Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2010, 20, 269–270
Mendeleev Communications

Oxidation of soot with NO + O_2 over Pt catalyst: direct evaluation of Pt catalyst efficiency in NO to NO_2 recycling

Aleksandr Yu. Stakheev,* Anton M. Gololobov, Galina N. Baeva, Galina O. Bragina and Nataliya S. Telegina

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: st@ioc.ac.ru

DOI: 10.1016/j.mencom.2010.09.009

In the new method for evaluation of Pt/Al_2O_3 efficiency in oxidation of soot with NO + O_2 + N_2 mixture the number of NO to NO_2 recycles is determined on the basis of surplus CO_2 emission resulted from the injection of known amount of NO into O_2 + N_2 stream.

Diesel particulate filter (DPF) is the most effective technology for achieving low emission of soot by diesel engines. However, they eventually become blocked as the soot accumulates on the filter. The most plausible method for regenerating the filter is to use a catalyst that promotes oxidation of soot at exhaust gas temperatures under engine operating conditions (*ca.* 300 °C). Among many catalysts for oxidation of soot so far reported, Pt exhibits a high level of catalytic activity.[1–3] It was demonstrated that Pt indirectly promotes oxidation of soot by catalyzing the oxidation of NO into NO_2 by O_2, the true oxidant being NO_2.[4,5] The reactions that are mainly responsible for lowering temperature of oxidation of soot are: (i) oxidation of soot with NO_2 followed by (ii) NO recycles to NO_2 over Pt catalyst. However, due to the complexity of soot combustion process, it is difficult to evaluate a number of NO to NO_2 recycles or other parameters (*e.g.*, activation energy).

In this study we evaluated performances of Pt catalysts on the basis of the number of NO to NO_2 recycles over a catalyst under conditions of oxidation of soot. Number of recycles was evaluated by injection of known amount of NO into 10% O_2 + N_2 gas mixture flowing through a reactor. Surplus amount of CO_x formed by NO injection was measured and a number of NO_2 to NO recycles was calculated on this basis.

We used two Pt/Al_2O_3 catalysts (1 wt% and 0.25% Pt) prepared by incipient wet impregnation of γ-Al_2O_3 with aqueous $Pt(NH_3)_4(NO_3)_2$ followed by drying and calcinations in flowing air at 550 °C. The catalyst–soot mixtures were prepared by gently mixing of catalyst and soot (Printex-U, Degussa) with spatula for 20 min, thus realizing a loose contact. A catalyst:soot ratio of 9:1 (w/w) was always employed. Two types of catalyst granulation were used for catalyst–soot mixture: catalyst powder with catalyst particle size < 0.05 mm and granulated catalyst with particle size of 0.2–0.4 mm.

In typical temperature-programmed oxidation (TPO) run a batch of the catalyst–soot mixture (100 mg) was loaded in the tubular quartz reactor and a flow of oxygen (10% O_2 in N_2) or oxygen–NO mixture (10% O_2, 400 ppm NO) was fed to the reactor at a flow rate of 100 cm^3 min^{-1}. TPO measurements were carried out at 10 K min^{-1} temperature ramp using a FTIR gas analyzer ‘Gasmet’ (Temet Instruments Dx-4000n).

For measuring Pt catalyst efficiency in NO to NO_2 recycling, the catalyst–soot mixture (100 mg) was loaded in tubular quartz reactor and 10% O_2 + N_2 mixture was fed to the reactor. After stabilization of CO + CO_2 emission ~1.8 μmol NO was injected into reactor as 0.4% NO + N_2 mixture during 1 min, and surplus CO_x emission was measured. These measurements were carried out isothermally within 350–500 °C temperature range with ~25 °C increment. Soot conversion was kept < 30%, and a new catalyst–soot mixture was loaded when soot conversion exceeds this level. Additionally catalyst activity in NO to NO_2 oxidation was measured at 150 °C under the same conditions over catalyst load without soot (90 mg).

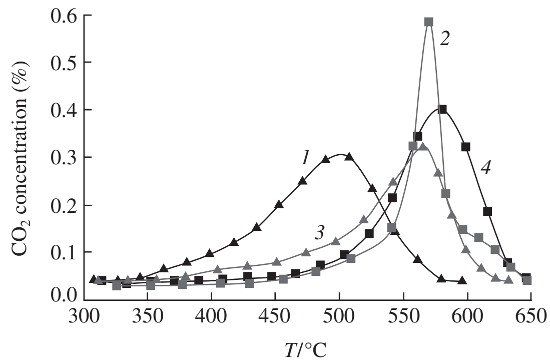

Figure 1 TPO profiles of oxidation of soot over 0.25% Pt/Al_2O_3 (loose contact): (*1*, *2*) powder, (*3*, *4*) granulated; (*1*, *3*) O_2 + NO, (*2*, *4*) O_2.

