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Mechanism of Selective Catalytic Reduction of Nitrogen Monoxide by Organic Compounds

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Carbonaceous radicals have been identified in a γ-alumina catalyst in the selective reduction of NO by organic compounds; these are probably produced from carbon deposits that accumulate on the catalyst and are proposed to be active species which preferentially react with NO.

Selective catalytic reduction of nitrogen monoxide (NO) under conditions of net oxidation has so far been achieved only by the use of ammonia as the reducing agent. Recently, hydrocarbons have been found to be effective as reducing agents for this reaction by using heterogeneous catalysts such as γ-alumina,[1] H-form zeolites[2] or metal-supported zeolites.[3] This phenomenon is now attracting the interest of workers in the area of catalyst research and environmental control engineering but little is known about the reaction mechanism, except that acid sites of the catalyst are suspected to be involved. We report here that carbonaceous radicals and reactive carbon deposits are formed in the catalyst layer during the selective reduction of NO by methyl *tert*-butyl ether (MTBE) or propylene on γ-alumina.

The catalyst was obtained by calcination in air at 600 °C of γ-alumina (1 g). The steady-state rate of NO reduction as well as the reactivity of the carbon deposits with NO and their accumulated amount were estimated with a flow reactor at atmospheric pressure. The concentrations of NO_x, CO, CO_2, N_2 and N_2O in the product gas were measured. Steady-state reactions were performed under a concentration of 1000 ppm NO in 5% O_2 using 140–1400 ppm of reducing agent in a He stream at a flow rate of 160 ml min^{-1}. The catalysts used were submitted to ESR measurements for which precautions were taken not to expose the sample to air.

For both reducing agents, N_2 and N_2O were the only nitrogen-containing products in the steady-state reaction and more than 98% of the NO removed was converted into N_2 above 400 °C. Although the maximum NO conversion was achieved by propylene at 500 °C, MTBE had a wider active temperature range, especially at lower temperatures.

ESR spectra were taken for the catalysts after the steady-state reaction and a symmetrical signal with a *g* value of 2.004 shown in Fig. 1 (inset), was observed in each case. This signal

was considered to arise from a carbonaceous radical. The relation between NO conversion in the steady-state reaction at 400 °C and the spin density, upon varying the concentration of the reducing agents, is shown in Fig. 1. Also shown is the relation between NO conversion and the accumulated amount of carbon deposits, apparent as a brownish to greyish colouration in the catalyst layer as the reaction proceeded. Both relations had a high correlation, and moreover, were very similar for both reducing agents.

Reactivity of the carbon deposits was further examined. After accumulating the carbon deposits by carrying out a steady-state reaction at 400 °C with MTBE as the reducing agent, the flow of MTBE was then cut off while NO (1070 ppm) and O_2 (5%) flow were maintained, and the rates of NO conversion and CO_2 + CO production were monitored at initially constant and then increasing temperature. The results are shown in Fig. 2, in which *r* is defined as [NO conversion (ppm)]/[CO + CO_2 production (ppm)] and can be regarded as an index of selectivity towards NO reduction. For the steady-state reaction condition prior to cut-off of MTBE (*A* in Fig. 2); the end of the constant-temperature phase after cutting off MTBE (*B*); and during the increasing-temperature phase (*C*) the values of *r* were 0.24, 0.42 and 0.29, respectively. By contrast, in the case of active charcoal and for a mechanical mixture of active charcoal and γ-alumina, the average *r* values during the latter phase (*C*) were only 0.018 and 0.032, respectively, *i.e.* of the same order as the ratio of partial pressures of NO and O_2 in the reacting gas (= 0.02). From these results, it is evident that the carbon deposits formed from MTBE or propylene have the ability to preferentially reduce NO. Similar findings have been reported for carbon deposits formed on an Fe-silicate catalyst. The reactivity of the deposits was rather rapidly lost at constant temperature but reactivation occurred on raising the temperature. In addition, while the *r* value of the carbon deposits was hardly affected by carbonization in He at 600 °C for 30 min, absence of O_2 in the reacting gas, led to inactivity of the carbon deposit towards NO below 550 °C.
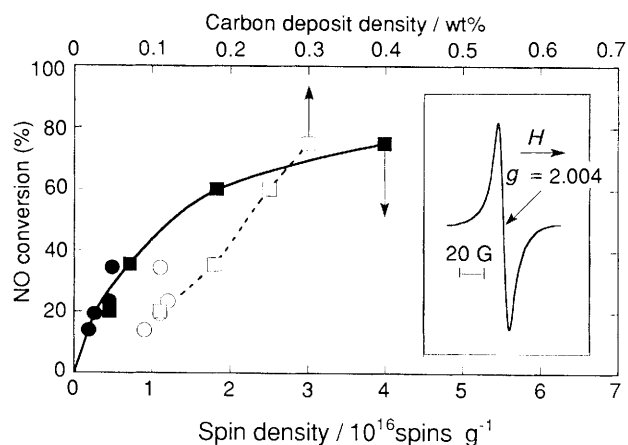

