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Hydrometallurgical processing of spent selective catalytic reduction (SCR) catalyst for recovery of tungsten

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ABSTRACT

This paper deals with the recovery of tungsten as synthetic $CaWO_4$ from spent V_2O_5-WO_3/TiO_2 (selective catalytic reduction, SCR) catalyst. The newly developed process included the systematic experimental steps (roasting, decomposition (using HCl solution), leaching (using NaOH), and precipitation) to recover tungsten as $CaWO_4$. The results revealed that the effect of roasting of spent SCR catalyst was significant for the extraction of tungsten. Furthermore, CaO addition in the roasting process promoted chemical equilibrium for the formation of $CaWO_4$, and extraction efficiency of tungsten was increased simultaneously. Decomposition process revealed that 4 $mol\cdot L^{-1}$ of HCl solution was the best condition with considerable degree of removal (92.5%) of vanadium along with negligible loss of tungsten. The most appropriate concentration of NaOH (*aq*) to dissolve tungstic acid (H_2WO_4) from the decomposed sample was 1 $mol\,L^{-1}$ (> 99% tungsten yield) in accordance with minimized concentration of foreign metals (Si, Al, Fe). The maximum amount of tungsten (> 99%) was obtained from the sodium tungstate solution as synthetic $CaWO_4$ using $CaCl_2$ (molar ratio ($CaCl_2$/WO_3): 1). The best experimental conditions for the precipitation were under following conditions: temperature, 50 °C; equilibrium pH, 8–10; molar ratio ($CaCl_2$/WO_3), "1". The content of $CaWO_4$ in the final product was 96.1 wt%. The overall yield of tungsten from the feedstock using the proposed process was 96.4%.

1. Introduction

Nitrogen oxides, usually denoted "NO_x", are the byproducts of high-temperature combustion in stationary and mobile applications. It is considered that an unwanted pollutant in the atmosphere, and controlling it using selective catalytic reduction (SCR) catalyst is of major environmental interest (Forzatti, 2001; Clean air technology center, 1999; US Department of Energy, 1998; Bosch and Janssen, 1988; Nakajima and Hamada, 1996). Among the reported catalyst systems, V_2O_5-WO_3/TiO_2 catalyst has been considered the most efficient and durable for stationary application environments (Marberger et al., 2015; Spivey, 2002). Because global demand for their use has increased, nowadays, spent V_2O_5-WO_3/TiO_2 catalysts contribute to the generation of significant amounts of solid wastes (Wallerstein, 2012; Kwon and Hong, 2016).

V_2O_5-WO_3/TiO_2 catalyst usually consist of TiO_2 anatase as a supporting oxide, vanadium (V) as a catalytic agent, and various promoters such as W, Si, and Ca (Alemany et al., 1996; Reddy et al., 1997). Although vanadium (vanadium) is the main catalytic agent, high tungsten (W) content (WO_3, 7–10 wt%) is usually chosen in relation to the content of V (0.5–1.5 wt%) due to the improvement in durability by sulfur endurance, resistance to thermal deterioration, and prevention of the formation of crystalline vanadium pentoxide (V_2O_5) (Marberger et al., 2015; Spivey, 2002).

V_2O_5-WO_3/TiO_2 catalyst has a finite lifetime due to abnormal operation, contamination, and degradation of catalytic performance. The typical lifetime of this catalyst is known to be approximately three years, depending on the composition and operating environment (Spivey, 2002). However, regeneration process such as chemical and physical treatment and soot blowing can prolong the typical lifetime (Spivey, 2002). Despite the use of regeneration processes, degradation of SCR catalysts is unavoidable because properties such as texture, porosity, and structure of SCR catalyst are degraded by repeated physical and chemical treatments. Therefore, considerable amounts of spent SCR catalysts have been treated by a specified waste-handling process, and disposed of in landfills as waste. Considering the industrial importance of W (Lassner and Schubert, 1999) and its harmful impact on humans, plants, and soil pollution (Imtiaz et al., 2015; Koutsopyros et al., 2006), the recycling of spent SCR catalyst is an environmentally-sound option for treating and utilizing W as a new secondary source.