Typical TPO profiles obtained in the case of the 0.25% Pt/Al_2O_3(powder)–soot and 0.25% Pt/Al_2O_3(granulated)–soot mixtures are shown in Figure 1. The combustion activity was monitored by the CO_2 and CO emission; only CO_2 emission is shown in Figure 1, since the CO formation was negligible, being below the detection limit of our FTIR apparatus (less than 20 ppm).

For 0.25% Pt/Al_2O_3(powder)–soot mixture (Figure 1) TPO profile is similar to that observed in studies of Pt-containing catalyst in oxidation of soot with NO + O_2 mixture.[6–8] When NO + O_2 + N_2 stream is used, oxidation of soot starts at approximately 330–350 °C with the maximum CO_2 evolution around 490 °C. Comparison of TPO profiles obtained with NO + O_2 + N_2 and O_2 + N_2 streams suggests that the main part of soot in the course of TPO with NO + O_2 + N_2 is oxidized by the reaction with NO_2 as proposed in refs. 2,4,9:

$$NO + 1/2O_2 \leftrightarrow NO_2 \quad \text{(over Pt)} \qquad (1)$$

$$NO_2 + C \rightarrow CO + NO \qquad (2)$$

$$CO + 1/2O_2 \rightarrow CO_2 \quad \text{(over Pt)} \qquad (3)$$

When the same catalyst is loaded in granulated form [0.25% Pt/Al_2O_3(granulated)–soot mixture] TPO profiles is changed significantly (Figure 1). Maximum of CO_2 evolution is shifted toward higher reaction temperature by 80 °C to 570 °C. For granulated

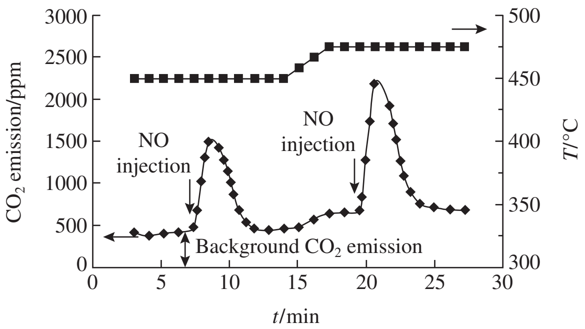

Figure 2 Variations of CO_2 emission upon NO injection (~1.8 mmol NO) into O_2 + N_2 stream in the course of oxidation of soot over 0.25% Pt/Al_2O_3 (powder).

Pt/Al_2O_3, temperature of maximum CO_2 evolution in the course of TPO with NO + O_2 + N_2 flow coincides with the temperature of CO_2 evolution in the course of TPO with O_2 + N_2 flow. Comparison of these TPO profiles suggests that the oxidation of soot with molecular oxygen prevails in the overall combustion process.

Emission of CO_2 below 480–500 °C (Figure 1) implies that a part of soot is oxidized by low-temperature reaction with NO_2 according to reactions (1)–(3). Moreover, analysis of low-temperature part of TPO profile obtained in the course of oxidation with NO + O_2 + N_2 flow indicates that oxidation of soot starts at ~330–350 °C, similar to 0.25% Pt/Al_2O_3(powder)–soot mixture (Figure 1). However, low-temperature emission over granulated catalyst is significantly diminished in comparison with TPO over 0.25% Pt/Al_2O_3(powder)–soot mixture.

Typical pattern of CO_2 evolution upon NO injection into feed O_2 + NO stream at 450 and 475 °C is shown in Figure 2. NO to NO_2 recycling efficiency was calculated assuming that oxidation of soot proceeds *via* reactions (1)–(3) and formation of one CO_2 molecule requires one NO to NO_2 recycle. Number of recycles was calculated according to the following equation:

$$\text{Number of recycles} = \frac{[\text{surplus } CO_2 \text{ emission}] - [\text{background } CO_2 \text{ emission}]}{[\text{amount of NO injected}]}$$

Surplus CO_2 emission was calculated by integration of the area of the peak resulted from NO injection. Background CO_2 emission was calculated on the basis of CO_2 emission before NO injection.

Results of evaluation of NO to NO_2 recycling efficiency for 0.25 and 1% Pt/Al_2O_3 catalysts (powder and granulated) are summarized in Figure 3 and Table 1.

