

Deactivation of V₂O₅/Sulfated TiO₂ Catalyst Used in Diesel Engine for NO_x Reduction with Urea

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Deactivation of V₂O₅/sulfated TiO₂ catalyst used for 24000 h in diesel engine for NO_x reduction with urea was investigated. The characteristics of the deactivated catalyst were compared with the fresh catalyst by XRD, ICP-AES, SEM and EDS. The catalytic activity of the catalysts was measured with a fixed-bed reactor. From the results, Ca and S were found as main poisons and XRD analysis showed their major phase was CaSO₄. The deposit of CaSO₄ blinded the catalyst and reduced the surface area from 51.0 m²/g to 30.5 m²/g. The NO_x conversion of the deactivated catalyst is 10% lower than that of the fresh catalyst due to CaSO₄ generated by sulfation of Ca.

1. Introduction

SCR catalyst deactivation is an important practical concern due to a significant technical and economical impact on the SCR process (Moulijn et al., 2001). In the treatment of a power plant flue gas, SCR catalysts can be poisoned and plugged with fly ash including alkali and alkali earth metals (Janssen and Meijer, 1993). There are many studies to understand the underlying phenomena leading to the deactivation of SCR catalysts used in coal fired power plant (Gutberlet and schallert, 1993), bio fuel power plant (Zheng et al, 2005) and municipal incineration plant. However, few studies have been done on the deactivation of V₂O₅/sulfated TiO₂ catalyst in real thermal power plant. In this study, the characteristics of deactivated catalyst used for 24000 h in diesel engine for NO_x reduction with urea have been investigated.

2. Experimental

2.1 Catalyst preparation

The deactivated catalyst used for this study is the honeycomb type catalyst aged in diesel engine using bunker C fuel oil. Sulfated titania (TiO₂) was used as a catalyst support to make sulfated V₂O₅/TiO₂ catalyst and the preparation method was reported elsewhere (Lee et al, 2002). The physical properties of the catalyst are shown in Table 1. The catalyst for characterization and activity measurement was extracted from the sample benches which were located above third layer of the reactor. The deactivated catalyst sample was exposed to the flue gas at temperature of 400 °C for 24000 h. The activity was measured using 24.8 mm × 24.8 mm × 49.0 mm honeycomb sample catalyst.

Table 1 Physical properties of the sulfated catalyst element

Type	Open Frontal Area(%)	Cell Density (cell/in ²)	Cell Size (mm)	Wall Thickness (mm)	Hydraulic Diameter (mm)	Geometric Surface Area(m ² /m ³)
Honeycomb	62	20	4.3	1.15	1.86	580

2.2 Catalyst characterization and catalytic activity measurement

SEM analysis was performed with a JEOL JSM-6360 apparatus equipped with an EDS (OXFORD Instrument INCA 7582) instrument. A Rigaku D/MAX 2500H diffractometer was employed for obtaining X-ray diffraction patterns (XRDs). The catalyst and the deposits were analyzed with a Thermal Element IRS DUO ICP-AES. BET surface area and pore size distribution were measured by N₂ adsorption at 77K with a Micrometrics ASAP 2010. The activities of a fresh catalyst sample and the deactivated monolithic catalyst sample were measured using a NO_x reducing system equipped with the fixed bed quartz reactor (46mm I.D.).

3. Result and Discussion

3.1 Characteristics of the deposits

As shown in Fig. 1, the dominant species found in the deposits are alkaline earth element Ca and sulfur. The XRD pattern shown in Fig. 2 identifies CaSO₄ as a major phase of the deposit. Fig. 3 shows the cross section of the deactivated catalyst where surface and pores were blocked with deposits. Chemical analysis of selected particles with EDS is summarized in Table 2. The chemical composition of selected deposit points (a, b, c, d) indicates the presence of high levels of calcium and sulphur. The composition of the catalyst point(e) shows high level of catalyst support TiO₂.