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During past decades, metallurgical processes for the recovery of valuable metals from spent catalysts have been intensively surveyed (Zheng and Cheng, 2009). A variety of processes including roasting, acid leaching, caustic leaching, anhydrous chlorination, smelting, and bio leaching have been proposed. After review of such processes for the recovery of valuable metals from spent catalysts, it is considered that a combination of methods, accompanied by roasting and leaching is likely the best option. Direct leaching under pressure also shows the feasibility of metal recovery with high yield. Compared to the number of processes and technologies proposed for the material recycling of spent desulfurization catalysts, the research for recycling of spent denitrification catalysts is insufficient.

$CaWO_4$, also known as scheelite, is the one of the most important feed material for production of W-related products (Gürmen et al., 1999; Martins et al., 2007). Currently, synthetic $CaWO_4$ is considered a strong candidate as another source of W (Martins et al., 2007). In general, W ore and concentrate contains a number of impurities (Si, Sn, Pb, As, and Mo) (Yih and Wang, 1979). The modern hydrometallurgical route for extractive metallurgy of W, involves complicated purification processes (Yih and Wang, 1979; Shamsuddin and Sohn, 1981; Lassner and Schubert, 1999). Removing impurities from W concentrate is intended to produce pure intermediate such as Na_2WO_4 (*s, aq*) and $CaWO_4$ (*s*). Therefore, the provision of high-grade of intermediates is the most important requirement for guaranteeing the purity of final products such as WO_3, H_2WO_4, and ammonium para tungstate (APT).

This paper deals with the recovery of W in the form of synthetic $CaWO_4$ from spent V_2O_5-WO_3/TiO_2 catalyst by the order of roasting, acidic decomposition, leaching and precipitation. From the results of this investigation, it is believed and expected that it will be feasible to establish a process for recovery of W from spent SCR catalyst and thereby to provide a new secondary source.

2. Experimental

2.1. Sample preparation

Spent SCR catalyst as feedstock was supplied from the Samcheonpo thermoelectric power plant, South Korea. All of the spent SCR catalyst as feedstock were physically cleaned to remove attached dust, and then pulverized by jaw crusher and grinding mill. The particle size distribution of the pulverized feedstock was mainly ranged from 1 to 100 μm, as determined through particle size distribution analysis (Mastersizer2000, Malvern Instruments, USA). Pulverized spent SCR catalyst was dried at 353 K in an oven for 24 h to remove residual moisture. Further pre-treatment was not conducted.

2.2. Experiments and analysis

The roasting temperature and time was varied between 923 and 1223 K for 3 h. The amount of CaO (98%, Junsei Chemicals, Japan) added differed 2 fold and 3 fold from CaO (wt%) in the feedstock. The roasting process was carried out in air using a muffle furnace. A high purity and dense alumina crucible was used to contain the feedstock during the roasting reaction. Every roasted feedstock underwent to HCl decomposition (Conc., $6\ mol{\cdot}L^{-1}$; temperature, ambient temperature; S/L (w/v) ratio, 0.1; time, 2 h; agitation speed, 350 rpm) and NaOH leaching (Conc., $1\ mol{\cdot}L^{-1}$; temperature, ambient temperature; S/L (w/v) ratio, 0.1; time, 2 h; 350 rpm) to determine the effect of roasting variables and extraction efficiency of W.

