



Selective recovery of catalyst layer from supporting matrix of ceramic-honeycomb-type automobile catalyst

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ABSTRACT

Natural resources of platinum group metals (PGMs) are limited and their demand is increasing because of their extensive uses in industrial applications. The low rate of production of PGMs due to low concentration in the related natural ores and high cost of production have made the recovery of PGMs from previously discarded catalytic converters a viable proposition. The ceramic-honeycomb-type automobile catalytic converter contains appreciable amount of PGMs. These valuable substances, which are embedded in the catalyst layer and covered on the surface of the supporting matrix, were selectively recovered by attrition scrubbing. The attrition scrubbing was effective for the selective recovery of catalyst layer. The process was convinced as the comminution and separation process by physical impact and shearing action between particles in the scrubbing vessel. The catalyst layer was dislodged from the surface of the supporting matrix into fine particles by attrition scrubbing. The recovery of Al₂O₃ and total PGMs in the fraction less than 300 μm increased with the residence time whereas their contents in the recovered materials slightly decreased. The interparticle scrubbing became favorable when the initial input size increased. However, the solid/liquid ratio in the mixing vessel was slightly affected by the low density of converter particles.

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1. Introduction

Catalytic converters are installed in the engine exhaust system of an automobile. They have been used increasingly since the mid-1970s to meet emission limits enforced by international legislation. They contain platinum group metals (PGMs) as catalysts that reduce the level of undesired exhaust gases such as carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO_x) which are the main by-products of internal combustion processes [1]. Although the PGMs are present in very small quantities in these types of catalysts, given their intrinsic value, it is worth recovering them from the spent catalytic converters. For the PGMs recovery to be economic, most of them must be recovered and the processes should be simple and cost-effective because the conservation and recycling of PGMs are irrefutable demand of our industry.

Several million tons of spent automobile catalytic converters are annually disposed of worldwide. An automobile catalytic converter generally contains 1–2 gm of all types of PGMs, including 0.5–1 gm of platinum. Recently, it has been expected that the demand of

PGMs will resume its growth because the number of new vehicles purchased increases [2]. Moreover, the demand for diesel powered vehicles, more stringent emissions legislation worldwide and shift from palladium- to platinum-rich automobile catalytic converter system in gasoline powered vehicles have increased the demand of platinum consumption [3,4]. Natural resources of PGMs are limited and because of their extensive use in catalysis, electronic devices, space materials, biomedical devices and other industrial applications, their demand is increasing. Therefore the low rate of production of these precious metals due to their low concentration in the related natural ores and their high cost of production have made the metal recovery from previously discarded catalytic converters a viable proposition [5].

The recovery technologies of PGMs from spent catalytic converters have been reviewed in the last few decades. Two types of process, namely, wet and dry methods, have been commercially operated. In a wet process, PGMs on the catalytic converters are dissolved mostly in the form of chloro-complex (MCl), by contacting them in aqueous solutions. Subsequently the resulting solutions are concentrated and then the precious metal ions are cemented by metals such as Al, Fe or Zn in the concentrated system [6–8]. In a dry process, they are melted, for example, with CaO at elevated temperatures to produce a slag with low viscosity. PGMs in the melt

