Autonomous Improvement in the Catalytic Activity of KVO_3/SiC for Soot Oxidation under Practical Gaseous Conditions

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(Received December 25, 1997; CL-970977)

The effect of reactant gas composition on the catalytic combustion of soot by KVO_3/SiC are investigated. The activity of KVO_3/SiC increased by repeating the measurement of temperature-programmed reaction (TPR) under reaction gases containing SO_2. SEM and EDX observations showed that only KVO_3 was present on the surface of the fresh sample, but a mixture of K_2SO_4, V_2O_5 and KVO_3 was formed on the used sample, suggesting that during the reaction process the mixed metal oxide change into simple sulfate and oxide which are more stable and catalytically active under practical conditions.

The diesel particulate contributes to a great extent to the environmental pollution especially in urban areas. Several methods to control the emission have been developed and tested. So far, engine modifications and use of oxidation catalysts which only oxidize the hydrocarbon fraction have turned out to be effective. However, the problem of the oxidation of solid soot has not yet been solved. It is urgent to develop efficient catalysts which can oxidize soot under practical conditions.

Vanadium containing oxides are active catalysts for soot oxidation[1] and KVO_3 is a representative among them. However, most of the researchers investigated the catalytic behavior only in the dry air conditions,[1-4] the effect (poisoning) of SO_2 having been considered in very few cases. There have been no report concerning the variation of catalyst and its activity with time. In this study, we have investigated the catalytic behavior of a soot combustion catalyst under conditions close to practical ones: a) catalytic components are coated on SiC filter material, b) reaction gases contain SO_2, NO, H_2O, N_2 and O_2, c) space velocity is high (60,000 h^{-1}) and d) the contact between carbon and catalyst is loose[5].

The catalytically active component, KVO_3 (5% in weight), was loaded on granular SiC (60~100 mesh), i.e., calcined at 800 °C for 2 hours. SiC was made by crushing a SiC filter material (Ibiden Co.). Carbon black (primary particle size, 28 nm; surface area, 80 m^2/g; Nippon Tokai Carbon 7350F) was used as model soot. The supported catalyst and carbon black were mixed for 10 minutes using an electric mixing machine without any crushing media. The contact between catalyst and carbon after the mixing procedure was loose: close to practical situations according to Neeft's classification[5]. The temperature-programmed reaction (TPR) was carried out to measure the activity of catalysts: reactant gases composed of 10% O_2, 7% H_2O, 1000 ppm NO and 100 ppm SO_2 diluted with N_2, was passed through a mixture of a catalyst sample (0.5 g) and carbon black (0.005 g), at a flow rate of 500 ml/min. Temperature was raised by 10 °C/min from room temperature to 600 °C, during which CO_2 and CO concentrations in the product gases were continuously measured with infrared CO_2 and CO analyzers. The catalytic activity was evaluated by the initial and peak temperatures of the CO_2 TPR signal, the former being the temperature where the CO_2 concentration exceeds 100 ppm. All the carbon black was burnt out after a TPR measurement. The morphology and composition of the catalyst surfaces were observed and determined by SEM (JEOL JSM5300) with EDX (Phillips PV9800) and XPS(Shimadzu ESCA 750).

Figure 1 shows TPR profiles of SiC support (blank) and KVO_3/SiC for the combustion of carbon black. For KVO_3/SiC, all the carbon were burnt out till 560 °C, while the carbon combustion just started, for SiC, at 560 °C. The peak temperature was lowered more than 100 °C and the selectivity to CO decreased for KVO_3 /SiC, compared with that of the blank.

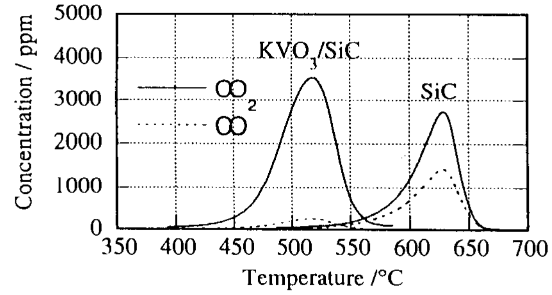

Figure 1. TPR profiles of SiC and KVO_3/SiC, reaction gases containing 10% O_2, 7% H_2O, 1000ppm NO and 100ppm SO_2 diluted with N_2.

In order to investigate the influence of reactant gas composition on the catalytic performance, the activity of KVO_3/SiC for soot combustion were tested repeatedly under different reaction gas conditions. The results are shown in Figure 2. At peak maximum points, the conversions of carbon are almost the same (about 55%). The activity of KVO_3/SiC increased by repeating the TPR measurement under reaction gases containing SO_2.

