216b Tap® and Bench-Scale Reactor Studies of Nox Storage and Reduction on Model Pt/Bao/Al2o3 and Pt/Al2o3

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NOx storage and reduction (NSR) is emerging as a potential NOx emission abatement technology for lean burn and diesel vehicles. There are two processes involved in Lean NOx trapping (LNR); in step one, NOx is adsorbed on the alkali earth oxide site of a bifunctional supported catalyst. In the second step, the nitrate is released by reduction of surface nitrates with intermittent hydrocarbon injection for a short time compared to trapping process. The reactions occurring on the noble metal catalyst are coupled with the storage process on the alkali earth metal catalyst. To improve trapping efficiency, the proximity of the noble metal to the alkaline earth metal particles plays a strong role. It is necessary to understand the roles played individually by the noble metal and the storage function to optimize the performance of catalyst. We employ Temporal Analysis of Products (TAP®) to probe the transient kinetics of NSR. The TAP method is well suited for the NSR system because of the ability to conduct the NSR process under well characterized catalyst state and transport conditions. The TAP reactor has higher resolution compared to conventional flow reactors since the number of molecules introduced are small compared to the number of active catalyst sites. Supporting experiments are carried out in a bench-scale monolith reactor system.

The TAP studies involve feeding pulses of reactants to model Pt/BaO/Al_2O_3 catalysts at ca. 10^{-7} Torr total pressure. The product gas emerging from the catalyst bed is analyzed by a Quadrupole Mass Spectrometer (QMS) in a separate chamber maintained at ~10^{-8} Torr of pressure. Before each experiment the catalyst is pre-reduced at 400 °C in H_2. NO or NO_2 were pulsed for a prescribed period for several fixed catalyst temperatures in the range of 300 to 450 ^{o}C. The QMS monitored effluent NO, N_2, O_2, and NO_2. Feed pulse intensities were kept below ~$5*10^{15}$ molecules to ensure Knudsen transport. "Pulse-probe" experiments are carried out in which a sequence of a NO or NO_2 "pulse" and H_2 "probe" was applied to simulate the complete NSR cycle. After each run, the temperature was increased to 400 ^{o}C in H_2 to remove surface O_2 or NOx, and to quantify the uptake of stored NOx species.

Experiments involving pulsing of NO over Pt/BaO/Al_2O_3 catalyst reveal the decomposition of NO to N and O ad-species on Pt surface. The N_2 evolution steadily increases; goes through maxima and then decreases. NO is released after N_2 on NSR catalyst while the order is reversed in case of Pt/Al_2O_3 indicating that NO interacts with the BaO function of the NSR catalyst. These findings reveal the following mechanism:

1: $NO + Pt \leftrightarrow NO\text{-}Pt$;

2: $NO\text{-}Pt + Pt \leftrightarrow N\text{-}Pt + O\text{-}Pt$;

3: $2\ N\text{-}Pt \rightarrow N_2 + 2\ Pt$;

4: $O\text{-}Pt + BaO \leftrightarrow BaO_2 + Pt$;

5: $NO + BaO_2 \leftrightarrow BaO_2\text{-}NO$;

Pulsing of NO_2 shows similar behavior with shorter induction period that coincided with the production of N_2. The ratio of NO produced to NO_2 fed increases monotonically from 0 to 0.33 indicating the disproportionation reaction of NO_2. Based on these findings, the reaction sequence is expanded to include following steps:

6: $NO_2 + Pt \leftrightarrow NO_2\text{-}Pt$

7: $NO_2\text{-}Pt + Pt \leftrightarrow NO\text{-}Pt + O\text{-}Pt$

8: $NO_2 + BaO \leftrightarrow BaO_2\text{-}NO$

9: $NO_2 + BaO\text{-}NO_2 \leftrightarrow BaO\text{-}(NO_2)_2$

10: $NO_2 + BaO\text{-}(NO_2)_2 \leftrightarrow BaO\text{-}(NO_3)_2 + NO$

Reactions 8 – 10 summed up give the disproportionation reaction giving the observed ratio of 0.33. As the number of NO_2 molecules introduced is increased, the N_2 maxima shift towards the ordinate. The NO breakthrough curve also shifts accordingly.

In order to elucidate the role of Pt in the storage process, TAP and bench-scale experiments are carried out on a series of $Pt/BaO/Al_2O_3$ catalysts with different Pt and Ba loadings. For example, a comparison of NO and NO_2 pulsing experiments on Pt/Al_2O_3 and $Pt/BaO/Al_2O_3$ provides important information on the kinetics of NOx uptake. The promotional effect of Pt on NOx uptake will be examined by comparing NOx uptake under different conditions of pre-exposure to oxygen.

Finally, the experiments will be complemented with reaction system modeling. The TAP reactor is effectively simulated because of its operation in Knudsen regime and the accompanying microkinetic modeling of the experiments with parameter estimation will be presented.