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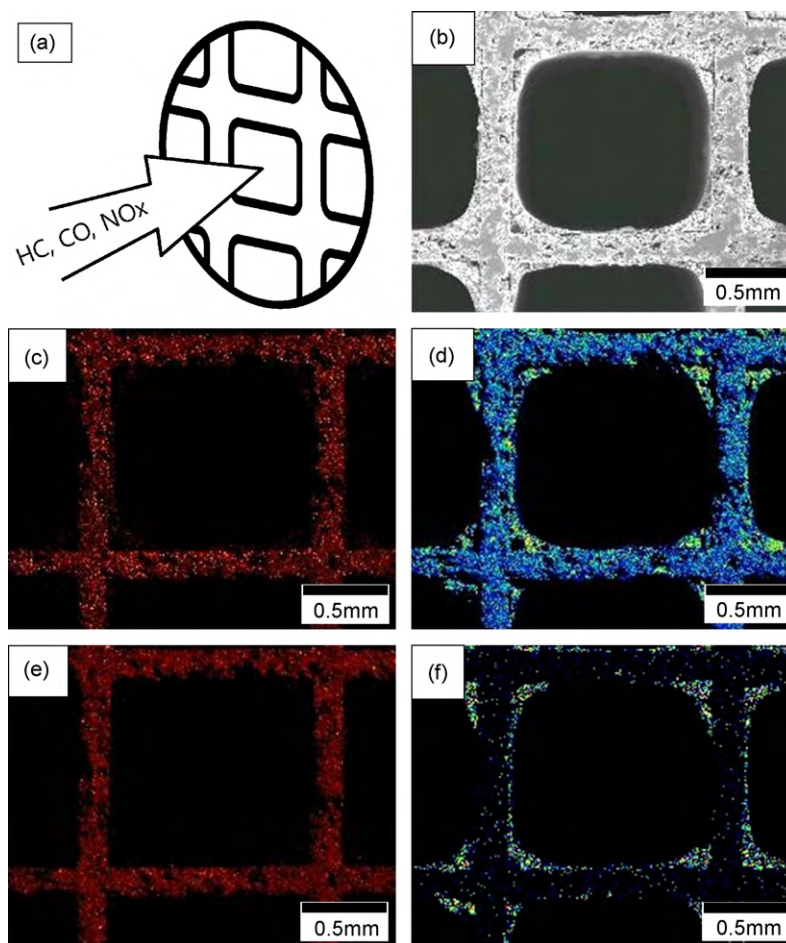


Fig. 1. Schematic diagram (a), SEM (b) and EDS mapping images (Mg (c), Al (d), Si (c) and Ce (f)) of the main parts of the typical catalytic converter.

are separated by allowing them to adsorb on Fe or Cu having high specific gravity [9].

Even though some technologies practiced for the commercial applications are sufficient to recover PGMs, the methods seem to be not cost-effective. Since the PGMs embedded in the catalyst layer of these types of automobile converters are present in very small quantities, it is, therefore, worth separating the catalyst layer from supporting matrix before they are processed. The separation and/or selective recovery of catalyst layer prior to any wet or dry recovery process can make a significant contribution to minimize the potential processing cost of these types of catalysts. Very little attempt, however, has been done yet.

The main purpose of this work is to provide information on the separation of catalyst layer from automobile catalytic converter by attrition scrubbing, a physical impact/shearing action between particles themselves and either the liquid phase or the walls and impellers in the mixing vessel [10–13]. At the point of impact, the

catalyst layers are dislodged from the supporting matrix or the bond between the layer and the surface of supporting matrix is weakened that the layer breaks under further impacts. The process variables that influence the efficiency of attrition scrubbing such as residence time, solid/liquid ratio and initial feed size of the catalyst sample have been explored in this work.

2. Experimental

2.1. Sample

The spent catalytic converters used in this work were collected from a local auto junkyard. The size and shape of converters, along with their catalyst loading, may vary according to the size of a vehicle's engine. The catalyst supporting matrix, which is of honeycomb structure, is made of magnesium aluminosilicate

Table 1
Size distribution and chemical composition of the different size fractions.

Size (μm)	wt%	Chemical composition (wt%, ppm*)								
		SiO ₂	Al ₂ O ₃	MgO	CaO	CeO ₂	ZrO ₂	Pd*	Pt*	Rh*
+1000	33.1	39.4	38.8	9.8	0.1	4.0	0.5	49	35	12
–1000+600	28.6	39.5	38.8	9.9	0.2	4.0	0.5	41	39	14
–600+300	14.1	41.0	38.6	10.3	0.2	3.5	0.4	36	30	11
–300+212	4.8	22.3	48.1	5.4	0.5	10.9	1.6	116	60	26
–212+106	8.5	7.9	57.3	1.8	1.5	17.5	1.7	125	132	43
–106+45	5.7	11.4	50.5	2.7	3.6	15.9	1.5	129	138	48
–45	5.2	7.5	49.8	1.7	2.4	20.4	1.3	136	146	59

