

## Utilization of Spent RHDM Catalyst Treated at Various Conditions as the de-NO<sub>x</sub> SCR Catalyst Material

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### Abstract

Increasing emphasis has been paid recently in the world wide on the utilization of spent RHDM catalyst as the de-NO<sub>x</sub> SCR catalyst material. Spent RHDM catalyst deactivated with contaminants on which were deposited such as carbonaceous materials, sulfur and vanadium metal was pretreated with oil washing (n-heptane) and high temperature roasting for the removal of carbons and sulfur. Followed by oxalic acid leaching process was carried out for controlling excess vanadium deposited on spent RHDM catalyst in search of appropriate vanadium loadings for the best SCR performance and the leaching conditions are 5~15wt% concentration of oxalic acid and 2~40min. leaching time at 50°C with the ultrasonic agitator. And De-NO<sub>x</sub> activities of treated/untreated spent RHDM catalysts and commercial SCR catalyst were measured by the atmospheric SCR catalyst performance test unit, their characterizations were also carried out by the chemical and physical analyzers such as ICP, BET, Porosimeter, C&S Analysis and XRF. Acid leached (10wt%-10min) catalyst had shown the highest de-NO<sub>x</sub> performance of all prepared catalysts. Therefore the possibility of using as SCR catalyst through adequate treatment process of spent RHDM catalyst was found and further research will be needed in detail for the commercialization of it.

**Keywords:** RHDM catalyst, SCR, Acid leaching, NO<sub>x</sub>

### INTRODUCTION

Upgrading of heavy petroleum oils and residues to more valuable and environmental-friendly clean transportation fuels by catalytic hydroprocessing has been paid considerably in recent years. Prior to upgrading, residue hydrotreating process is essential to remove sulfur and heavy metals (Ni, V) to protect upgrading catalysts such as FCC or hydrocracking catalysts and to preserve environments. To remove these impurities, residue hydrodesulfurization (RHDS) catalyst to remove sulfur and residue hydrometallation (RHDM) catalyst for removal of heavy metals have been used in large quantities for a long time world-widely [1-3]. However these catalysts have limited life time and are gradually deactivated during use in a process [4-7]. The deactivated catalysts are usually regenerated and reused. However when it is uneconomical to regenerate and reuse them they are discarded as spent catalysts. These spent catalysts are hazardous wastes, their disposal in landfills is restricted in many countries [8-9]. In recent years, increasing emphasis has been placed on the development of processes for recycling the waste catalyst

materials as much as possible. Several possible options such as metals recovery, remanufacturing and reuse, treatment to produce active new catalysts and other useful materials have been considered by refiners and researchers to handle the spent catalyst problem [10-13]. Recovery of metals and other valuable products from spent catalysts are an attractive option. Recovery metals such as V and Mo from spent hydroprocessing catalysts have been reported in many studies. Several processes such as chlorination [14-15], acid leaching [16-20] have been reported in the literature for recovery of metals from spent hydroprocessing catalysts.

This study focused on the utilization of spent RHDM catalyst as new de-NO<sub>x</sub> SCR (Selective Catalytic Reduction) catalyst material by acid leaching at various research conditions.

RHDM catalyst is mostly composed of (Ni or Co)/(Mo or W)/Al<sub>2</sub>O<sub>3</sub> and deactivated by V in heavy residue oil. Deactivated RHDM catalyst components are V/Ni/Mo/Al<sub>2</sub>O<sub>3</sub>. Meanwhile SCR catalyst composed of V/(W or Ni)/(TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>). V component is a poisoning material to RHDM catalyst but on the other hand it is known as an active component of SCR catalyst. Furthermore, Mo is the main active component of RHDM catalyst and can be used as a promoter for SCR catalyst because Mo has the same group of periodic table of elements and almost same characteristic of W which is being used as a promoter of SCR catalyst. Therefore this study was carried out in order to confirm whether spent RHDM catalyst can be utilized as SCR catalyst for NO<sub>x</sub> removal [21-24].

In recent years, Some R&D progress for remanufacturing of spent RHDS catalyst was made by our research team in Korea and prototype of remanufactured RHDS catalyst produced in pilot plant line are shown as near fresh RHDS catalyst in activity and performance for sulfur removal.

