



# Mechanochemical processing of molybdenum and vanadium sulfides for metal recovery from spent catalysts wastes



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## ARTICLE INFO

### Article history:

Received 28 April 2016

Revised 27 June 2016

Accepted 27 June 2016

Available online 12 July 2016

### Keywords:

Recycling

Spent catalysts wastes

Sulfide

Molybdate and vanadate

Mechanochemical

## ABSTRACT

This work describes the mechanochemical transformations of molybdenum and vanadium sulfides into corresponding molybdate and vanadate, to serve as a new environment-friendly approach for processing hazardous spent hydrodesulphurization (HDS) catalysts solid waste to achieve an easy recovery of not only molybdenum and vanadium but also nickel and cobalt. Co-grinding the molybdenum and vanadium sulfides with oxidants and sodium carbonate stimulates solid-state reactions without any heating aid to form metal molybdates and vanadates. The reactions proceed with an increase in grinding time and were enhanced by using more sodium carbonate and stronger oxidant. The necessary conditions for the successful transformation can be explained on the basis of thermodynamic analyses, namely a negative change in Gibbs free energy.

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## 1. Introduction

Catalysts have been widely used in the desulphurization operations of petroleum refining industry to minimize hazardous sulfur dioxide emission from fuel combustion for decades. After certain time of use, the catalysts will eventually be deactivated and discharged as hazardous solid wastes (Akciil et al., 2015b). Annually, over hundred thousand tons of the spent HDS catalysts are yielded, which abound in valuable metals, especially as Mo and V sulfides and nickel-cobalt sulfides supported in a alumina base (Beolchini et al., 2012; Marafi and Stanislaus, 2008).

Environmental management of hazardous solid wastes has become a major concern around the world due to the serious risks of uncontrolled solid waste to ecological system (Jadhao et al., 2016). Simultaneously, the abundance of valuable metals in various solid wastes offers an alternative way for resources supply. Precious metal recycling from PCB (Akciil et al., 2015a; Behnamfard et al., 2013; Birloaga et al., 2013), yttrium recovery from exhaust fluorescent lamps (De Michelis et al., 2011) and lead recovery from cathode ray tube funnel glass (Okada et al., 2015; Okada and Yonezawa, 2014) have been widely reported in various literatures.

As the global demands on molybdenum and vanadium resources are rising continuously, primary resources supplies are

becoming more and more insufficient, resulting in the natural attention shifted to the secondary sources. Molybdenum and vanadium-rich spent catalyst naturally become the corresponding secondary resources due to the large output. The usage of HDS catalysts is about 30% of total global catalyst consumption, thus the treatment and metal-recycling from spent HDS catalysts are highly desirable, from the stances of resource preservation, sustainable development, and environmental protection (Zeng and Cheng, 2009; Zeng and Yong Cheng, 2009).

The states of metals in spent catalyst wastes are usually in the form of sulfide and numerous industrial processes, based on hydrometallurgy, pyrometallurgy or the combination of both have been used to recycle valuable metals from these catalysts (Akciil et al., 2015b).

Roasting followed by sulfuric acid leaching can dissolve all valuable metals, however, the subsequent process to separate various metals with high purity are quite complex and uncontrollable (Akciil et al., 2015b; Zeng and Yong Cheng, 2009). Roasting with sodium carbonate followed by water leaching is reasonably simple by converting molybdenum and vanadium sulfides into water soluble compounds of sodium molybdate and vanadate. Nevertheless, during roasting, nickel, cobalt and alumina carrier may remain in residues and react to form stable spinel compounds which are difficult to dissolve for recovering nickel and cobalt (Akciil et al., 2015b; Park et al., 2006). Roasting followed by alkali leaching with dilute NaOH (Pinto and Soares, 2013b) may extract molybdenum

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efficiently due to its strong basicity, while it is not suitable for HDS catalyst with high SiO<sub>2</sub> content because of the formations of sodium silicates and filtering difficulty.

Hydrometallurgy process, with the essence of extracting metal from aqueous solution, exhibits advantages of low temperature operation and suitable for low grade materials to pyrometallurgy (Akciil et al., 2015b). More than 90% valuable metals could be dissolved from spent catalyst through low temperature (200–450 °C) sulfuric acid baking followed by mild leaching process (Kim et al., 2009). Acid solutions, mainly sulfuric, hydrochloric acid and various combined acid, have been widely used as solvents during extraction of metals from spent HDS catalysts. Concentrated solutions are needed to obtain high recovery percentage of metals but with no selectivity. Therefore, subsequent separation and purification step, which normally involve repeated solvent extraction and precipitation, are still required (Nguyen and Lee, 2015; Pinto and Soares, 2013a). Caustic leaching can also be used to selectively dissolve molybdenum and vanadium from the spent HDS catalyst (Sahu et al., 2013; Zhao et al., 2015). It can dissolve Mo, V and partial Al but leave Ni, Co and Fe in the residue to some degree.

New recycling process is strongly required to simplify the subsequent separation and purification process, prevent secondary pollution during high temperature roasting and avoid particularly the formation of stable spinel phases from which valuable cobalt and nickel are difficult to recover. The roasting process with sodium carbonate at high temperature has the advantage of recovering Mo and V at high yield, however, it is not easy to avoid the emission of toxic gases such as hydrogen sulfide or sulfide oxides. In other words, heating operation is not a good choice to process the non-oxide samples like the HDS catalyst from the stance of save waste management.