Fig. 1 Rate of NO conversion as a function of spin density or carbon deposit density in a γ-alumina catalyst, with (inset) the observed ESR signal. Catalyst load = 1 g, Reactants: 1000 ppm NO, 5% O_2, 140–840 ppm MTBE or 230–1400 ppm propylene in a He stream at a rate of 160 ml min^{-1}, temperature = 400 °C. Reductant = MTBE (square), propylene (circle).
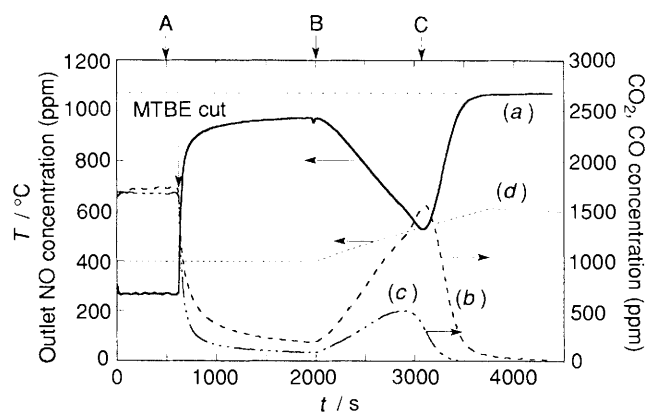

Fig. 2 Time profiles of the outlet NO, CO and CO_2 concentrations during the reaction between carbon deposits and a mixture of NO (1070 ppm) and O_2 (5%) in a He stream. Total flow rate = 160 ml min^{-1}; (*a*) NO, (*b*) CO_2, (*c*) CO, (*d*) temperature.

These results indicate that both the carbonaceous radical and the carbon deposits play a crucial role, perhaps as intermediates, in the selective reduction of NO by organic compounds. The radical is likely to be produced from the carbon deposits through partial oxidation with O_2. The reactive carbon deposits need not contain much hydrogen but must be close to γ-alumina surface.

Although a stable molecule, NO is a radical and shows very high reactivity with other radicals. Oxygen likewise also has unpaired electrons but compared with NO has a lower reactivity. For instance, with the methyl radical, the activity of NO (1.2×10^{-11})[5] is higher than that of O_2 $(0.3-5 \times 10^{-12}$ cm^3 $molec^{-1}$ $s^{-1})$.[6] On the basis of the mechanisms for the production and destruction of fuel NO_x in homogeneous systems[7] and in coal char combustion,[8] we suggest that NO is converted to N_2 through the formation of C–NO bonds at the carbon deposit by a radical reaction, in which the reactivity of NO, normally a weaker oxidant than O_2 towards carbon deposits, surpasses that of O_2. A second molecule then reacts with the C–NO group to give the final observed products.

The role of the catalyst is considered to promote the formation of carbon deposits from the reactant organic compounds by cracking or partial oxidation, to produce and stabilize carbonaceous radicals perhaps on Lewis-acid sites,[9] at which NO can react to form N_2.

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