In this study, the possibility of utilization of spent RHDM catalyst as SCR catalyst material by way of proper treatment (oil washing, high temperature roasting, acid leaching) was studied at various conditions [25-26] with the experience of remanufacturing spent RHDS catalyst.

### EXPERIMENTS

#### Sample of spent RHDM catalyst

The spent RHDM catalyst was obtained from domestic refinery company and was analyzed the deposited coke, sulfur and metals by C&S analyzer (CS-2000, ELTRA GmbH Co. in

Germany) and ICP-OES(5100, Agilent Tech. Manufacturing GmbH and Co. KR. in Malaysia) respectively after the process of n-heptane washing to remove heavy oil from spent RHDH catalyst.

### Treatment process for spent RHDH catalyst

The treatment process for spent RHDH catalyst can be categorized as heavy-oil washing, high temperature roasting and acid leaching.

In this study, to find out conditions of the utmost de-NO<sub>x</sub> performance as SCR catalyst, after complete removal of the deposited coke and sulfur by high temperature roasting, acid leaching was carried out with the condition of acid solution concentration and leaching time.

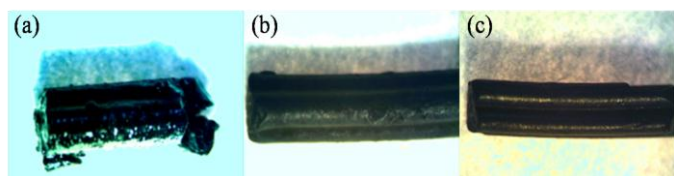
The catalyst notation is shown as Table 1 with respect to treatment progress. It notes as de-oiling (DO), high-temperature roasting (HR) and acid leaching (AL).

**Table 1.** Notation of processing condition.

Processing condition	Notation
De-Oiling(oil washing)	DO
High temperature Roasting	HR
Acid Leaching (concentration: A wt% - time: B min)	ALA-B

### Heavy oil washing process

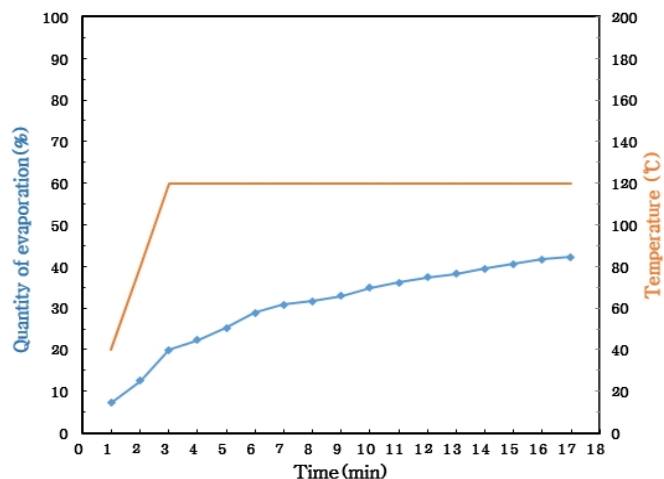
The solvent n-heptane (98.0%, Daejung Chemical Co. Ltd. in Korea) was used for heavy oil washing. The spent RHDH catalyst was put into stainless steel bath and washed with n-heptane of which volume is 1.5 times than that of catalyst using agitator for 2h. Repeated the same process for 2~3 times. In Fig. 1, checked with optic microscope and confirmed the original shape of the catalyst what is called quadrilobe.



**Figure 1.** Optical microscopic pictures (×20) of spent RHDH catalyst in the processing of heavy-oil washing (a) Spent RHDH catalyst (b) After oil washing (c) Dried RHDH catalyst.

Completely washed catalyst was dried naturally for 24h and then heated at 120°C for about 20min. This heating

temperature was determined by evaporation test with analyzer (MAC series, Radwag balance and scales Co. Ltd. in Poland) of which operation is completed in case of no sign of evaporation in 30s. The result is shown in Fig. 2.



**Figure 2.** Result of evaporation analysis.

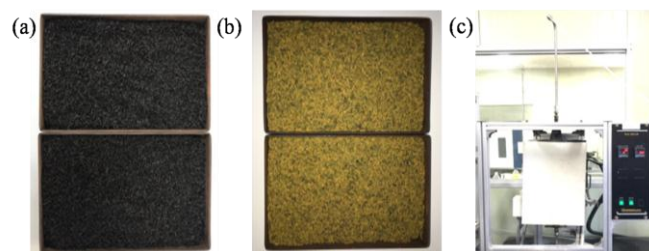
### High temperature roasting process

The high temperature roasting process is very important to primarily open the catalyst pores which was plugged with deposited coke and sulfur. The roasting furnace has 4 trays and each tray was charged with 25g heavy oil washed catalyst. The experimental condition and procedure of roasting process are specified as Table 2 and Fig. 3.