Mechanochemistry is the coupling of mechanical and chemical phenomena on a molecular scale as an interface between chemistry and mechanical engineering. It is possible to synthesize chemical products by using only mechanical action without any heating operation on starting samples of stable minerals or super molecules. The mechanisms of mechanochemical transformations are often complex and different from usual thermal or photochemical mechanisms (Carlier et al., 2013; Munnings et al., 2014).

Mechanochemical processing has wide-ranging applications from the syntheses of semiconductor materials to the treatment of various wastes including metallurgical residues and leaded glass (Baláž et al., 2013; Wang et al., 2007; Yuan et al., 2012). Hydrometallurgical process after mechanical activation also provides a more efficient and selective approach for mineral concentrating and hazardous materials removing (Baláž and Achimovičová, 2006; Bujňáková et al., 2014).

In this paper, we report a novel non-thermal process to treat molybdenum or vanadium sulfides by grinding them with oxidants and sodium carbonate. The mechanically induced solid-state reactions result in the formation of soluble molybdate or vanadate for an easy recovery by simple water washing and the solid residues after water washing are easily dissolved by acid solution further to recover nickel and cobalt. In addition, the necessary conditions in this process are discussed. Our results may serve as the basis for further treatments of petroleum desulphurization catalysts.

## 2. Experimental procedure

Chemical reagents of molybdenum sulfide (MoS<sub>2</sub>), vanadium sulfide (V<sub>2</sub>S<sub>3</sub>), manganese dioxide (MnO<sub>2</sub>), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium chlorite (NaClO<sub>2</sub>) were supplied from Wako Chemical Co., Ltd., Japan and used as received. Starting samples (MoS<sub>2</sub>-MnO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub>), (V<sub>2</sub>S<sub>3</sub>-MnO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub>) and (MoS<sub>2</sub>-NaClO<sub>2</sub>-Na<sub>2</sub>CO<sub>3</sub>) with various molar ratios of three

chemicals, specifically described in the following results and discussion section, were prepared for grinding operation.

Grinding device used in this work was a planetary ball mill (Pulverisette-7, Fritsch, Germany). The mill consists of a pair of pots made of stainless steel, each having 45 ml in inner volume and a rotational disk. The grinding media (steel balls) were mono-size spheres having 15.9 mm diameter. 2.0 g of the starting mixtures were charged in the pot and ground at 700 rpm for different periods of time.

After grinding, the mill was stopped and the samples were removed for characterizations as well as water leaching. As for the water leaching, 0.5 g of the ground product was dispersed in 100 ml distilled water and agitated for 1 h. Subsequently the slurry was filtered by a No. 5C filter from Advantec, Japan with pore size 1 μm and cellulose as main compositions, to obtain the filtrates. Parallel experiments were carried out throughout the whole experimental stages to obtain the accurate results.

The X-ray diffraction (XRD) analysis (Rigaku, Japan, RAD-B system, Cu Kα) was conducted for the ground and the washed samples to determine the phases and compositions. Quantitative analyses of molybdenum and vanadium in the filtrates were performed by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Optima 3300SYS, Perkin Elmer, USA) to determine the water soluble rates.

## 3. Results and discussion

### 3.1. Characterization and recycling of Mo

Fig. 1 shows the XRD patterns of the ground mixture of MoS<sub>2</sub>, MnO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> with the molar ratio of 1:6:4 at 700 rpm for 4 h. Compared to the sample mixed by hand (designated as 0 h) with three initial substances as marked, sodium molybdates (Na<sub>2</sub>MoO<sub>4</sub>) is clearly observed in the pattern of the ground sample together with two new compounds, S and Mn<sub>3</sub>O<sub>4</sub>. Three starting substances cannot be observed in ground samples, meaning that all the starting ones had reacted to obtain the reaction products.

When oxidant MnO<sub>2</sub> is ground, as presented by Eq. (1), it tends to emit oxygen with Mn<sub>3</sub>O<sub>4</sub> (sometimes together with Mn<sub>2</sub>O<sub>3</sub>) as stable product, which is demonstrated in Fig. 2.



Then MoS<sub>2</sub> may be oxidized to form molybdenum oxide and sequentially to react with sodium carbonate. Eventually, water-soluble sodium molybdate is generated, as represented by Eqs. (2) and (3). These two reactions can be explained by calculating

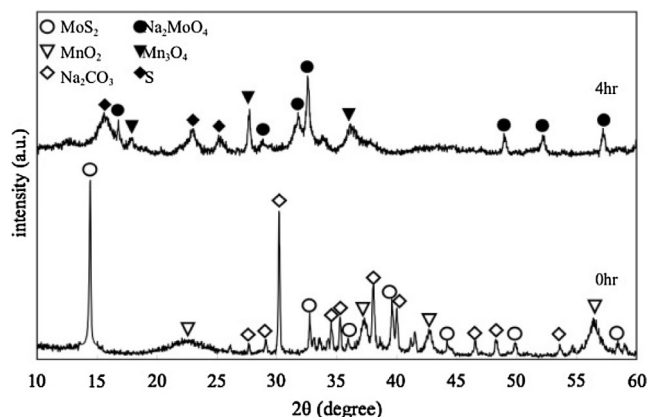


Fig. 1. XRD patterns of the mixture of MoS<sub>2</sub>, 6MnO<sub>2</sub> and 4Na<sub>2</sub>CO<sub>3</sub> mixed by hand (0 h) and co-ground for 4 h.

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