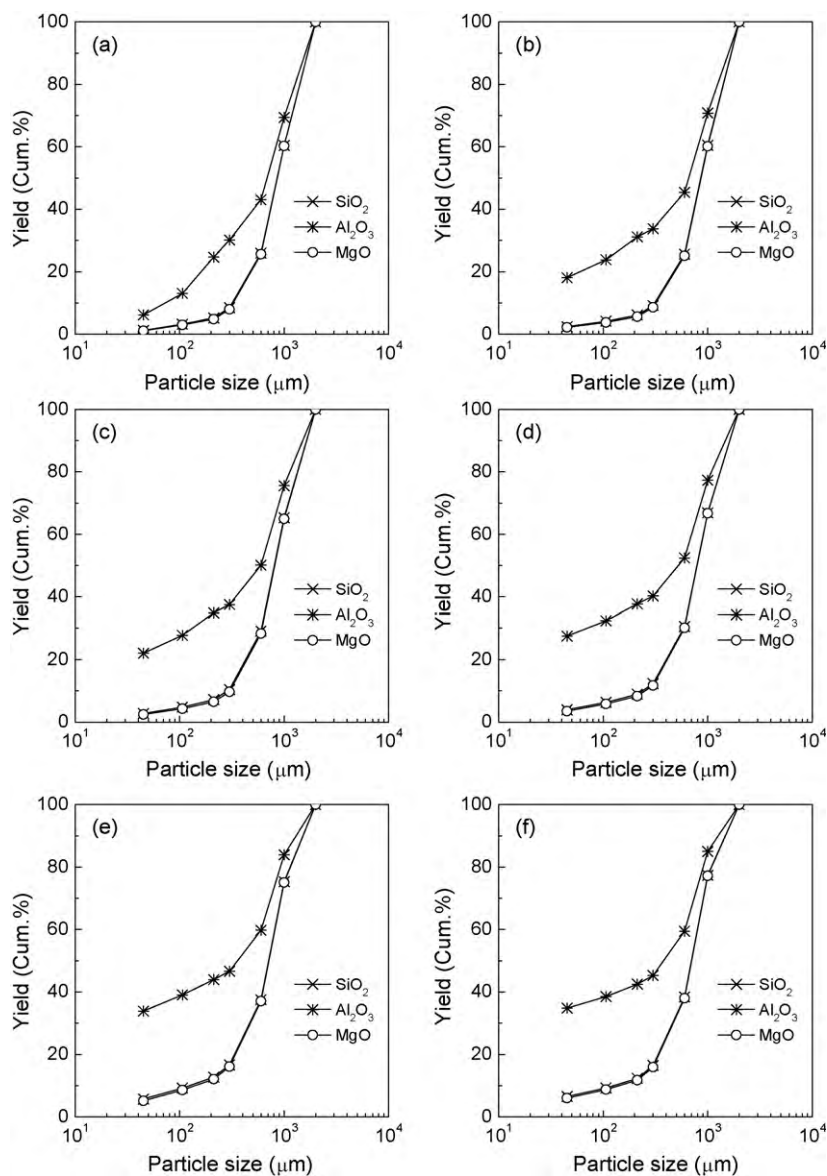


Fig. 3. Yield of SiO₂, MgO and Al₂O₃ of the sample, not scrubbed (a), scrubbed for 5 min (b), 10 min (c), 20 min (d), 40 min (e) and 60 min (f).

in the fraction less than 300 μm. This was attributed to more brittle structure of catalyst layer than supporting matrix. Namely, the catalyst coating, which covers the surface of the supporting matrix, has a porous structure in order to increase the effective surface area of catalysts. Thus it can be understood that the layer would be easily dislodged from the supporting matrix and broken into fine particles under the impact of stamp mill. Fig. 2 shows the X-ray diffraction patterns of the fractionated particles. The main peaks of the coarse fraction over 600 μm (a) were exactly matched with those of cordierite (JCPDS No. 13-0029) although weak peaks of CeO₂ (JCPDS No. 43-1002) were also detected. On the other hand, the peaks of CeO₂ increased as the particle size decreased and they were predominant in the pattern of the particle less than 45 μm. Although the peaks of γ-Al₂O₃ are not observable in the patterns owing to its very poor crystallinity, the γ-Al₂O₃ content should be high based on its chemical analysis. These results indicate that the catalyst layer rather than supporting matrix tends to be easily broken into fine particles less than 300 μm. In addition, it can be also expected that the contents of PGMs and other metal oxides increased simultaneously as the particle size decreased since they are mostly imbedded in the catalyst layer.