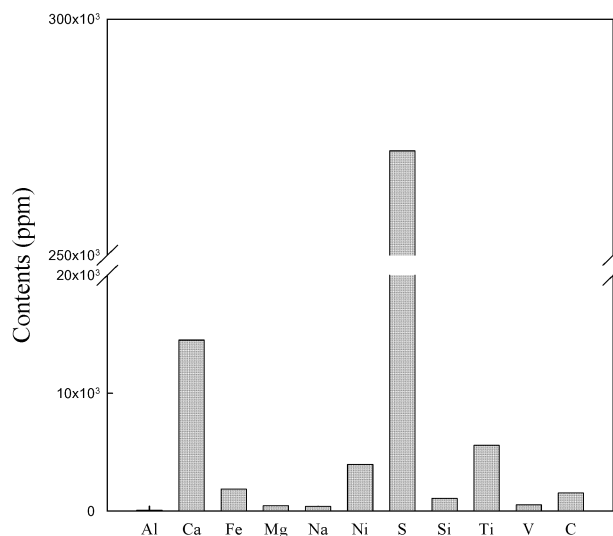


Fig. 1. Contents of the deposits measured with ICP-AES.

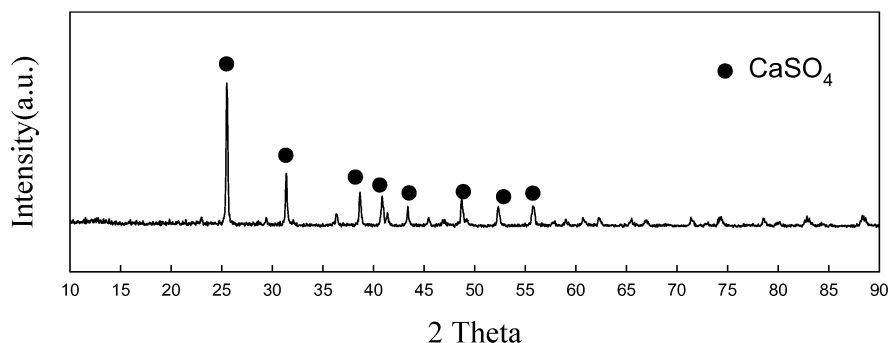


Fig. 2. XRD pattern of the deposits

Line scans were obtained for various elements (Ti, V, S, Ca) across the catalyst originating from its outer region and terminating catalyst inner region as shown in Fig. 4 and Fig. 5. It can be seen that the V_2O_5 /sulfated TiO_2 catalyst starts at a point indicated by 30 μm while the region between 0 and 30 μm represents the deposit zone composed of Ca and S. V and Ti appear to be homogeneously distributed across the catalyst. The element distribution and the structure of the deactivated catalyst are confirmed by elemental mapping with EDS (Fig. 6). The external zone of the layer is rich in Ca and S while the inner layer shows the support material TiO_2 .

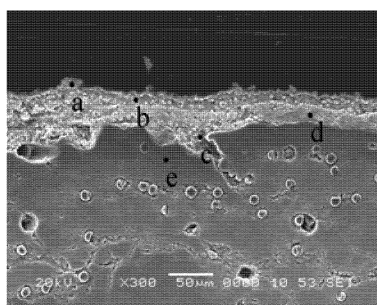


Fig. 3. Cross section of the deactivated catalyst and selected points for EDS analysis.

Table 2 Chemical composition of selected point on cross section of the deactivated catalyst

Element	Point a(wt%)	Point b(wt%)	Point c(wt%)	Point d(wt%)	Point e(wt%)
Si	0.00	3.43	17.73	11.56	3.73
S	14.48	40.15	32.96	36.00	0.00
Ca	58.52	51.01	31.38	34.45	0.00
Ti	0.00	0.00	2.56	0.00	88.33
V	0.00	0.00	1.47	2.24	2.63
Fe	0.00	0.00	1.28	2.17	0.00
Ni	0.00	5.42	12.63	13.38	5.31

