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Mechanism of H_2-promoted oxidation of nitrogen monoxide over Ag/Al_2O_3

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H_2-promoted oxidation of NO to NO_2 over Ag/Al_2O_3 proceeds *via* two-step mechanism: (1) formation of surface nitrate species, and (2) reduction of this species with NO. Hydrogen plays a crucial role at the first step.

Addition of H_2 is known to dramatically enhance selective catalytic reduction (SCR) of NO_x with hydrocarbons[1] or ammonia[2] over Ag/Al_2O_3. However, a mechanism of this effect is still discussed. Reviewing of the recent literature indicates the role of adsorbed nitrates in the H_2-promoted SCR over Ag/Al_2O_3, which are formed on the catalyst surface in significant amount when H_2 is added to the reaction mixture.[3,4] Our recent studies demonstrate that accumulation of surface nitrates can be closely related with H_2-promoted NO oxidation.[5] Taking into account important role of surface nitrates in the overall mechanism of H_2-assisted SCR, herein we studied surface nitrate formation on Ag/Al_2O_3 catalyst in the presence and absence of hydrogen, by means of the isothermal transient response method (TRM).[6] Transient reaction measurements were complemented by conventional catalytic tests.[†]

The catalyst was characterized by atomic absorption spectroscopy (AAS), and X-ray photoelectron spectroscopy (XPS) by a SPECS spectrometer. The accurate correlation between data obtained by means of AAS and XPS indicated uniform distribution of Ag species over Al_2O_3 surface.

Within temperature range of 100–250 °C, Ag/Al_2O_3 is essentially inactive in conventional SCR without H_2 addition (Figure 1). NO_x conversion starts at ~250 °C and approaches 100% at ~320 °C. Addition of 1000 ppm H_2 significantly enhances NO_x conversion within temperature range from 100 °C to 320 °C. At $T_{\mathrm{react}} > 320$ °C NO_x conversions in conventional C_6H_{14}-SCR and H_2-assisted C_6H_{14}-SCR processes are identical. The data are in a good agreement with the results of our previous studies[7] and reveal a pronounced enhancing effect of H_2 on C_6H_{14}-SCR within 100–300 °C temperature range. Since H_2-promoting effect in SCR is mostly evident below 300 °C, our TRM measurements were carried out at 250 and 140 °C (see below).

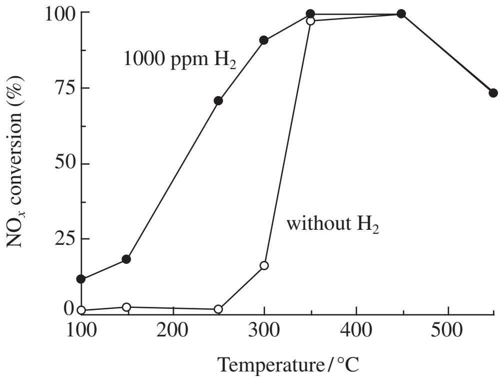

Figure 1 Effect of hydrogen in C_6H_{14}-SCR over Ag/Al_2O_3. Feed gas composition: 300 ppm NO, 300 ppm C_6H_{14}, 1000/0 ppm H_2, 10% CO_2, 7.5% O_2, N_2.

Figure 2 shows typical transient run focusing on H_2 effect on NO adsorption–oxidation at 250 °C. It is noteworthy that NO

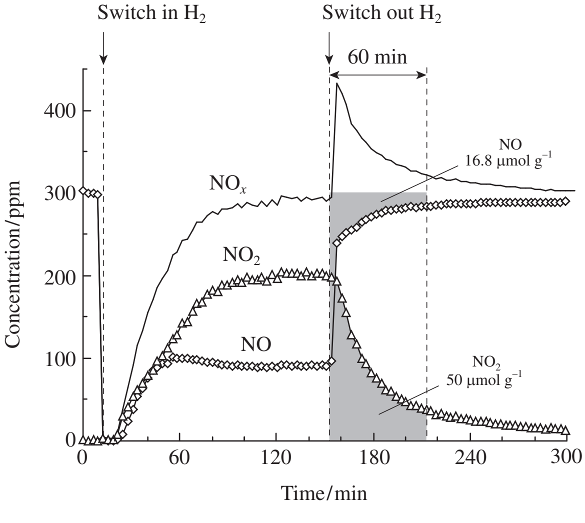

Figure 2 Transient study of H_2-induced NO_x adsorption over Ag/Al_2O_3 at 250 °C. Feed gas composition: 300 ppm NO, 1000/0 ppm H_2, 10% CO_2, 7.5% O_2, N_2.

[†] Catalyst Ag/Al_2O_3 containing 1 wt% Ag was prepared by incipient wetness impregnation of Al_2O_3 (γ-Al_2O_3, 'Sasol', $S_{\mathrm{BET}} = 152$ m^2 g^{-1}) by an aqueous solution of $AgNO_3$ followed by drying at room temperature and calcination at 550 °C in flowing air.

