



Recovery of molybdenum from alkaline leach solution of spent hydrotreating catalyst by solvent extraction using methyl tricaprilylammonium hydroxide

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ABSTRACT

Detailed extraction of molybdenum(VI) from alkaline sodium hydroxide solution by quaternary ammonium salt (Aliquat 336, R_3CH_3NOH) mixed with kerosene was investigated. The different factors affecting the extraction system such as time of shaking, alkali, extractant, metal ion concentrations, temperature and the organic to aqueous volume phase ratio were studied in order to obtain the best conditions for separating molybdenum(VI). Based on the slope analysis method, the extracted molybdenum(VI) species was suggested to be $[(R_3CH_3N)_2MoO_4]$. Increasing the temperature was found to slightly increase the extraction affinity indicating the endothermic character of the process. Stripping was successfully accomplished by 2.0 M NaOH solution. The extraction procedures were applied to recover molybdenum(VI) from a sample of spent hydrotreating catalyst containing a significant amount of Al(III), Cu(II) and Ni(II). The recovery yield was found to be 96% and a hydrometallurgical flowsheet was also proposed.

1. Introduction

Hydrotreating catalysts (HDT) account for about one-third of the total worldwide catalyst consumption. They are used for sulfur removal in petroleum refineries. Spent HDT catalysts containing Ni, Mo, Co, Rh, Pt, Pd and/or V; are generally supported on porous materials like alumina and silica through precipitation or impregnation processes (Furimsky, 1996). Molybdenum is a strategic metal which in general has an extensive demand for its use in industrial applications such as a catalyst in petrochemicals, alloying agent in steel, nuclear energy, radios, thermocouples and aircraft parts (Saily et al., 1996). Due to the increasing demand of molybdenum and rapid depletion of its land-based ores, there is a growing need to find alternate sources to meet the future demands. Thus, spent HDT catalyst is one of the vital sources. Various secondary molybdenum sources contain high values of metals such as U(VI), V(V), W, Re, Al, Ni, Cu, Co, etc. (Chen et al., 2006). During the refining of pure petroleum from crude oils, Mo(VI) is used as a catalyst and after a number of cycles of use the activity of these catalysts gradually decreases with time, hence it is necessary to regenerate and reuse these catalysts. The economic interest of the spent HDT catalyst is due to the presence of the major constituents generally contain molybdenum(VI) (4–12%), aluminum(III) (15–30%), nickel (1–5%), cobalt (0–4%), sulfur (5–10%), silicon (1–5%), vanadium(V)

(0–0.5%), which makes them economically viable for recovery of valuable metals (Kim et al., 2009). A number of processes and technologies for the recycling of the metals from spent catalysts were studied and developed (Kar et al., 2005; Van den Berg et al., 2002). Basically, there are two main processes, hydro- and pyro-metallurgical processes to recover valuable metals from spent catalysts. These processes include roasting, acid, and caustic leaching.

Solvent extraction is one of the most effective methods as hydro-metallurgical technique and extensively used in separation science, including recovery and preconcentration of Mo(VI). In recent decades, a number of extractants were investigated to extract molybdenum(VI) from acidic solutions. Firstly, amine extractants, such as Alamine 336 (Kim et al., 2015), Alamine 308 (Sahu et al., 2013) and Alamine 304–1 (An et al., 2009a; Ghadiri et al., 2014) are the popular choice for the extraction of molybdenum(VI) from solutions in the pH range of 2–3. However, phase separation might be a problem due to the formation of the third phase (Parhi et al., 2011) when the organic phase overloaded with molybdenum(VI) or the concentration of the extractant was high. Secondly, neutral extractants, including TBP (Nguyen and Lee, 2014a) and TOPO (Banda et al., 2012) were found to extract molybdenum(VI) in the form of MoO_2Cl_2 from solutions with a high concentration of hydrochloric acid. Thirdly, chelating or acidic extractants can be used to extract molybdenum(VI) as cations in solutions at $pH < 1$.

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Table 1
Chemical analysis data for the spent catalyst (mass fraction, %).

Component	Na	Al	Si	P	S	Cl	K	Ca	Fe	Ni	Cu	Nb	Mo
Content, %	0.07	32.79	0.67	0.15	0.37	0.03	0.06	0.11	0.25	25.39	18.19	0.08	21.74

On the other hand, various organic complexing extractants such as di(2-ethylhexyl) phosphoric acid (D2EHPA), Cyanex 301, Cyanex 272 and LIX 84-I exhibit good performance for the extraction of molybdenum(VI) in solutions with high concentration of sulfuric acid (Li et al., 2012; Wang et al., 2014; Wu et al., 2012). But the drawback of the D2EHPA system was its low separation coefficient of molybdenum(VI) over iron(III), while the problem of the Cyanex 272 system was the formation of the third phase during stripping of molybdenum(VI) from loaded organic solutions using ammonia.

Chen et al. (2006) indicated that the Mo(VI) and V(V) contained in leach liquor and obtained by roasting of spent catalyst with sodium carbonate at 1023 K were extracted by using of 20% (v/v) trialkyl amine and 10% (v/v) secondary octyl alcohol in kerosene. When 10% (w/w) ammonia/water was used as stripping agent, 0.375 M NH_4NO_3 was added to the stripping solution. So, over than 99% of V(V) can be crystallized as ammonium metavanadate at pH = 7–8.5 while over than 98% of Mo(VI) can be crystallized as ammonium polymolybdate at pH between 1.5 and 2.5.

