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Hydrocarbon reaction pathway in selective NO reduction over a bifunctional SnO_2/Al_2O_3 catalyst

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Propene reduction of NO on SnO_2/γ-Al_2O_3 proceeds *via* the formation of acrolein and acetaldehyde, and the latter reduces NO_x to N_2 over Al_2O_3.

Catalytic reduction of nitric oxide (NO) from the exhaust of a lean-burn engine, which contains only a very low concentration (500 ppm level) of NO_x but much higher concentrations of oxygen (5–10%) and water (10–15%), has been a great challenge. Zeolite-supported catalysts are among the most promising known using a hydrocarbon reductant, but they lack the necessary durability because of hydrothermal degradation.[1] Alumina-based catalysts are more hydrothermally stable. Recently, they have shown promising activities for this reaction (*e.g.* refs. 2 and 3), especially under conditions of higher temperatures and partial pressures of oxygen that are suitable for treating heavy duty diesel engine or lean-burn gasoline engine exhausts. Nonetheless, higher activities are still very desirable for a practical catalyst, as well as a broader temperature window.

Understanding the reaction mechanism could facilitate improvement of these catalytic systems. On zeolite-based catalysts, a commonly observed first step of the reaction is the oxidation of NO to NO_2, which is a strong oxidant that activates the hydrocarbon.[4–7] However, the steps beyond that are not known. Various surface intermediates have been detected, and their involvement in the reaction implicated, such as organic nitro compounds,[8,9] isocyanate and nitrile,[10–12] and oxime,[13] but the steps leading to their formation and further reaction remain mostly speculative. As for alumina-supported catalysts, it is known that alumina itself is active for hydrocarbon reduction of NO,[14] and especially for NO_2,[2] but relatively inactive for NO oxidation to NO_2.[15] Various surface species are detected by IR spectroscopy in the reduction reaction, including nitrate, isocyanate, nitrile or cyanide.[16–18]

We have recently discovered that SnO_2/γ-Al_2O_3 is a bifunctional catalyst.[3,19,20] Using a standard reaction feed mixture of 0.1% propene, 0.1% NO, 10% H_2O and 15% O_2, it was found that a mixture of SnO_2/SiO_2 and γ-Al_2O_3 was as effective in reducing NO_x as an active SnO_2/γ-Al_2O_3 catalyst, while SnO_2/SiO_2 was completely unable to produce N_2.[20] In addition, the mixture of SnO_2/SiO_2 and γ-Al_2O_3 was only effective if SnO_2/SiO_2 was positioned upstream of Al_2O_3 and not *vice versa*. Since the NO_2 concentration at the exit of a reactor containing SnO_2/SiO_2 was the same as the background level within experimental uncertainty. Thus oxidizing NO to NO_2 is not the function of SnO_2. Therefore, this system provides a new opportunity to elucidate the hydrocarbon reaction pathway, which is the subject of this report.

When 0.1 g of SnO_2/SiO_2 was placed in a separate reactor upstream of 0.1 g γ-Al_2O_3, it was found that no N_2 was detected at the exit of the SnO_2/SiO_2 reactor, even when the propene conversion was 40%. Instead, a significant concentration of acrolein (C_3H_4O, *ca.* 120 ppm) and some acetaldehyde (CH_3CHO, *ca.* 40 ppm) were detected. Thus, the function of SnO_2 was selective oxidation of propene, primarily to acrolein. Removing NO from the reaction feed did not change the yield of acrolein. Thus, this selective oxidation step utilizes molecular oxygen as the oxidant.