The variable parameters for HCl decomposition of W in the roasted feedstock was HCl concentration (3–$6\ mol{\cdot}L^{-1}$, Junsei Chemicals, Japan). Every decomposed product was dissolved in NaOH solution (Conc., $1\ mol{\cdot}L^{-1}$; temperature, ambient temperature; S/L (w/v) ratio, 0.1; time, 2 h; 350 rpm) to determine the conversion rate of tungstic acid. Before leaching, the decomposed samples were ground into particles < 45 μm. The solubility of $CaWO_4$ in the NaOH solution was not taken into account (Zhao and Li, 2008). The addition of Ca for the precipitation of W using $4\ mol{\cdot}L^{-1}$ of $CaCl_2$ (*aq*) was varied between 1, 1.1, and 1.2 (molar ratio, $CaCl_2/WO_3$). The temperature of the precipitation reaction was 25 or 50 °C. Precipitation reaction time was given by 30 min. The solution pH was controlled in the range between 8 and 10 using concentrated HCl solution. Fig. 1 summarizes the process flow chart for the recovery of W from spent SCR catalyst in this experiment.

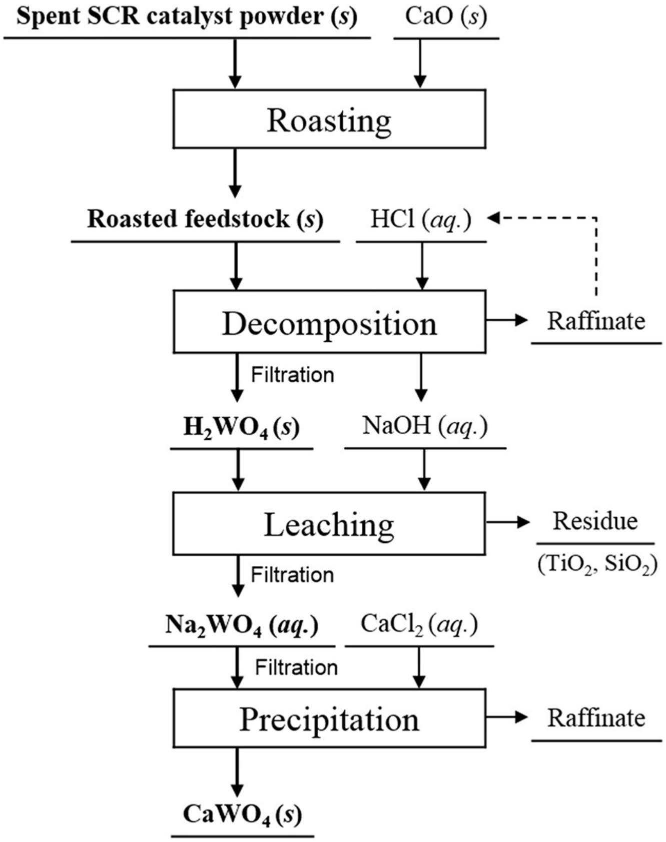

Fig. 1. Process flow chart for recovery of W as synthetic $CaWO_4$ from spent SCR catalyst.

All the metals in the solution and solid samples were assayed using inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP Duo6300, Thermo Scientific, UK). For the analysis of chemical composition for solid samples (feedstock, residue, and precipitates), alkali fusion using the flux Na_2O_2 (96%, Acros Organics, France) as a pre-treatment was conducted before the ICP-OES analysis. Structural characterization of solid samples was performed using Raman spectrometer (LabRAM HR-800 UV–visible-NIR, HORIBA Jobin Yvon, Japan), and X-ray diffractometer (XRD, X'pert MPD, Philips, USA). The morphological characteristics of TiO_2 in the feedstock were determined by transmission electron microscopy (TEM, Tecnai G2 F30, FEI Company, USA).

3. Characteristics of feedstock

Table 1 shows the chemical composition of the feedstock. W as the catalytic promoter existed at the rate of 7.11 wt% by their oxide base, TiO_2 (70.9 wt%), SiO_2 (9.32 wt%), CaO (2.50 wt%), and Al_2O_3 (2.41 wt %) were the notable amount in the spent SCR catalyst. Although V as a catalytic agent was composited in a SCR catalyst, it was confirmed that content of V existed in minor amount (0.98 wt%) relative to the total weight of feedstock.

The catalytic agent in V_2O_5-WO_3/TiO_2 catalysts simultaneously existed in several different states such as bulk crystallite, two-