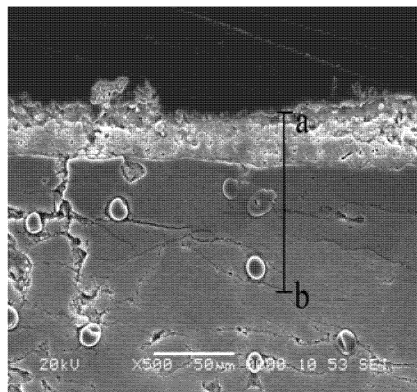


Fig. 4. Cross section of the deactivated catalyst and selected line for element line scanning.

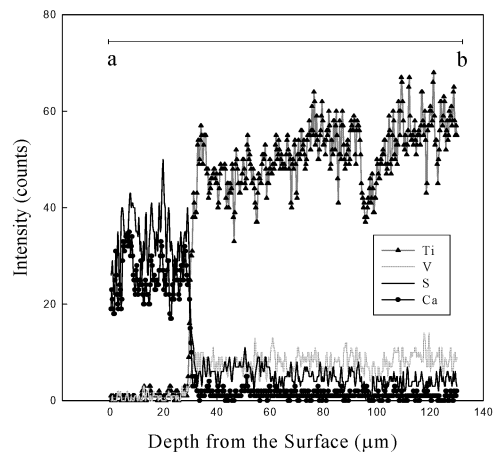
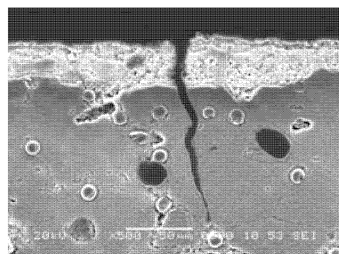
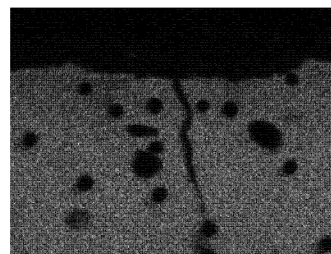


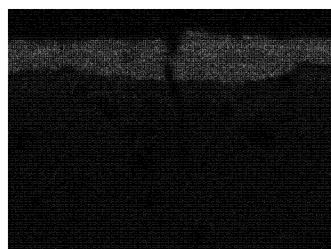
Fig. 5. Element profiles of Ti, V, S and Ca from deposit into the catalyst.



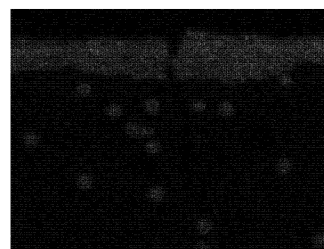
(a)



(b)



(c)



(d)

Fig. 6. Elemental mapping of deactivated catalyst. (a) SEM image of the catalyst, (b) Ti, (c) S, (d) Ca

3.2 Characteristics of the catalyst

The ICP-AES analysis of the fresh and the deactivated catalyst indicates that only insignificant amounts of Fe, Mg, Na and Ni were accumulated in the catalyst after 24000 h on the stream. On the other hands, the amount of Ca and S accumulated in the deactivated catalysts increased up to 1.6% and 1.8% respectively (Fig. 7).

Table 3 BET surface area and pore volume of the fresh and exposed samples

Catalyst	BET Surface Area(m ² /g)	Total Pore Volume(cm ³ /g)	Average Pore Diameter(nm)
Fresh Catalyst	51.0	3.43	17.73
Deactivated Catalyst	30.5	5.42	12.63