Transient reaction measurements and catalytic tests were carried out in a fixed-bed flow reactor at GHSV = 10000 h^{-1} using the feed gas containing 300/0 ppm NO, 300/0 ppm C_6H_{14}, 1000/0 ppm H_2, 7.5% O_2, 10% CO_2, balance N_2. In typical TRM run, the catalyst was kept at constant temperature (250 or 140 °C) under flow of 7.5% O_2 + 10% CO_2 + N_2, and stepwise changes of NO (0 → 300 ppm), and/or H_2 (0 → 1000 ppm) concentrations were imposed. NO_x-TPD measurements were carried out by heating the sample in flowing N_2 from adsorption temperature to 550 °C with temperature rump of 7.5 K min^{-1}. Reaction products were analyzed by an Eco Physics CLD 70 S chemiluminescent NO/NO_x analyzer and conventional gas chromatograph.

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adsorption in the absence of H_2 is essentially negligible and the amount of $NO_{x,ads}$ does not exceed 5–7 μmol g^{-1}. On the contrary, when H_2 (1000 ppm) is switched in to the feed gas, significant NO_x adsorption is observed for a period of ~60 min. Total amount of adsorbed NO_x was evaluated by integrating NO_x adsorption profile and by the following NO_x-TPD measurements. Both methods revealed that the amount of adsorbed NO_x was ~110–120 μmol g^{-1}.

After saturation of the catalyst with $NO_{x,ads}$, outlet NO_x concentration reaches inlet value of 300 ppm, and significant amount of NO_2 is detected in outlet gas. NO_2 and NO concentrations steadily increase upon saturation of the catalyst surface and approach steady-state level of ~200 ppm and 100 ppm, respectively, when saturation is completed (t = 140 min). Evidently, H_2-induced NO adsorption is accompanied by intense NO oxidation in accordance with literature data.[1]

Further insight into mechanism of NO adsorption–oxidation was gained by transient runs consisted of a step removal of H_2 from a feed stream after saturation of the catalyst surface with NO_x adspecies. After removal of H_2 from the gas stream (t = 160 min), NO_2 evolution is not ceased, but gradually decreases during next few hours. Simultaneously, NO concentration increases stepwise, though does not reach inlet level of 300 ppm immediately, but slowly increases in parallel with decreasing NO_2 concentration. Note that upon removal of H_2 from gas stream, we observed a stepwise increase in outlet NO_x concentration to ~450 ppm followed by gradual decrease to inlet level during ~1 h.

These data suggest that NO_2 formation proceeds over '$NO_{x,ads}$-saturated' catalyst even in the absence of hydrogen, and accompanied by consumption of NO. Detailed analysis of variations of NO and NO_2 outlet concentrations (after removal of H_2) indicated that consumption of one NO molecule is accompanied by evolution of three NO_2 molecules. The data obtained can be interpreted as follows. According to literature data,[8] NO_2 formation may proceed *via* reduction of surface nitrates by NO. At the first stage surface nitrates $NO^-_{3\,surf}$ are reduced to surface nitrites $NO^-_{2\,surf}$ with evolution of equimolar amount of NO_2 [reaction (1)]. At the following stage highly reactive $NO^-_{2\,surf}$ is decomposed producing NO_2 and NO molecules, and releasing surface adsorption site O^{2-}_{surf} [reaction (2)].

$$2NO^-_{3\,surf} + 2NO \rightarrow 2NO_2\uparrow + 2NO^-_{2\,surf} \tag{1}$$

$$2NO^-_{2\,surf} \rightarrow NO_2 + NO + O^{2-}_{surf} \tag{2}$$

$$2NO^-_{3\,surf} + NO \rightarrow 3NO_2\uparrow + O^{2-}_{surf} \tag{3}$$

Combination of (1) and (2) yields equation (3) showing that consumption of one NO molecule results in releasing three NO_2 molecules. Stoichiometry of this reaction is in a good agreement with the observed ratio $NO_{2\,released}/NO_{consumed}$. Thus, during first 60 min after removal of H_2 from the gas stream, evolution of 50 μmol g^{-1} NO_2 was detected. At the same time, 16.8 μmol g^{-1} NO was consumed, which gives $NO_{2\,released}/NO_{consumed} = 2.97$.

At the steady-state, when hydrogen is fed to the gas stream, surface nitrates can also be reduced by hydrogen:

$$2NO^-_{3\,surf} + H_2 \rightarrow 2NO_2\uparrow + H_2O + O^{2-}_{surf} \tag{4}$$

Efficiency of this process is lower, as evidenced by TRM measurements comprising removal of NO from a feed stream after saturation of the catalyst surface with NO_x adspecies (Figure 3). When NO was switched out from the feed gas, NO_2 evolution continues due to $NO^-_{3\,surf}$ reduction *via* reaction (4). However, this evolution is significantly less intense than NO_2 released by reduction with NO (compare Figures 2 and 3). For example, integral NO_2 evolution *via* reaction (4) during the first 60 min after removal of NO from the gas stream does not exceed 23 μmol g^{-1}, which is more than 2 times lower than 50 μmol g^{-1} NO_2 evolution *via* reaction (3).