By this process, deposited coke and sulfur could be almost completely eliminated.

**Table 2.** Conditions of high-temperature roasting.

	Conditions
Temperature	400°C- 1h, 500°C- 2h
Heating rate	5°C/ min
Air flowrate	8ml / min



**Figure 3.** Processing procedure of high-temperature roasting (a) Before roasting (b) After roasting (c) Roaster.

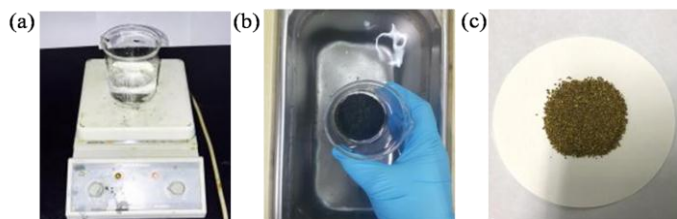
### Acid leaching process

After high temperature roasting process for deposited coke and sulfur removal, acid leaching process was conducted for increasing catalyst specific surface area and porosity by controlling the leaching degree of V which affects the NOx removal performance.

The reagent is oxalic acid(99.5%, Daejung Chemical Co. Ltd.) and acid solution was prepared with range of concentration. Ultrasonic cleaning device was used (ESW-2820B, WhashinTech Co., Ltd. in Korea) at 40kHz ultrasonic wave. The following Table 3 and Fig. 4 showed the experimental conditions and procedure of acid leaching process.

**Table 3.** Conditions of acid leaching.

	Conditions
Concentration of acid solution / Leaching time	5wt% / 2min, 5min, 10min 10wt% / 2min, 5min, 10min, 15min, 30min, 35min, 40min 15wt% / 2min, 5min, 10min
Temperature	50°C
(Catalyst / Solution)wt. ratio	1 / 2



**Figure 4.** Processing procedure of acid leaching (a) Preparation of acid solution (b) Acid leaching (c) Catalyst after acid leaching.

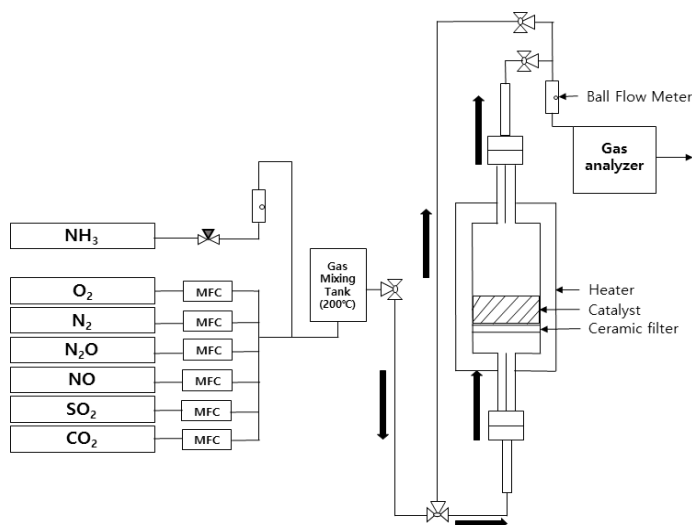
### Characterization of prepared catalysts

The prepared catalysts with treatment conditions were analyzed by various analytical instruments for physical /chemical surface analysis.

After heavy oil washing, various element of spent RHDM catalyst was identified by Inductively coupled plasma optical emission spectrometer(ICP-OES, 5300DV, Perkin Elmer in USA). The residual content of coke and sulfur after high temperature roasting was analyzed by C&S(CS-2000, ELTRA GmbH Co. in Germany) analyzer. The specific surface area was analyzed by BET(TriStar II 3020, Micromeritics Co. in USA) and the porosity of catalyst was done by Porosimeter (AutoPore™ IV Series, Micromeritics Co. in USA). After acid leaching, the contents of metals in the catalyst was analyzed by XRF(Delta professional, Olympus Co. in Japan).

