

CARBON-NO_x REACTION CATALYZED BY VANADIUM OXIDE

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Introduction

It is well known that soot, namely carbon, plays important role for NO_x formation in combustion. Therefore, many works[1,2] have been done to use carbon as reducing agent of NO_x, including catalytic work[3]. It should be attempted that unburned soot is injected again into furnace to reduce NO_x.

At Kashima-Kita electric power plant, heavy end oils like asphalt and orimulsion are used as fuel and valuable metals such as vanadium or nickel which is included in the end oils are recovered from dust ash by wet technique. Here, soot is produced as by-product. This soot is estimated as reducing agent of NO_x. It was found that the soot has higher activity to react with NO_x comparing other carbonaceous materials such as carbon black, and also this high activity is mainly due to vanadium oxide which is contained in the soot as contaminant.

Experimental

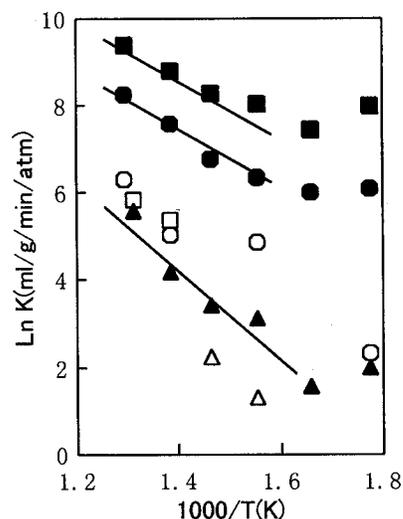
The soot is from metal recovery plant and the properties are as follows, surface area: 19.0m²/g, SiO₂:2.21wt%, NH₄:1.16wt%, Fe:2.04wt%, Ca:0.08 wt%, Mg:1.02wt%, V:2.41wt% Na:0.10wt%, Ni:1.76 wt%. Carbon black is also used as reference carbonaceous material. The soot is demineralized by hot HCl and metals are loaded on the demineralized soot by impregnation method.

TGA(Shinku-Riko TA-7000) was used to measure reactivity. The weight of sample is 6-7mg and the sample is heated up at reaction temperature for 30 minutes and kept at this temperature for 250 minutes. Gases used are 464ppm of NO₂, 2008ppm of NO(balance UHP He) and air. The gas flow rate was fixed at 100ml/min. In order to calculate reaction rate, it was assumed that the rate is first order to the concentration of reaction gas and NO_x and oxygen react with carbon to produce carbon dioxide.

Results and discussion

Figure 1 shows the Arrhenius plots of the reaction

rates of two types of carbon with three gases, NO₂, NO and O₂.



○●:NO □■: NO₂ ▲▲:O₂
Closed:Soot, Open:Carbon black

Figure 1. Carbon-gas reaction rate

The soot shows higher reaction rate than carbon black at every temperature and for all gases. Namely, the soot has higher activity not only for NO₂ and NO but also for oxygen. The good linear relationship can be observed at higher temperature over 350 °C for the three gases in case of the soot. The reason of high reaction rate at lower temperature under 310 °C is not apparent so far, but it is thought that ammonia in the soot affects the weight loss of the sample.

The reactivity of gases with the soot is NO₂>NO>O₂ and the ratios at 370 °C are about 140, 25 and 1 for NO₂, NO and O₂, respectively. This fact suggests that over half of the soot reacts with NO_x even if effluent gas contains few percent of oxygen and few hundreds ppm of NO₂ and NO.

The activation energies for NO₂ and NO are almost same and higher value is observed for O₂. It can be said from this fact that lower temperature is profitable for NO_x reduction with less carbon

consumption by O₂.

NO_x shows higher reaction rate than O₂ even for the carbon black. However, when the soot and carbon black are compared as ability of reducing NO_x in the presence of O₂, the reaction rate ratio between NO_x and O₂ looks smaller for the carbon black than for the soot. At least, the rate of NO₂ compared with O₂ is apparently smaller than the soot because the rates with NO and NO₂ are almost same for the carbon black. Therefore, the soot has larger possibility to be used as NO_x remover from exhaust gas than the carbon black not only for high reactivity but also again for less carbon consumption by O₂.

Next, the reason of high reactivity of the soot is examined. The reason should be the morphology of the soot, properties as carbonaceous material or catalytic effect of metal compounds included in the soot as contaminant. First, the soot is demineralized and reactivity with NO is measured. Very low weight loss is observed at 370 °C. This fact shows that the soot itself has low reactivity for NO reduction and the reactivity is smaller than the carbon black, because the carbon black shows reactivity at 370 °C as shown in Figure 1. So, the catalyzation of metal compound, especially nickel and vanadium, is most likely. Here, both metals exist as salt, not as metal, in the soot.

Table 1 shows reaction rate of nickel nitrate loaded demineralized soot.

Table 1 Catalytic effect of nickel (gas:NO)

Pre treat.	React. Temp. (°C)	Reaction rate (ml/g/min/atm)
Non	370	0.12X10 ³
900°C	370	0.55X10 ³
Non	500	2.13X10 ³
900°C	500	2.51X10 ³

Though nickel shows catalytic activity for NO reduction, this activity is marked at higher temperature and when the sample is heat treated before reaction. That is, almost same rate is observed at 500 °C, but, at 370°C, about four times higher rate is seen for pre-heat treated sample than for non pre-heated one. This fact is probably due to reduction of nickel nitrate to metal nickel and only metal nickel shows high catalytic activity, as clarified in carbon gasification by H₂O and H₂.

Then, the catalytic effect of vanadium oxide is measured. The reaction rate to NO at 370 °C is

depicted in Figure 2 when the vanadium pentoxide is used and the loading level is changed. The vanadium oxide is little soluble in water, so aqueous ammonium is added until the oxide becomes completely soluble in water.

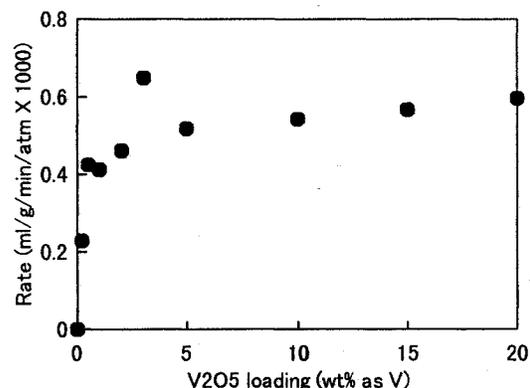


Figure 2. Catalytic effect of vanadium

Vanadium oxide has catalytic activity at its very low loading level without no pre-heat treatment, rate increased rapidly with V₂O₅ loading up to 3wt% and almost leveling-off is observed over about 5wt%. The rate at this level is higher than that of the nickel nitrate loaded soot without pre-heat treatment and furthermore, almost same with as-received soot. The catalytic activity of V₂O₅ for carbon-NO_x reaction is first revealed here in our knowledge, though it is known vanadium shows catalyzation for carbon gasification and NO_x-NH₃ or NO_x-CO reaction. This rate is almost same as that of the nickel loaded soot with pre-heat treatment at 900 °C.

It is concluded from the results obtained here that the soot can be used as NO_x remover from exhaust gases with less carbon consumption by oxygen and this ability is mainly caused by catalytic activity of vanadium oxide included in the soot.

Further study will be presented at the conference when other carbons are used and vanadium oxide is loaded on the carbons.

References

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