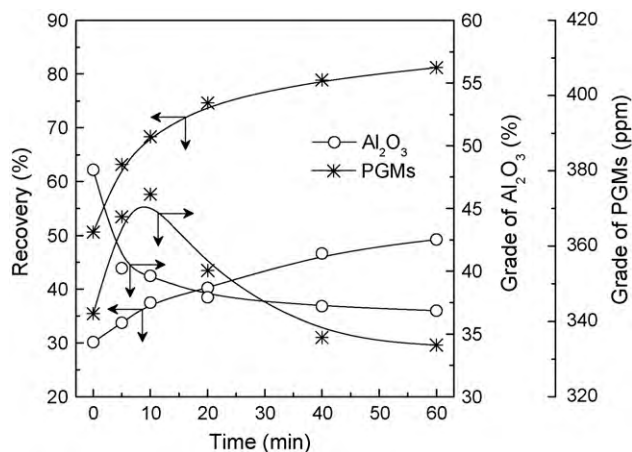


Fig. 4. Recovery and grade of Al₂O₃ and total PGMs in the fraction below 300 μm as a function of scrubbing time.

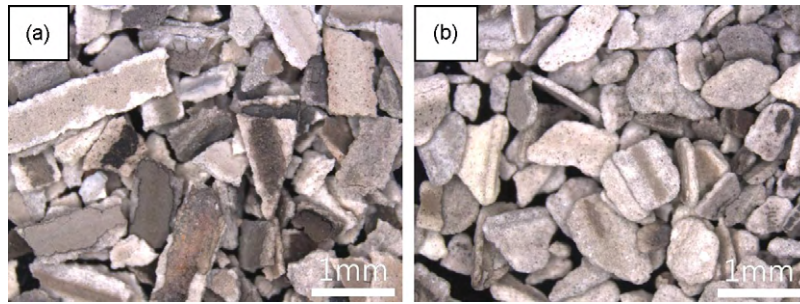


Fig. 5. Optical microscopic images of the raw particles (a) and the particles attrition scrubbed for 60 min (b).

In this ceramic-honeycomb-type automobile catalytic converter, neither thermal shock nor chemical leaching is sufficient to recover the precious metal catalyst components from the supporting matrix. This is attributed to the fact that the catalyst layer has a quite strong bond with the supporting matrix [7]. On the other hand, attrition scrubbing is considered as a comminution or a separation process enough to separate the catalyst layer. Actually, as shown in Fig. 3, the supporting matrix was less brittle than catalyst layer against attrition scrubbing in the mixing vessel where the converter particles underwent the shearing and impact forces. In the case of the particles less than 45 μm , as the residence time increased to 60 min, the yield of Al_2O_3 increased from 6.2 wt% to 33.8 wt%. Most of Al_2O_3 in the fractions less than 45 μm is believed to be originated from the catalyst layer rather than the supporting matrix. Fig. 4 shows the grade and recovery of Al_2O_3 and total PGMs in the sample less than 300 μm according to the scrubbing time of 60 min. The recovery of Al_2O_3 and total PGMs increased by 48.2% with an increase until the scrubbing time to 60 min although their contents in the treated materials decreased as the attrition scrubbing progressed. Table 2 shows the variation of γ -alumina and cordierite contents in different size fractions as a function of scrubbing time. It is noticeable that the attrition scrubbing led to make the γ -alumina concentrated into fine particles less than 45 μm , while cordierite remained in the coarse particles over 300 μm .