### NOx removal activity measurement

The performance test of NOx removal for treated spent RHDM catalyst which was grinded into powder with 150~200 mesh was carried out in the fixed-bed reactor under atmospheric pressure as is shown in Fig. 5.



**Figure 5.** Schematic diagram of catalyst performance test unit.

The gas flowrate was automatically controlled by mass flow controller (MFC : F-100C, manufactured by Bronkhorst Co. in UK) and simulated gas composition was selected as the exhaust gas conditions in the coal fired power plant's operating condition as follows. The 200ppm NO gas(10% in N<sub>2</sub> balance, Sungkang Specialty Gas Co. Ltd.) and NH<sub>3</sub> gas(10% in N<sub>2</sub> balance, Sungkang Specialty Gas Co. Ltd.) were made to flow with the mole ratio of 1:1. The concentration of O<sub>2</sub> gas (99.9%, Sungkang Specialty Gas Co. Ltd.) was maintained at 8% and all gases analysis was done by gas analyzer (Greenline MK2, Eurotron Instruments UK Ltd.). The range of reaction temperature was 200~400°C with increment of 25°C, which was controlled by PID controller. And the catalyst volume was 1cm<sup>3</sup>and the space velocity was set to bet 100,000h<sup>-1</sup>. For precise activity test, stabilization was executed for 30min at each reaction temperature. The test condition is shown in Table 4.

**Table 4.** Experimental condition of NOx removal activity.

		Condition
sample type		Powder
S·V		100,000h <sup>-1</sup>
Temperature		200~400°C
NH <sub>3</sub> / NO mole ratio		1
Catalyst Volume		1cm <sup>3</sup>
Gas Composition	NO	200ppm
	O <sub>2</sub>	8%
	N <sub>2</sub>	Balance

## RESULTS & DISCUSSION

### The evaluation of characteristics for treated RHDM catalyst

#### ICP analysis

ICP analysis was conducted to confirm the content of V, Mo, and Ni of DO catalyst and the result is shown in Table 5.

Based on the result, the content of V can be used as active component of SCR catalyst is 169,111ppm and the content of Mo can be used as a promotor of SCR catalyst is 14,567ppm. It was confirmed that poisoning element for SCR catalyst such as As and Pb was not detected.

**Table 5.** Result of ICP analysis of spent RHDM catalyst.

Elements	Content(ppm)
W	204
Al	153,391
As	n.d.
Co	3,562
Fe	1,288
Mo	14,567
Na	2,176.
Ni	43,636
Pb	n.d.
V	169,111

#### Carbon & Sulfur Analysis

The elimination of deposited coke which has blocked pores and poremouth of the spent RHDM catalyst is essential because it prevents reactant from contacting with active components. High temperature roasting was accomplished with the condition in Table 3 and the result is shown in Table 6.

It was confirmed that coke was completely eliminated and at that time residual content of sulfur was less than 1.0wt%.

**Table 6.** Results of Carbon & Sulfur analysis.

Catalysts	Carbon (wt%)	Sulfur (wt%)
DO	18.43	14.08
HR	0.0167	0.7237

#### XRF analysis

The acid leaching process with respect to variables such as acid solution concentration and leaching time was carried out and analyzed by XRF for residual contents of V, Mo and Ni which are the components for SCR catalyst. The analysis

results are shown in Table 7 and represented there are little differences among AL 5-10, AL 10-10, and AL 15-10 conditions. However, at the condition of over 10 min leaching time, the residual V content significantly decreased. It was inferred that optimum leaching time is required to control the leaching rate.

**Table 7.** Results of XRF analysis.

Catalysts	Ni (ppm)	Mo (ppm)	V (ppm)
DO	26,263	2,531	123,158
HR	33,142	7,908	181,151
AL 5-10	28,873	6,973	160,593
AL 10-2	29,376	5,832	174,526
AL 10-5	33,154	4,922	168,315
AL 10-10	30,236	3,517	152,369
AL 10-15	29,962	2,477	95,386
AL 10-30	27,611	1,872	78,067
AL 10-35	25,868	1,655	53,534
AL 10-40	28,726	718	35,179
AL 15-10	34,127	1,336	133,913

#### BET analysis

The specific surface area is the main factor to affect the catalytic activity and its activity can be restored through acid leaching process. The analysis results are shown in Table 8. Based on the result, the specific surface area of AL catalysts was increased 10 times than that of DO catalyst and also increased proportional to the leaching time.

