Outstanding effect of SO_2 addition on the rate of carbon oxidation with a Pt catalyst

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Addition of trace SO_2 (*ca.* 8 ppm) to a reactant gas containing NO substantially enhanced the oxidation rate of carbon black mixed with a Pt/SiO_2 catalyst, which is attributed to SO_3 (or H_2SO_4) catalyzing the oxidation of carbon by NO_2.

The emission of soot from diesel engines is a serious environmental problem. Among the many catalysts for soot oxidation that have so far been reported, Pt exhibits high levels of catalytic activity.[1–5] Platinum is thought to promote soot oxidation indirectly, *i.e.* by oxidizing the NO normally coexisting in the exhaust gas into NO_2, which actually oxidizes soot to CO and CO_2. Here we report the effect of adding SO_2 to the reactant gas, which dramatically promoted the oxidation of carbon black.

Platinum (1 wt%) supported on silica gel (Pt/SiO_2) was prepared by impregnating SiO_2 (0.1 to 0.25 mm in diameter, 374 $m^2\ g^{-1}$) with a solution of $Pt(NH_3)_4(OH)_2$, followed by drying, reduction with H_2 at 400 °C and calcination in air at 600 °C. Commercially available carbon black (CB; Nippon Tokai carbon 7350F; primary particle size = 28 nm; specific surface area = 80 $m^2\ g^{-1}$; CHN analysis: C, 97.99; H, 1.12; N, 0.06%; H_2O = 0.58 wt%) was used as model soot. The Pt/SiO_2 catalyst (0.5 g) and CB powder (0.005 g) were simply mixed together with a spatula and placed in the reactor. Mixing in this way results in a 'loose' contact between the catalyst and carbon, which is thought to be close to that found in practical cases.[6] Temperature-programmed reactions (TPRs) were carried out in a tubular quartz reactor. Reactant gases—10% O_2, 7% H_2O, 0 or 1000 ppm NO, 0 to 100 ppm SO_2 and N_2, a composition which is typical of diesel exhaust gas, except for the absence of CO_2—were passed through the mixture of catalyst and CB at a flow rate of 0.5 dm^3 (STP) min^{-1}. The temperature of the reactor was raised from 80 to 700 °C by 10 °C min^{-1}. A non-dispersive IR gas analyzer was used to continuously measure the concentrations of CO and CO_2 emitted by the carbon oxidation. In addition, TPR measurements using an FTIR gas analyzer were separately conducted to measure the concentrations of NO, NO_2 and SO_2 in the product gas.

Fig. 1 shows the effect of the composition of the reactant gas on the CO_2 emission during the TPR. The CO concentration was almost zero in all cases ($\leqslant$0.8 ppm). In the gas mixture $N_2 + O_2 + H_2O$ [Fig. 1(○)], carbon was not oxidized at all below 500 °C, above which temperature the reaction rate increased abruptly and the oxidation was finished at 675 °C. Platinum had no accelerating effect on the carbon gasification under these conditions, since the TPR result using SiO_2 alone (not shown) was almost the same as that shown in Fig. 1(○). Fig. 1(●) shows the result when 100 ppm SO_2 was added to the reactant gas. Sulfur dioxide had no effect on the oxidation under these conditions. On the other hand, the addition of NO instead of SO_2 brought about an acceleration of carbon oxidation Fig. 1(△). The initial temperature, which we define as the point where the CO_2 concentration exceeds 100 ppm, was about 200 °C lower than that in $N_2 + O_2 + H_2O$. In the case of SiO_2 alone, such a promotional effect of NO was not observed, but when NO_2 was used instead of NO, the CO_2 emission curve shifted to nearly the same temperature region as Fig. 1(△). These results suggest that NO_2, which is formed by the oxidation of NO over Pt, oxidizes carbon black more strongly than O_2. The effect of NO_2 on soot oxidation has been already reported by several researchers.[4,5,7]