Fig. 5 shows the optical microscopic images of the raw particles (not scrubbed) and the particles attrition scrubbed for 60 min. Even though a small amount of particles still remains unchanged and, moreover, the prolonged scrubbing rounded off the sharp edges of the particles, it is noticeable that attrition scrubbing removed the catalyst layer from supporting matrix effectively. Consequently the impact and shearing forces caused by intensive scrubbing and

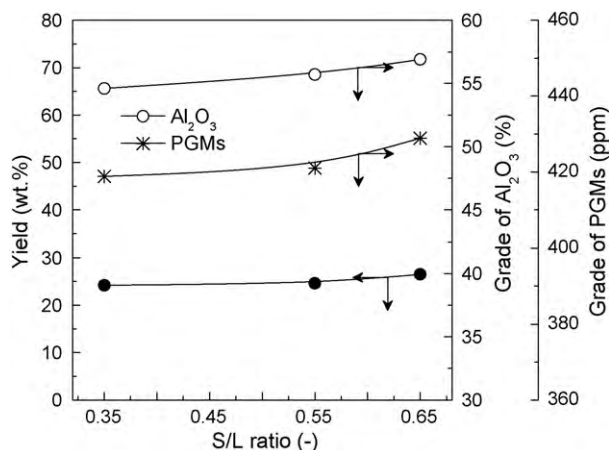


Fig. 6. Yield and grade of Al_2O_3 and total PGMs in the fraction less than 45 μm as a function of S/L ratio.

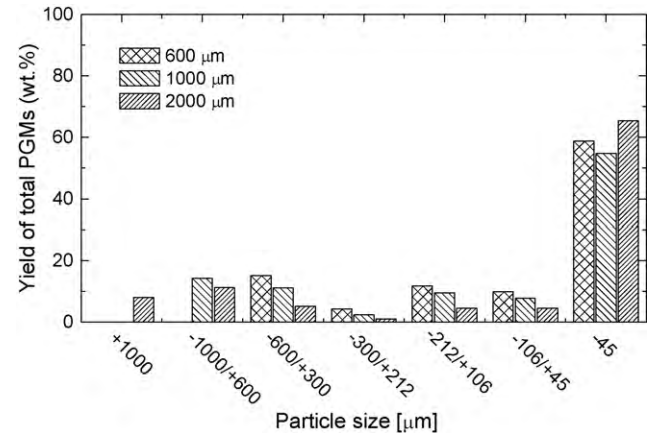


Fig. 7. Yield of total PGMs in the fractionated particles as a function of initial feed size.

mixing acted predominantly on the surface of the particles to make the catalyst layers be delaminated into fine particles.

In the case of attrition scrubbing of contaminated soils or mineral particles, it has been generally accepted that the efficiency of scrubbing increases as the solid/liquid ratio (S/L ratio) in the mixing vessel increases owing to more effective scrubbing actions between particles [17]. However, it was found to be little affected by the S/L ratio in the present work although the yield and the grade of Al_2O_3 and PGMs slightly increased as shown Fig. 6. This result might be contributed to the comparatively low density of converter particles. Thus, in this case, it is possible to say that the scrubbing efficiency does not depend only on the particle concentration in the mixing vessel. The production of fine particles less than 45 μm increased when the input size of the sample increased as shown in Fig. 7. It implies that the interparticle scrubbing became favorable as the initial input size increased. On the contrary, the production of fine particles reduced when the initial input size decreased owing to the increment of total surface area of feed so as to reduce the contact of catalyst layer.

4. Conclusion

- (1) The catalytic converter sample is mainly composed of 32.9% SiO_2 , 42.0% Al_2O_3 and 8.2% MgO in the form of γ -alumina and cordierite. The sample also contains 6.9% CeO_2 , 0.7% ZrO_2 and 0.6% CaO in the form of oxide as well as 62 ppm Pd, 56 ppm Pt, 19 ppm Rh in the form of metal.
- (2) As the particle size of sample decreases, the content of SiO_2 and MgO decreases. On the contrary, the content of PGMs and other oxides increases. It indicates that the catalyst layer rather than supporting matrix tends to be easily broken into fine particles less than 300 μm .

- (3) The attrition scrubbing as a comminution and separation process is determined to be a viable route to recover the catalyst layer. The physical impact and shearing action between particles in the scrubbing vessel causes the PGMs-containing catalyst layer to delaminate from the supporting matrix.
- (4) The recovery of γ -alumina in the fraction less than 300 μm increases as the residence time increases. The recovery of PGMs increases simultaneously by 81.2% PGMs at a residence time of 60 min. However, there seems practically no relationship between solid concentration and γ -alumina recovery in the present work.
- (5) The interparticle scrubbing becomes favorable when the input size of the sample increases. The solid/liquid ratio in the mixing vessel was, however, little affected owing to low density of converter particles.

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