**Table 8.** Results of BET analysis.

Catalysts	BET Surface Area (m <sup>2</sup> /g)	Single point Surface are at P/Po (m <sup>2</sup> /g)
DO	26.90	24.90
AL 10-10	138.66	134.74
AL 10-30	238.70	232.38
AL 10-40	249.90	242.40

#### Porosimeter analysis

The value related with catalyst pore is the important factor in judging the availability as SCR catalyst and the results are shown in Table 9. As the similar result was found in BET analysis, porosity was significantly increased compare with

untreated spent catalyst and also increased proportional to the leaching time.

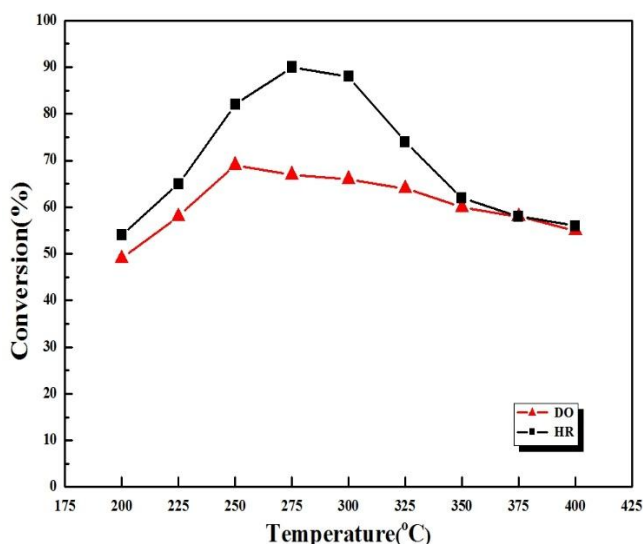
**Table 9.** Results of Porosimeter analysis.

Catalysts	Total Intrusion Volume (mL/g)	Total Pore Area (m <sup>2</sup> /g)	Porosity (%)
DO	0.247	0.98	35.48
AL 10-10	0.815	88.26	63.48
AL 10-30	1.327	184.84	69.10
AL 10-40	1.345	208.04	70.51

**The evaluation of NO<sub>x</sub> removal activity for treated RHDM catalyst.**

*The comparison for NO<sub>x</sub> removal activity between DO and HR catalyst*

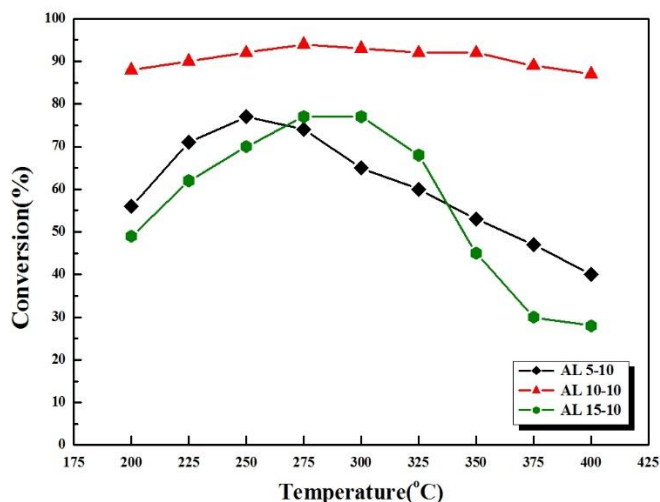
DO catalyst was prepared by heavy oil washing process and HR catalyst was also prepared by oil washing and high temperature roasting process. Those catalyst's samples were grinded into a powder and then screened with 150~200 mesh. The performance test for NO<sub>x</sub> removal was carried out and the result is shown in Fig. 6. The maximum NO<sub>x</sub> conversion efficiency of DO catalyst was 69% at 250°C, On the other hand that of HR catalyst was up to 90% at 275°C. But it showed that the activity temperature window is unstable and narrow over both catalysts.