The striking effect of SO_2 was observed when it was further added to $N_2 + O_2 + H_2O$ + NO over the Pt/SiO_2. By adding only 1 ppm of SO_2, the CO_2 emission level at 350 °C increased by 210 ppm [Fig. 1(▲)]. As the concentration of SO_2 was increased, a new peak appeared at around this temperature; when the SO_2 concentration exceeded 23 ppm, CO_2 emission was at its maximum at this temperature [Fig. 1(◇) and (◆)]. The temperature of maximum CO_2 emission was about 300 °C lower than that in the $N_2 + O_2 + H_2O$ mixture and more than 200 °C lower than that in $N_2 + O_2 + H_2O$ + NO. The initial temperature decreased to as low as 250 °C. The CO_2 concentrations at 350 °C in the experiments containing NO were plotted as a function of SO_2 content in the reactant gas (Fig. 2). The CO_2 concentration dramatically increases until the SO_2 content reaches 8 ppm and then almost levels off with further increases in SO_2 content. Such a promotional effect of SO_2 is not observed with SiO_2 alone, even when NO_2 is used instead of NO.

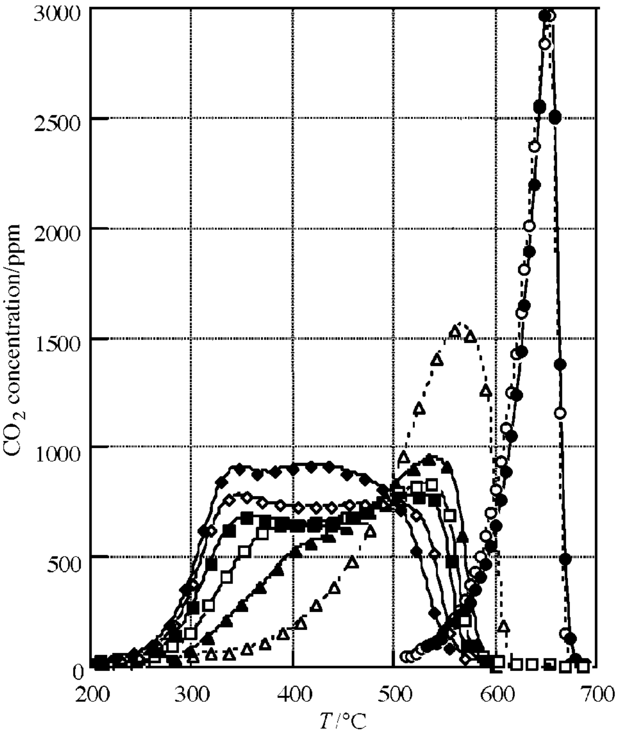

Fig. 1 TPR profiles of Pt/SiO_2 in carbon oxidation. Conditions; catalyst = 0.5 g, carbon = 0.005 g, flow rate = 0.5 $dm^3\ min^{-1}$ (0 °C, 1 atm) (**X** = 10% O_2 + 7% H_2O in N_2, **Y** = 10% O_2 + 7% H_2O + 1000 ppm NO in N_2): (○) **X**, (●) **X** + 100 ppm SO_2, (△) **Y**, (▲) **Y** + 1 ppm SO_2, (□) **Y** + 4 ppm SO_2, (■) **Y** + 8 ppm SO_2, (◇) **Y** + 23 ppm SO_2, (◆) **Y** + 100 ppm SO_2.

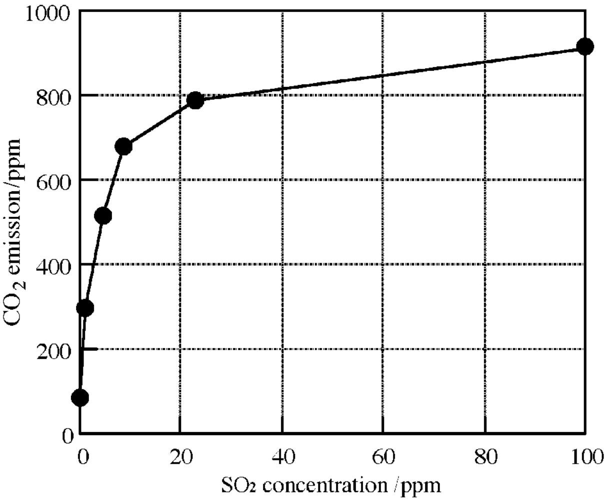

Fig. 2 Effect of the concentration of SO_2 on the activity of Pt/SiO_2 catalyst in carbon oxidation (T = 350 °C). Conditions are as in Fig. 1.