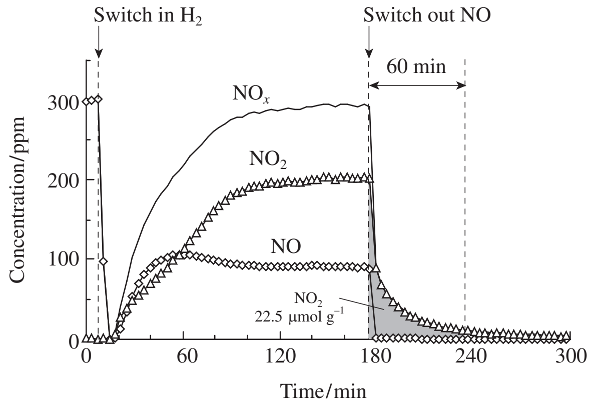

Figure 3 Transient study of H_2-induced NO_x adsorption over Ag/Al_2O_3 at 250 °C. Feed gas composition: 300/0 ppm NO, 1000 ppm H_2, 10% CO_2, 7.5% O_2, N_2.

It is informative to analyze contributions of pathways (3) and (4) in NO_2 formation at lower reaction temperature. Our recent TPD-study of H_2 and NO effect on $NO^-_{3\,surf}$ decomposition[5] indicated that below 160 °C rate of reaction (4) becomes negligible, while surface nitrate decomposition *via* reaction with NO [reaction (3)] remains significant. This provides better discrimination of contributions of pathways (3) and (4) in NO_2 formation.

Results of transient response measurements at 140 °C are shown in Figure 4. When NO is removed from the gas stream (t = 260 min), NO_2 formation is immediately ceased, and only traces of NO_2 are detected (<5 ppm). On the other hand, replacement of H_2 with NO in the feed gas (t = 350 min) restores NO_2 concentration almost to the steady-state level: 80 ppm at t = 250 min and 60 ppm at t = 350 min. These data indicate that at 140 °C reaction (3) becomes essentially a sole pathway of NO_2 formation (Figure 4), while contribution of reaction (4) is negligible. Moreover, a close match of NO_2 concentration at steady-state (t = 250 min), and in the course of surface nitrate decomposition by NO (t = 350 min), implies that the main pathway of NO_2 formation at steady-state proceeds *via* reaction (3) and does not require hydrogen.

On the other hand, hydrogen plays crucial role in NO_x storage on Ag/Al_2O_3 surface leading to the formation of $NO^-_{3\,surf}$. Studying the mechanism of H_2-promoting in NO_x storage is beyond the scope of experiments reported here. Nevertheless, analysis of the literature data suggests that, presumably, hydrogen continuously reduces Ag_2O species to Ag^0, making Ag-species capable of

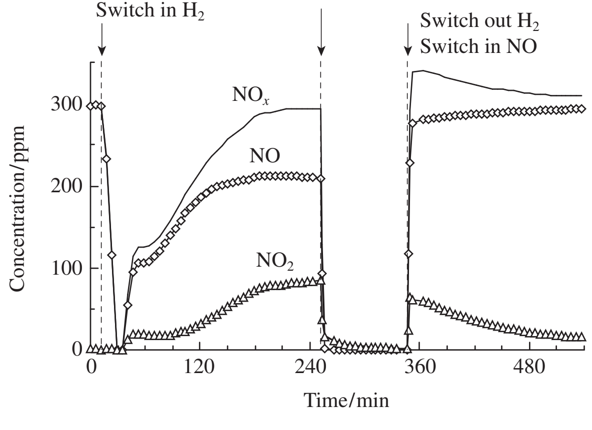

Figure 4 Transient study of H_2-induced NO_x adsorption over Ag/Al_2O_3 at 140 °C. Feed gas composition: 300/0 ppm NO, 1000/0 ppm H_2, 10% CO_2, 7.5% O_2, N_2.

activating oxygen molecule. In turn, activated oxygen oxidizes NO molecule to NO_2 or surface nitrates.[9]

Analysis of the literature data and experimental results obtained in this study allow us to suggest the following hypothetical scheme of H_2-promoted NO_2 formation over Ag/Al_2O_3:

$Ag_4O_2 + 2H_2 \rightarrow Ag_4^0 + H_2O$ (ref. 9)

$Ag_4 + 2O_2 \rightarrow Ag_4O_2 + 2[O^*]$ (ref. 9)

$NO + [O^*] \rightarrow NO_2$ (ref. 9)

$3NO_2 + O^{2-}_{surf} \rightarrow 2NO^-_{3\,surf} + NO$ (ref. 8)

$2NO^-_{3\,surf} + NO \rightarrow 3NO_2 + O^{2-}_{surf}$ (ref. 10)

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