Isotope labeling provides additional information. When 0.1% ^{13}C-prop-2-ene (99% purity) was used as the reductant, and the reaction feed mixture was passed over SnO_2/SiO_2, only 2-^{13}C-labeled acrolein was detected. This was similar to the results obtained using a Bi–Mo–O catalyst. Thus, the oxidation reaction proceeds *via* a symmetric π-allyl intermediate commonly observed in selective oxidation of propene [eqn. (1)].

$$CH_2{=}C^*H{-}CH_3 \xrightarrow[SnO_2]{O_2} CH_2\underline{{-}C^*H{-}}CH_2 \xrightarrow[SnO_2]{O_2} CH_2{=}C^*H{-}CHO \quad (1)$$

The selective oxidation product acrolein is transported to γ-Al_2O_3 where its subsequent reaction resulted in the formation of N_2. This reaction was studied by using acrolein as the reductant at a concentration of 160–170 ppm instead of 0.1% propene. The concentrations of various products formed at 475 °C as a function of residence time are shown in Fig. 1. Sometimes, small amounts (<10 ppm) of HCN could be detected. HCHO (not shown) was also formed but was difficult to quantify because of the high concentration of water used. The data showed that acrolein was rapidly converted to acetaldehyde over γ-Al_2O_3. Interestingly, this reaction was not accompanied by the production of N_2. Further reaction of acetaldehyde was much slower, and N_2 was produced.

This reaction sequence is substantiated by the experiment using acetaldehyde as the reductant instead of acrolein. CO, CO_2 and N_2 were formed, and their concentrations increased with increasing residence time. A large CO to CO_2 ratio was observed, similar to that shown in Fig. 1. Sometimes, trace amounts of HCN were detected.

When 2-^{13}C-labeled acrolein was passed over γ-Al_2O_3 at short residence time, the acetaldehyde in the product consisted of 85% $^{13}CH_3CHO$. Thus, the formation of acetaldehyde from acrolein is by cleavage of the C=C bond. Water is important for this cleavage reaction and the evolution of acetaldehyde from Al_2O_3. When NO reduction by acrolein on γ-Al_2O_3 was repeated but without water in the feed stream, no acetaldehyde was detected in the product. In addition, the N_2 yield dropped to *ca.* 60% of the yield with water. Since at 475 °C, it is unlikely that desorption of acetaldehyde requires displacement by water, the data suggest that the formation of acetaldehyde involves hydrolysis of a surface intermediate.

The following reaction [eqn. (2)] explains the formation of acetaldehyde that is consistent with the observations. It is the

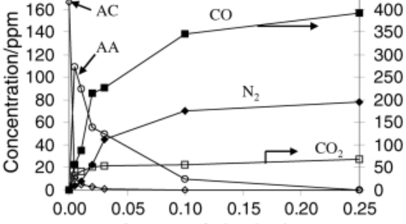

Fig. 1 Product distribution as a function of residence time for the NO_x reduction reaction over γ-Al_2O_3 using *ca.* 160 ppm acrolein. The residence time was changed by using different amounts of γ-Al_2O_3. AA: acetaldehyde, AC: acrolein.

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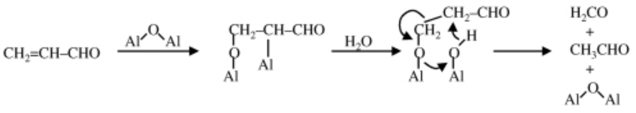
reverse of an aldol condensation reaction. We postulate that a bridging Al–O–Al is the catalytic site.



(2)

Thus, the primary hydrocarbon pathway in NO_x reduction for this catalyst system can be summarized in Fig. 2. The interesting features of this mechanism are the role of SnO_2 in the selective oxidation of propene using molecular O_2 and the role of γ-Al_2O_3 in N_2 formation. The reaction of acetaldehyde on alumina probably leads to the formation of surface nitrocompounds, nitrile or cyanide, isocyanate, and eventually N_2. The reactions of nitromethane have been studied over Cu-ZSM-5[9] and Al_2O_3.[16] Over Al_2O_3, nitromethane reacts to form isocyanate, carbamite, and eventually NH_3, the latter then reacts with NO to form N_2. It is quite possible that these steps apply to the system here.

In separate experiments, the reaction of acetaldehyde with O_2 on 0.1 g Al_2O_3 was compared with reaction with NO or NO_2 with and without O_2 under otherwise standard conditions. It was found that the reaction of acetaldehyde with NO alone was slow. Less than 40% of the acetaldehyde was converted. The reaction with a mixture of NO and O_2 was substantially faster and about the same as with only O_2. This is consistent with the low activity for NO oxidation to NO_2 on Al_2O_3.[15] The reaction of acetaldehyde with NO_2 or $NO_2 + O_2$ was the fastest, such that all the acetaldehyde was consumed. Thus, the initial step in the subsequent reaction of acetaldehyde under our reaction conditions does not involve adsorbed NO_x species. Instead, a possible pathway is its oxidation by oxygen to form adsorbed acetate, which has been observed by others.[21] The acetate decarboxylates in the presence of NO to form nitromethane.