Separate TPR experiments using an FTIR gas analyzer were also carried out under the conditions of 10% O_2, 0.5% H_2O, 1000 ppm NO, 100 ppm SO_2 and N_2. Over Pt/SiO_2, NO starts to be oxidized to NO_2 at 160 °C. The concentration of NO_2 reached a maximum at 330 °C and then decreased in accordance with levels expected from the thermodynamic equilibrium between NO_2, NO and O_2. The concentration of SO_2 in the product gas started to decrease at 165 °C, reached a negligible level between 220 to 500 °C, and then gradually increased in accordance with levels expected from the thermodynamic equilibrium between SO_3, SO_2 and O_2. Evidently, the oxidation of NO into NO_2 and SO_2 into SO_3 (or H_2SO_4 below 300 °C) proceeded over Pt/SiO_2. Incidentally, the oxidation of SO_2 to SO_3 by gaseous NO_2 did not proceed to an observable extent over SiO_2 alone under the conditions of 10% O_2, 0.5% H_2O, 1000 ppm NO_2, 100 ppm SO_2 and N_2. Nitrogen dioxide is regarded as an oxidizer that directly attacks the carbon and turns into NO; the NO may be oxidized to NO_2 over Pt/SiO_2 and reused. On the other hand, the outstanding effect of SO_2 with Pt/SiO_2 only appeared in the presence of NO suggesting that SO_3, produced from SO_2 over Pt, plays a role as a catalyst that accelerates the oxidation of carbon by NO_2.

To confirm this possible role of SO_3 (or H_2SO_4), we tested the effect of NO_2 and H_2SO_4 addition on the carbon oxidation over SiO_2 alone. When 1000 ppm NO_2 and 100 ppm H_2SO_4 were added to the feed containing 10% O_2 + 7% H_2O in N_2, the oxidation was initiated at 280 °C and there were peaks in CO_2 concentration at 380 and 490 °C. By contrast the addition of 100 ppm H_2SO_4 alone did not have any effect on the CO_2 emission rate: the initial and peak temperatures were around 560 and 680 °C, respectively. These results strongly suggest that SO_3 (or H_2SO_4) formed over Pt surfaces catalyzes the oxidation of carbon by NO_2.

Lur'e *et al.*[7] reported that the process of CO_2 formation from the interaction of NO_2 with soot proceeds through the oxidation of active sites on the soot surface, *via* abstraction of oxygen atoms from NO_2, to produce partially oxidized surface species (> C=O) and NO. We suspect that the effect of SO_3 (or H_2SO_4) can be attributed to the enhancement of decomposition of the partially oxidized surface species. It is well known that H_2SO_4 promotes dehydration and decarboxylation of organic compounds.[8] The partially oxidized surface species created by NO_2 may be rather inactive against further oxidation, but can be readily decomposed by a strong acid such as SO_3 or H_2SO_4. After this secondary process, the ability of the carbon surface to be oxidized may be restored.

Notes and References

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1 G. Neri, L. Bonaccorsi, A. Donato, C. Milone, M. Grazia M. and A. M. Visco, *Appl. Catal. B*, 1997, **11**, 217.
2 H. J. Stein, *Appl. Catal. B*, 1996, **10**, 69.
3 M. Hosoya and M. Shimoda, *Appl. Catal. B*, 1996, **10**, 83.
4 P. Hawker, N. Myers, G. Huthwohl, H. T. Vogel, B. Bates, L. Magnusson and P. Bronnenberg, SAE Technical Paper Series, 970182, 1997.
5 B. J. Cooper, H. J. Jung and J. E. Thoss, *US Pat.* 4902487.
6 J. P. A. Neeft, O. P. Pruissen, M. Makkee and J. A. Moulijn, *Appl. Catal. B*, 1997, **12**, 21
7 B. A. Lur'e and A. V. Mikhno, *Kinet. Catal.*, 1997, **38**, 535
8 *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 4th edn., ed. J. March, Wiley, New York, p. 389, p. 563, p. 1011

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