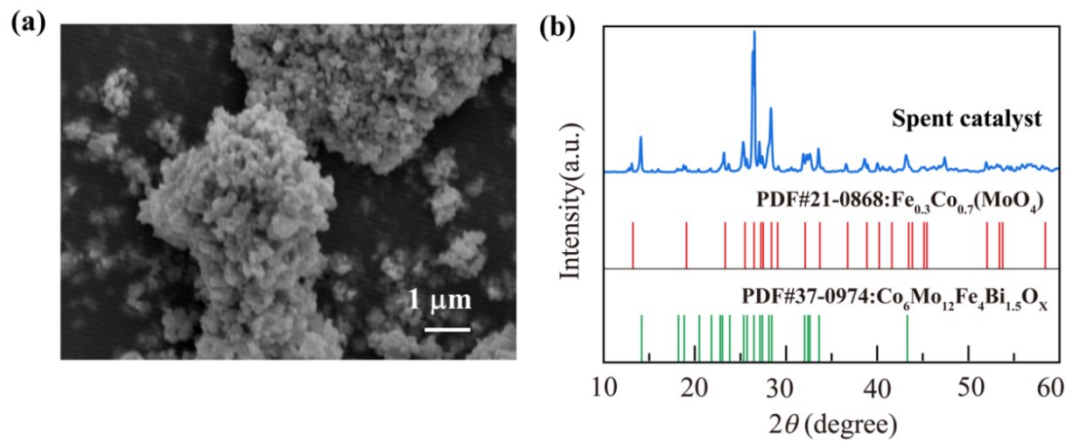
3. Results and discussion

3.1. Composition, phase and leaching behavior analysis of the spent catalyst
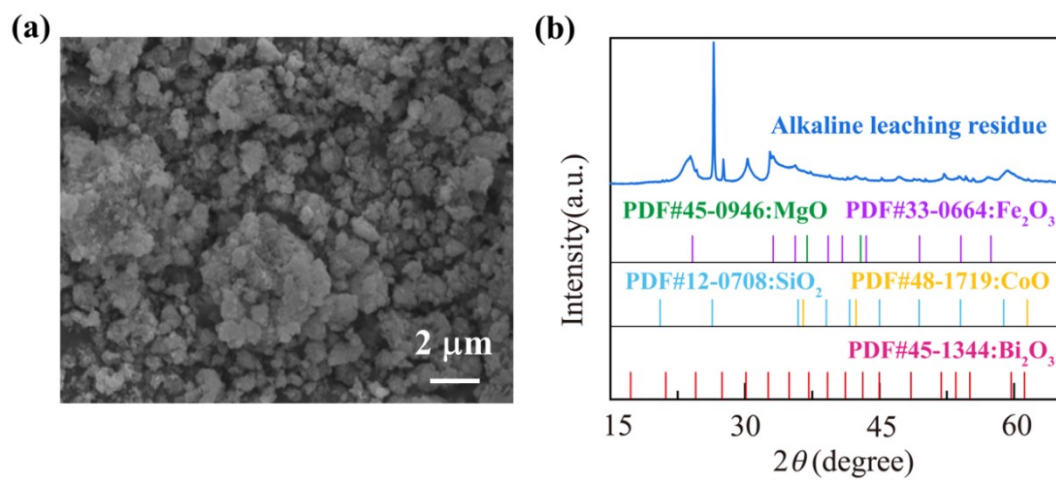
Table S1. Chemical composition of the spent catalyst.