In another study, a wash liquor containing 10 g/L of Mo(VI) was treated for the extraction and the selective recovery of Mo(VI) in a two-stage extraction using 10% (v/v) Alamine 304–1 diluted in Anisole 150 diluent (An et al., 2009b). An acidic solution containing the molybdenum(VI) was significantly recovered using Cyanex 301, dissolved in kerosene (Saberyan et al., 2003). Sastre et al. (2000) demonstrated the extraction of Mo(VI) from the sulfate solution using oxime extractant such as LIX 622, in which the extraction was carried out as the function of pH, different stripping reagents, time, temperature and extractant concentration. Amongst the three solutions (H_2SO_4 , HNO_3 , and NH_4OH) used for stripping Mo from metal loaded LIX 622, NH_4OH was found to be the best, while the stripping efficiency of the two acids was quite low.

Since aluminum(III) is associated with molybdenum(VI) in some types of spent catalysts, the extraction and separation of Al(III) were studied and reported. In this concern, the alkaline leaching of spent alumina-based catalysts from the petroleum industry yields a solution rich in Mo(VI), V(V) and Al(III). In order to recover the two heavy metals aluminum(III) must be first quantitatively separated. The extraction of aluminum(III) with oxine was chosen and LIX 26 was used (Olazabal et al., 1991). The best separation conditions were found to be $7 < \text{pH} < 8$, 0.3% LIX 26 and 10% n-octanol. A two-step counter-current extraction with equal volumes of the two phases gave 99.6% extraction of Al(III) with < 1 ppm of Mo(VI) and V(V). The organic phase was regenerated by contacting with sulfuric acid, at $\text{pH} < 2$, where aluminum(III) is quantitatively stripped. Xiao et al. (2017) made a thermodynamic analysis for the separation of tungsten(VI) and aluminum(III) in alkaline medium. The thermodynamic results revealed that the tungsten(VI) and aluminum(III) exist as WO_4^{2-} and $\text{Al}(\text{OH})_4^-$, respectively, in the pH range of 11.5–14. The authors found that the extractant of quaternary ammonium salt (N263 in HCO_3^- form) has stronger affinity with W(VI) than that with Al(III). By controlling the pH of the raffinate, the extractions of tungsten(VI) and aluminum(III) were 99.2% and 1.2%, respectively.

A representative sample, from a typical gas oil hydrotreating unit at the Cairo Oil Refinery Company (CORC), Egypt was used in the present study. The work in this paper is directed to study and develop a hydrometallurgical process flowsheet based on alkali leaching of spent HDT catalyst with sodium hydroxide solution followed by separation and recovery of molybdenum(VI) from leach liquor by the solvent extraction method using methyl tricaprilylammonium chloride (Aliquat

336) as extractant which offer an effectively and economically viable process.

2. Experimental

2.1. Materials and feed solution preparation

The HDT spent catalyst $\text{NiMo}/\text{Al}_2\text{O}_3$ was procured from CORC, EGYPT (4.7 mm cylinder extruded, 1.2 mm diameter). The sample was washed with distilled water, dried overnight in an oven maintained at 85 °C. Finally, it was ground to $-75 \mu\text{m}$ size and mixed thoroughly to obtain a uniform sample for chemical analysis and leaching experiments. The chemical composition of the spent catalyst was determined by energy dispersive X-ray fluorescence (XRF) with SiLi detector and presented in Table 1. All the chemicals used were Analar reagent grade. Hydrochloric acid and sodium hydroxide were obtained from BDH, Aliquat 336 (purity 98%) and 1-octanol was supplied by Merck while molybdenum oxide was purchased from Loba Chemie PVT Ltd., India and aluminum nitrate was obtained from Alpha Chemika, India. Kerosene (non-aromatic) was supplied by Misr Petroleum Ltd. Company, Egypt and used without further purification.

Being transition metal, molybdenum exhibits multiple valence states. It belongs to group 6 and displays valencies of +3, +4, +5 and +6. The stable valence of +6 is important for solvent extraction. Depending on the pH of molybdenum(VI) solution, it forms a large number of cations and anions as well as electrically neutral molecules (Olazabal et al., 1992). Thus, cationic molybdenum(VI) species become predominant in the most acidic region ($\text{pH} < 1$) and the polynuclear anionic species are predominant in the region $1 < \text{pH} < 6$, while the mononuclear anionic species is the only one at $\text{pH} > 6$ (Karagiozov and Vasilev, 1980). Therefore, dissolving molybdenum trioxide in alkaline solution results in obtaining anionic species most probably of the type tetrahedral monomeric molybdate ion (MoO_4^{2-}) (Baes and Mesmer, 1976) which is very stable in aqueous solution and could be easily extracted by basic extractants (Rayner-Canham and Overton, 2014).

Leaching experiments were conducted by taking 10 g of spent catalyst with 100 mL, 8% of caustic soda, during a time period of four hours, at a constant temperature of 90 °C in a round bottom flask fitted with a seal to avoid evaporation loss. The contents were stirred with a mechanical stirrer maintained at 300 rpm throughout the leaching experiments. After completion of the reaction, the contents were separated from the residue by vacuum filtration using 0.2 μm pore size membrane filter paper and analyzed for determining the metal ions content using Agilent Technologies ICP-OES 720.

2.2. Solvent extraction procedures

Since Aliquat 336 extractant was usually supplied in a chloride form and because the aqueous medium in the present work is mainly sodium hydroxide, it is necessary to convert Aliquat 336 into the hydroxide form by following the procedure that was previously reported (Salazar et al., 1992).

The extraction experiments were performed by shaking equal volumes of the aqueous and organic phases in stoppered glass tubes for 15 min (sufficient to reach the extraction equilibrium) using a thermostated shaking water bath adjusted at 25 ± 1 °C.

To determine the molybdenum(VI) concentration using Shimadzu 160-A UV-Visible spectrophotometer, Japan, known aliquot volumes

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