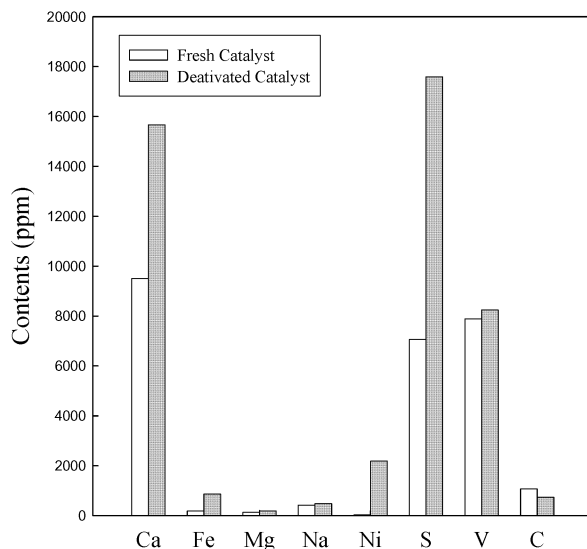


Fig. 7. Contents of catalysts measured with ICP-AES.

The change of BET surface area was measured for the fresh catalyst and the deactivated catalyst. As shown in Table 3, the surface area of the fresh catalyst is 51.0 m²/g and the surface area of the deactivated catalyst is about 30.5 m²/g. The decreased surface area of the deactivated catalyst might be originated from CaSO₄ that has been deposited on the catalyst. The total pore volume of the fresh is 0.208 m³/g and the total pore volume of the deactivated catalysts is 0.127 m³/g. There are no significant difference changes of average pore diameter of the fresh catalyst and the deactivated catalyst.

The XRD pattern of the fresh and the deactivated catalysts were detected. Anatase is the only TiO₂ phase detected in all samples, indicating that no significant rutilization occurred under all applied operating condition.

3.3 Catalytic activity

The NO_x removal activities of the fresh and the deactivated catalysts were measured in the fixed bed quartz reactor. The effect of reaction temperature on the conversion of NO_x is shown in Fig. 8. NO_x conversion of the deactivated catalyst is about 74% at 400 °C which is 10% lower than that of the fresh catalyst. This primary change of activity may be attributed to masking of catalyst surface by CaSO₄. The particles of Ca are transported into the pores of the catalyst and subsequently reacted with SO₃ to form CaSO₄. The CaSO₄ causes catalyst surface masking and prevents the reactant from diffusing into catalyst, especially active component vanadium.

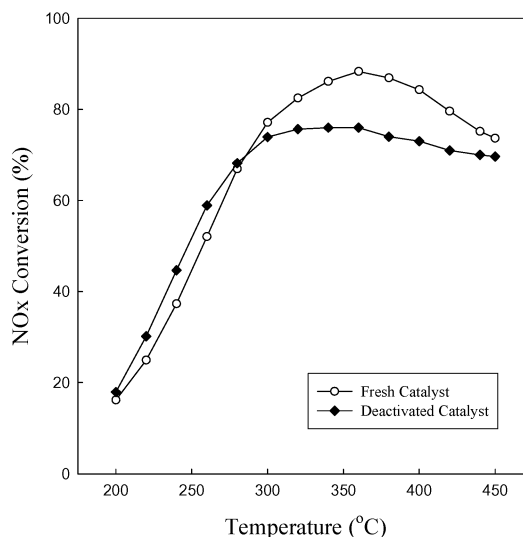


Fig. 8. NO_x conversion for the fresh and the deactivated catalyst.

4. Conclusions

The characteristics of the V₂O₅/sulfated TiO₂ catalyst used for 24000 h in diesel engine for NO_x reduction with urea have been investigated. From the result, the dominant species found in the deposits are alkaline earth element Ca and sulfur. The XRD pattern identifies CaSO₄ as a major phase of the deposits. The surface area of the fresh catalyst is 51.0 m²/g and the surface areas of the deactivated catalyst are about 30.5 m²/g. The decreased surface area of the deactivated catalyst might be originated from CaSO₄ that has been deposited on the catalyst. However, there are no rutilization of the deactivated catalyst. Anatase is the only TiO₂ phase detected in all catalysts. The NO_x conversion of the deactivated catalyst is 10% lower than that of fresh catalyst due to CaSO₄ which physically blinds the pore of the catalyst.

References

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