Chemicals	Co	Mo	Fe	Bi	Si	Al	Ca	Mg	P

Content (wt%)	15.30	39.58	6.70	4.64	1.88	0.23	0.14	0.83	0.005

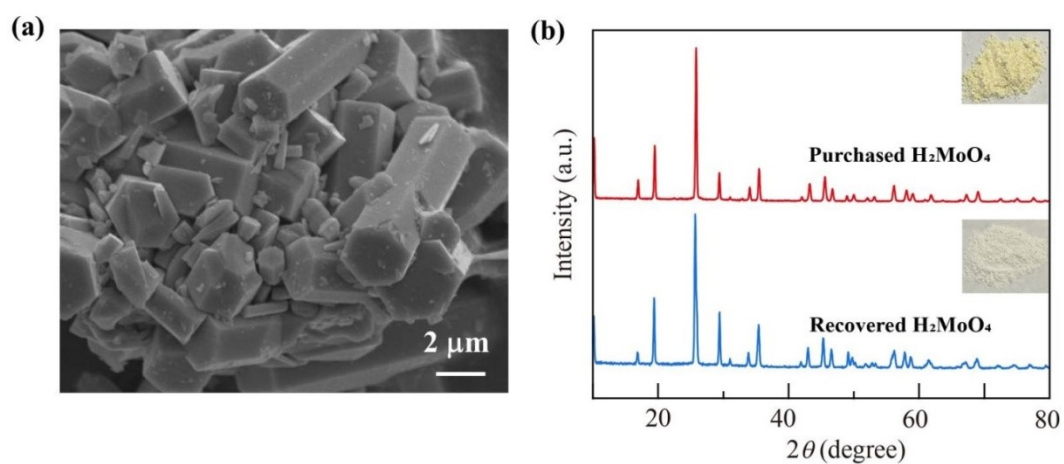**Fig.S1.** (a) SEM image and (b) XRD spectrum of the spent catalyst.

3.2. Recovery of Mo

Fig.S2. (a) SEM image and (b) XRD spectrum of the alkaline leaching residue.

Table S2 Chemical compositions of the alkaline leaching residue.

Element	Co	Mo	Fe	Bi	Si	Al	Ca	Mg
Alkaline leaching residue after washing (wt%)	29.03	3.76	12.87	8.60	3.47	0.42	0.26	1.54

Fig.S3. (a) SEM image of the recovered H_2MoO_4 and (b) XRD spectra of the purchased and recovered H_2MoO_4.

3.3. Hot acid leaching

**Table S3.** Levels and factors affecting the leaching yield.

Level	Factors			
	A	B	C	D
	H_2SO_4 concentration (mol·L^{-1})	Solid-liquid ratio	Temperature (°C)	Time (h)
1	3	1:4	70	2
2	4	1:5	90	4
3	5	1:6	110	6

Table S4. Chemical compositions of hot-acid leaching residue and leach liquor.

Element	Co	Mo	Fe	Bi	Si	Al
Hot-acid leaching residue after	0.32	0.34	1.68	27.28	12.64	0.14

|						
washing (wt%)						
Hot-acid leaching filtrate with concentrated washing water (g·L^{-1})	41.70	4.98	15.06	3.39	0.079	0.062
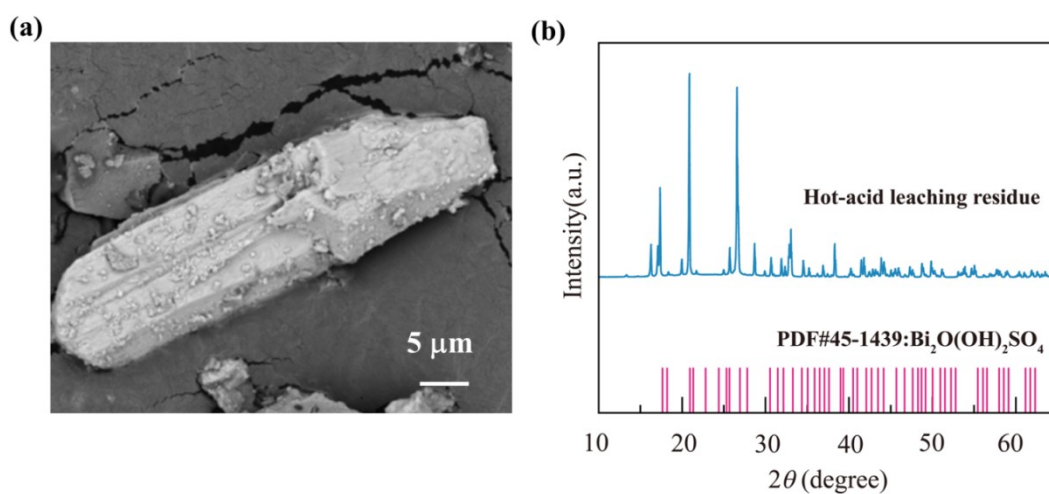
Fig.S4. (a) SEM image and (b) XRD spectrum of the hot-acid leaching residue.