**Figure 6.** Conversion of NO<sub>x</sub> over DO and HR catalyst.

*The comparison for NO<sub>x</sub> removal activity of AL catalysts(AL 5-10, AL 10-10, AL 15-10)*

The test catalysts were prepared with acid concentration of 5wt%, 10wt%, 15wt% respectively at 10min leaching time. The result is shown in Fig. 7. The maximum NO<sub>x</sub> conversion efficiency of AL 5-10 was 77% at 250°C, AL 15-10 was 77% at 275°C~300°C and AL 10-10 was 94% at 275°C. In conclusion, AL 10-10 catalyst showed best and stable conversion efficiency over entire test temperature ranges.



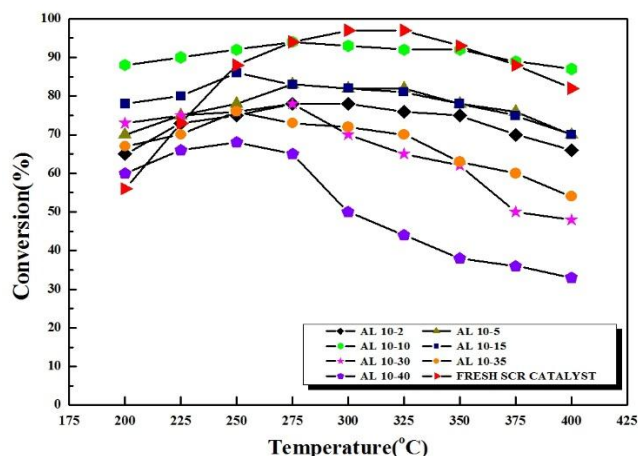
**Figure 7.** Conversion of NO<sub>x</sub> over AL catalysts.

*The comparison for NO<sub>x</sub> removal activity of AL catalysts(AL 10-2, Al 10-5, AL 10-10, AL 10-15, AL 10-30, AL 10-35, Al 10-40) and commercial fresh SCR catalyst*

From the above result, further tests were conducted by controlling leaching time such as less than 10min(2min, 5min) and more than 10min(15, 30, 35, 40min) at 10wt% acid solution to find out the effect of residual V content on NO<sub>x</sub> removal activity. The residual V content of each catalyst sample was 174,526ppm(2min), 168,315ppm(5min), 152,369ppm(10min), 95,386ppm(15min), 78,067ppm(30min), 53,534ppm(35min), 35,179ppm(40min). The efficiency of NO<sub>x</sub> conversion is shown in Fig. 8. The AL 10-10 catalyst showed the highest NO<sub>x</sub> efficiency and was equivalent to the performance of commercial fresh SCR catalyst. The maximum conversion of AL 10-10 catalyst was 94% at 275°C and that of commercial fresh SCR catalyst powder 97% at 300°C. The NO<sub>x</sub> conversion profile of AL 10-10 and commercial fresh SCR catalyst showed the very similar tendency.

In the condition over 10min leaching time, as the leaching time increases, NO<sub>x</sub> conversion decreased. It was inferred that because catalyst specific surface area and porosity increased but simultaneously the active components of catalyst were leached out significantly





**Figure 8.** Conversion of NO<sub>x</sub> over AL catalysts and fresh SCR catalyst.

## CONCLUSION

This study was carried out to confirm the possible usage of treated spent RHDH catalyst as SCR catalyst material. In consideration of research and results from treatment conditions of spent RHDH catalyst (oil washing, high temperature roasting, acid leaching), NO<sub>x</sub> conversion performance and catalytic characteristics analysis, the conclusions were as follows.

- 1) The optimum condition for acid leaching process is 10wt% acid solution. It was the best and stable condition for NO<sub>x</sub> conversion performance tested at 200°C~400°C than 5wt% and 15wt% samples.
- 2) In accordance with the results of BET and Porosimeter for AL 10-10, AL 10-30, AL 10-40, as the leaching time increases, catalyst specific surface area and porosity increased. But NO<sub>x</sub> conversion performance was relatively poor in spite specific surface area and porosity increased. In other words, to increase the leaching time may contribute to increasing the catalyst specific surface area and porosity but make the active component (V) and promoter (Mo) of SCR catalyst leach out significantly. Thus it was not effective in increasing the NO<sub>x</sub> conversion efficiency.
- 3) From the catalyst performance test on atmospheric fixed-bed reactor, The AL 10-10 catalyst showed the highest NO<sub>x</sub> efficiency and was equivalent to the performance of commercial fresh SCR catalyst.

Therefore it was confirmed that the spent RHDH catalyst can be possibly used as SCR catalyst through proper treatment process as described in this paper.

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