It has been found that KVO_3/SiC has a high "loose contact activity" for soot oxidation. The activity is similar to that of the most active catalyst ever reported, Cu-K-Mo-Cl/TiO_2 (or ZrO_2).[5] However, Cu-K-Mo-Cl catalyst won't be able to be used for practical purpose because the activity is soon lowered with loss of chlorine. The formation of chloro-carbon compounds which are very toxic, may become another problem.

The morphology of the fresh and used KVO_3/SiC surface are shown in Figure 3a and 3b, respectively. For the fresh KVO_3/SiC, the agglomerates of KVO_3 adhere to the surface of SiC particles. They were in different shapes: rod-, plate-shaped and bulk. The morphologies of agglomerates changed after a TPR

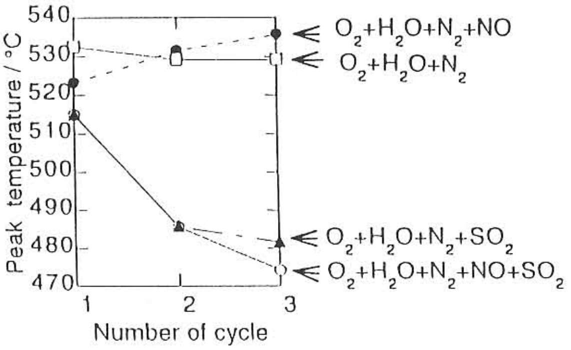

Figure 2. Effect of the composition of reaction gases on the activity of KVO_3/SiC.

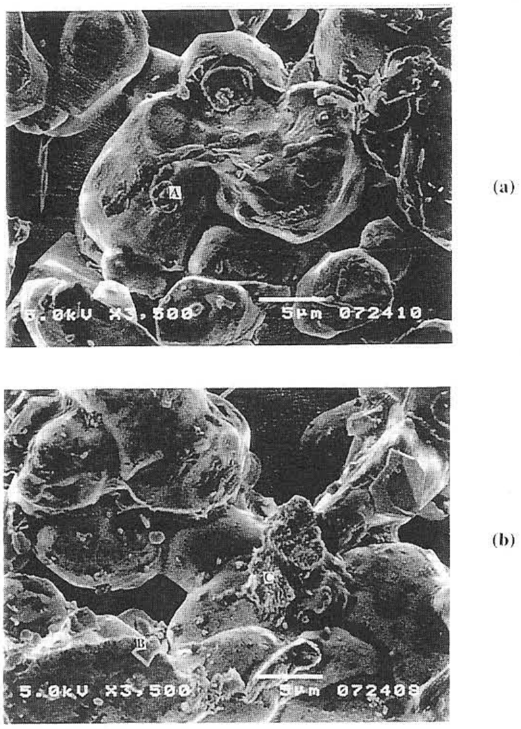

Figure 3. SEM pictures of KVO_3/SiC (a) before use (b) after use.

measurement. The EDX analysis results of the agglomerates on the fresh and used samples are shown in Table 1. For the fresh sample, K and V with the atomic ratio of 1:1 were present on the SiC support (point A), while for the used sample, a very strong S signal was found (point B).

Table 1. Elemental composition of the fresh and used KVO_3/SiC

Element		K(mol%)	V(mol%)	S(mol%)
Before use	Total	50.4	49.6	0.0
	A	51.6	48.4	0.0
After use	B	64.5	0.8	34.7
	C	31.3	59.6	9.1

XPS analysis was consistent with that of EDX, showing a strong S_{2p} peak at 168.6 eV, which indicates that S is in the form of sulfate on the used KVO_3/SiC.[6]

The elemental compositions were different for the different morphology agglomerates on the used KVO_3/SiC. The ratio of K: S: V was 1.86: 1.00: 0.02 at point B indicating that the main phase is K_2SO_4. For point C the ratio of K: S: V was 3.44: 1.00: 6.55. Such an abundance of vanadium indicates that V_2O_5, besides KVO_3, was present at point C. This also suggests that during the reaction process KVO_3 may partly change into K_2SO_4 and V_2O_5. The increase in activity by repeating the measurement can be attributed to a partial formation of an eutectic mixture of V_2O_5, and K_2SO_4 which has a lower melting point,[7] and thus higher mobility toward carbon particles, than KVO_3. It is supposed that a soot oxidation catalyst becomes more active when it is in liquid form, since the contact between catalyst and carbon get substantially better than that in a solid form.

References and notes

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