**Table S5.** Chemical compositions of pre-neutralization leaching residue and leach liquor.

Element	Co	Mo	Fe	Bi	Si	Al
Pre-neutralization leaching residue after washing (wt%)	2.99	12.09	2.05	23.44	8.48	0.46
Pre-neutralization leaching filtrate with concentrated washing water (g·L^{-1})	67.43	3.05	24.08	2.79	0.11	0.079
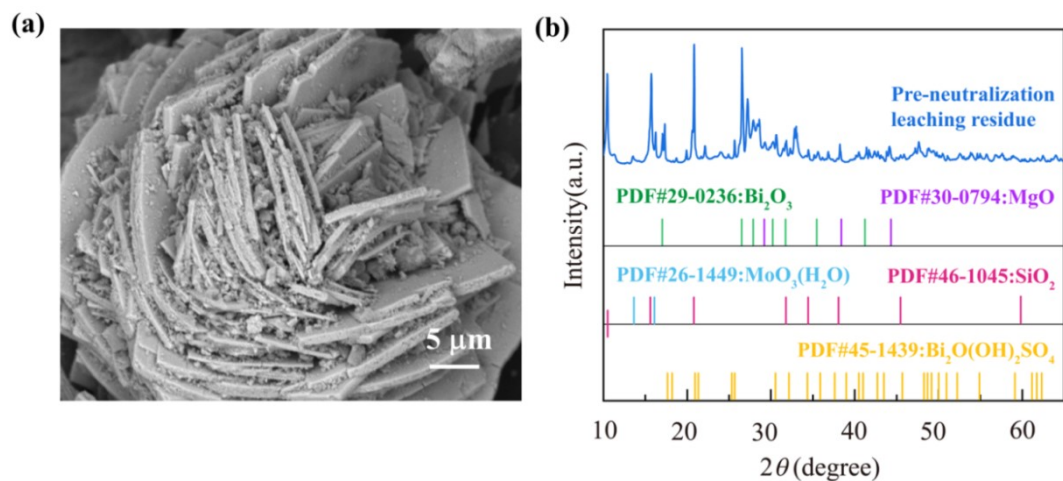
Fig. S5. (a) SEM image and (b) XRD spectrum of the pre-neutralization leaching residue.

3.4. Recovery of Bi

3.4.1. Co-precipitation of Fe
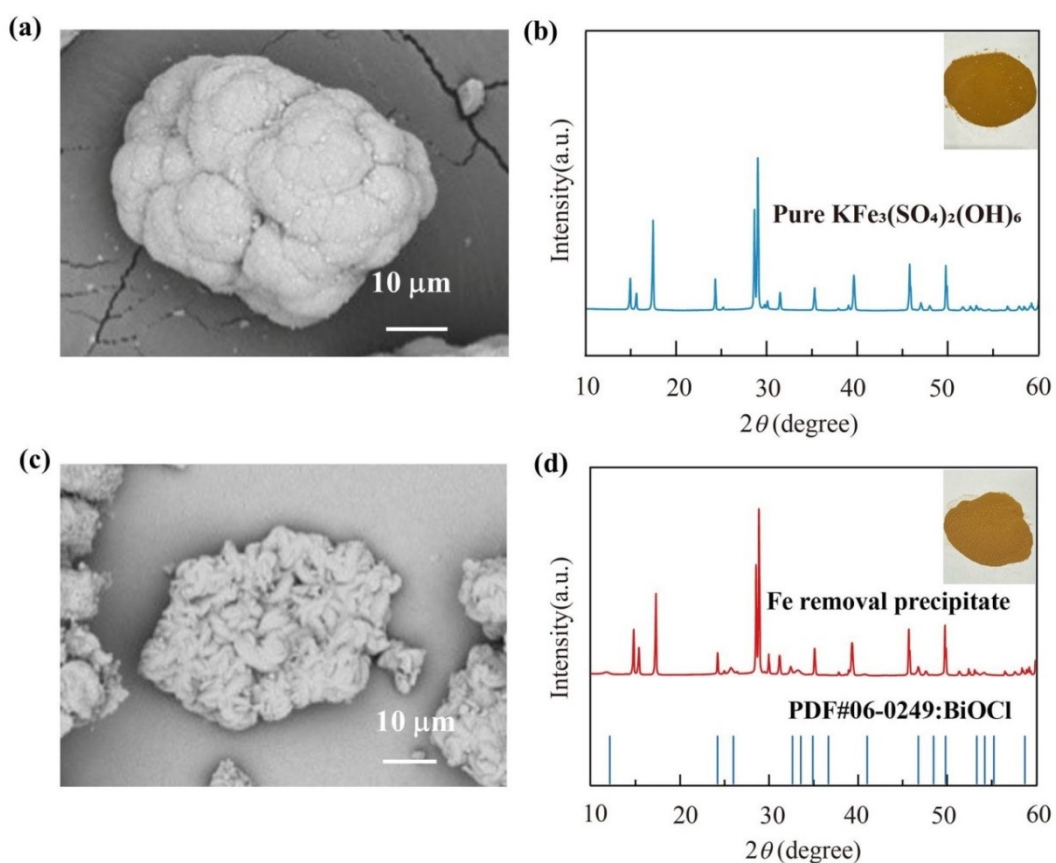
Fig. S6. (a, c) SEM images and (b, d) XRD spectra of the pure $KFe_3(SO_4)_2(OH)_6$ and Fe removal