In order to confirm the absence of a significant parallel reaction pathway for acrolein on γ-Al_2O_3, the N_2 production efficiencies of acrolein and acetaldehyde were compared. The results are shown in Fig. 3 for various NO_x/reductant ratios in the feed. Over a wide range of these ratios, the number of N_2 molecules produced for every reductant molecule consumed was independent of the reductant. Thus, the conversion of acrolein to acetaldehyde must be quantitative, and this step does not produce N_2. The N_2 production efficiencies for these two reductants approached the limit of unity, that is, one reductant molecule consumed per N_2 produced, consistent with the reaction mechanism in Fig. 2. Furthermore, the N_2 production efficiencies were higher using NO_2 than NO at low NO_x/reductant ratios.

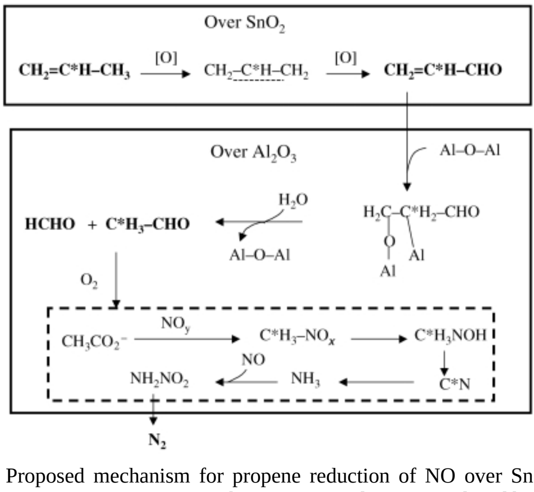


Fig. 2 Proposed mechanism for propene reduction of NO over SnO_2/γ-Al_2O_3. Reactions occurring over the SnO_2 or γ-Al_2O_3 are enclosed by solid lines, and reactions enclosed by dashed lines are formulated using literature information. Compounds in bold letters denote detected gaseous products and the remainder are surface intermediates. C* denotes labeled positions.

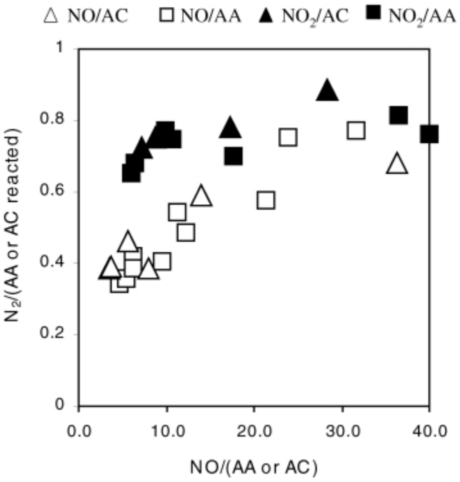


Fig. 3 N_2 formation efficiency, defined as number of molecules of nitrogen formed per acetaldehyde (AA) or acrolein (AC) molecule reacted, as a function of NO_x/reductant ratio in the feed. The NO_x/reductant ratio was changed by varying the concentration of NO (open symbols) or NO_2 (filled symbols) from 703 to 5921 ppm, and the concentration of the organic from 27 to 282 ppm. Standard concentrations of O_2 and H_2O were used, and the total flow rate was 200 ml min^{-1} with 0.1 g of Al_2O_3. The temperature was between 475 and 525 °C to obtain high conversions of the organic.

In summary, we have elucidated a substantial portion of the reaction pathway of the hydrocarbon for propene reduction of NO over SnO_2/γ-Al_2O_3. The slow step of this reaction has been identified to be the reaction of acetaldehyde on alumina. This information can be used to improve the catalytic activities for N_2 formation.

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