Number of NO recycles for 1.0% Pt/Al_2O_3(powder)–soot mixture varied from ~3 to ~47 with increasing the temperature from 350 to 475 °C. For 0.25% Pt/Al_2O_3 the numbers are lower in agreement with lower activity in NO to NO_2 oxidation (Table 1). Apparent activation energy of oxidation of soot calculated on the

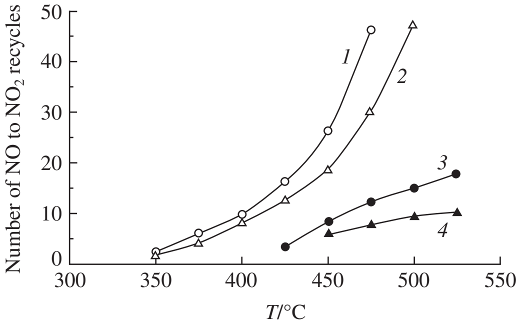

Figure 3 Effect of the reaction temperature and the catalyst granulation on the number of NO to NO_2 recycles over Pt/Al_2O_3 catalysts in the course of oxidation of soot (loose contact): (*1*, *3*) 1% Pt, (*2*, *4*) 0.25% Pt; (*1*, *2*) powder; (*3*, *4*) granulated, particle size 0.2–0.4 mm.

Table 1 Parameters of the performance of Pt/Al_2O_3 in oxidation of soot and NO to NO_2 conversion.

Pt content, loading	Number of NO to NO_2 recycles at 450 °C	E_{app}/ kJ mol^{-1}	Rate of NO to NO_2 oxidation at 150 °C/ μmol s^{-1} g^{-1}
0.25% granulated	5.8	49.2±2.1	36.4
0.25% powder	18.5	75.1±1.8	34.4
1% granulated	8.4	36.1±2.3	64.7
1% powder	26.4	72.3±1.6	59.1

basis of temperature dependences of NO to NO_2 recycling was found to be ~72–75 kJ mol^{-1}, which is in a reasonable agreement with the data reported by Jeguirum *et al.*[10] and Krishna *et al.*[11]

For Pt/Al_2O_3(granulated)–soot mixture efficiency in NO recycling is significantly lower despite similar activities of granulated and powdered catalysts in NO to NO_2 oxidation (Table 1). Calculations of the apparent activation energies of oxidation of soot on the basis of the data on NO to NO_2 recycling efficiency indicated that E_{app} was reduced by 25–30 kJ mol^{-1}.

The data obtained provide a rational explanation for the observed shift of TPO profile of Pt/Al_2O_3(granulated)–soot mixture toward higher temperature as compared to TPO profile of Pt/Al_2O_3(powder)–soot (Figure 1). Presumably, NO to NO_2 recycling over granulated catalyst is impeded since it requires a number of longer passages of NO_x molecules between oxidation centers (Pt) and soot particles. Therefore, the overall process of combustion of soot becomes limited by NO_x diffusion as evidenced by decreasing apparent activation energy (Table 1).

Thus, the technique proposed for evaluation of oxidation of soot catalyst efficiency provides a convenient method to determine a number of NO to NO_2 recycles provided by the catalyst. Calculations of apparent activation energy on the basis of temperature dependence of recycle numbers in combination with TPO data provide valuable additional information on the reaction mechanism.

This work was supported by the Russian Foundation for Basic Research (grant no. 08-03-01016a).

References

1 A. Setiabudi, J. Chen, G. Mul, M. Makkee and J. A. Moulijn, *Appl. Catal. B: Environ.*, 2004, **51**, 9.
2 D. Uner, M. K. Demrikol and B. Dernaika, *Appl. Catal. B: Environ.*, 2005, **61**, 334.
3 M. Seipenbusch, J. V. Erven, T. Schalow, A. P. Schalow, A. P. Weber, A. D. Langeveld, J. C. M. Marijnissen and S. K. Friedlander, *Appl. Catal. B: Environ.*, 2004, **55**, 31.
4 S. Liu, A. Obuchi, J. Oi-Uchisawa, T. Nanba and S. Kushiyama, *Appl. Catal. B: Environ.*, 2001, **30**, 259.
5 J. Oi Uchisawa, A. Obuchi, R. Enomoto, S. Liu, T. Nanba and S. Kushiyama, *Appl. Catal. B: Environ.*, 2000, **26**, 17.
6 J. Oi-Uchisawa, A. Obuchi, Z. Zhao and S. Kushiyama, *Appl. Catal. B: Environ.*, 1998, **18**, L183.
7 J. Oi-Uchisawa, A. Obuchi, A. Ogata, R. Enomoto and S. Kushiyama, *Appl. Catal. B: Environ.*, 1999, **21**, 9.
8 L. Castoldi, R. Matarrese, L. Lietti and P. Forzatti, *Appl. Catal. B: Environ.*, 2006, **64**, 25.
9 S. J. Jelles, R. R. Krul, M. Makee and J. A. Moulijn, *Catal. Today*, 1999, **53**, 623.
10 M. Jeguirum, V. Tschamber and P. Ehrburger, *Appl. Catal. B: Environ.*, 2007, **76**, 235.
11 K. Krishna, A. Bueno-Lopez, M. Makkee and J. A. Moulijn, *Appl. Catal. B: Environ.*, 2007, **75**, 201.

Received: 2nd April 2010; Com. 10/3501