precipitate.

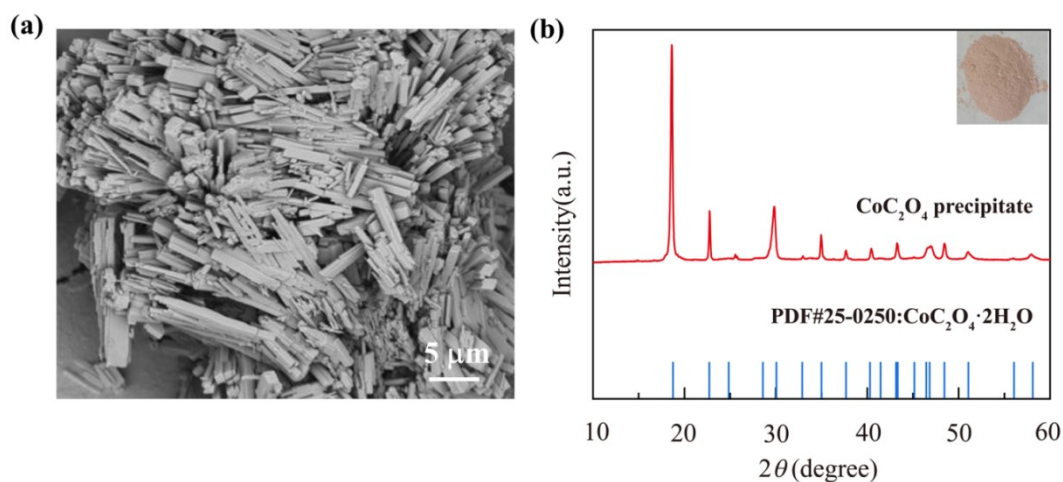**Table S6.** Chemical composition of the Fe removal precipitate.

Element	Co	Mo	Fe	Bi	K	S
Fe removal precipitate (wt%)	1.57	7.01	20.81	1.79	7.21	10.61

3.4.2 Preparation of CoC$_2$O$_4$

Table S7. Chemical composition of the purified Co solution.

Element	Co (g·L^{-1})	Mo (mg·L^{-1})	Fe(mg·L^{-1})	Bi(mg·L^{-1})
Content	84.09	90.04	3.61	<1.0

Fig.S7. (a) SEM image and (b) XRD spectrum of CoC$_2$O$_4$ precipitate.

4. Economic analysis

Under a representative conventional hydrometallurgical scheme, treating 1 t of spent catalyst requires roughly MgCl$_2$ (3 kg), HCl (0.95 t), 98% H$_2$SO$_4$ (0.73 t), KCl (0.06 t), and oxalic acid (0.27 t), for a reagent cost of about USD 427 at current prices. Caustic is the major additional expense: 2.39 t of 30% NaOH, costing about USD 345. The conventional total is therefore about USD 772 per tonne of feed.

The pre-neutralization strategy used here materially lowers caustic demand. Average use of 30%

NaOH falls by 0.87 t per tonne, so only 1.52 t is required (about USD 220), with other reagents on the same price basis. The resulting process cost is about USD 647 per tonne, a 16.2% reduction relative to the conventional approach.

References

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