NO oxidation and NOx storage kinetics on Pt/Al2O3 and Pt/BaO/Al2O3

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Reference:
A kinetic study of NO oxidation and NOx storage on Pt/Al2O3 and Pt/BaO/Al2O3, J. Phys. Chem. B, 2001, 105

Methodology :
Experiments were conducted using monolith reactor with 69 (1mm x 1mm) catalyzed channels. Reaction rates (pre-exponential factors, activation energies and coverage dependencies) are computed using laminar flow models.

Range of conditions :
Pressure : 1 atm (fixed)
Temperature : 300 C - 650 C NOx concentrations : 0 - 700 ppm.
Space velocity : 87000 hr^{-1}

Experimental features :
Experiments were conducted using a monolith reactor with 69 (1mm x 1mm) channels of 15mm length. Ar and N2 were used as inert gases. Effectivess of Pt was reduced significantly (about 15 times for the catalysts used in these experiments) in the presence of BaO. Pre-exponential factors for adsorption were estimated using kinetic theory at a fixed temperaturte of 600 K (and their temperature dependence was neglected). Transition state theory is used to prevent unreasonable entropy changes. Catalyst is regenerated thermally without using a reductant.

Measurement techniques :
Pt site dispersions were measured using CO TPD by assuming maximum coverage of 0.7 CO molecule per Pt site. Dispersions were measured in a FTIR study of CO adsorbed on Pt when BaO was present. Pt dispersion

reduced by 5 times when BaO was present. Temperature measurements were made using thermocouples. Gases are detected using a mass spectrometer. NO and NO2 were however measured using a chemiluminescence detector and N2O was measured using an IR instrument.

Materials/catalysts preparation :
In-house NOx adsorber catalyst was prepared by applying an alumina-based washcoat onto a monolith. The specific procedure used is detailed in "A Kinetic Study of Oxygen Adsorption/Desorption and NO Oxidation over Pt/Al2O3 Catalysts," Louise Olsson, Bjˆrn Westerberg, Hans Persson, Erik Fridell, Magnus Skoglundh, and Bengt Andersson, J. Phys. Chem. B, 1999, 103.

Detailed Description/Comments:
A NOx storage and release cycle is assumed to consist of 4 steps.

i) NO oxidation to NO2 on Pt/Al2O3.
O2 + 2PT <=> 2O(PT)
NO + PT <=> NO(PT)
NO2 + PT <=> NO2(PT)
NO(PT) + O(PT) <=> NO2(PT) + PT

ii) NO2 storage on BaO/Al2O3
NO2 + S <=> NO2(S)
NO2(S) <=> O(S) + NO
NO2 + O(S) <=> NO3(S)
NO2 + NO3(S) <=> NO2NO3(S)
2O(S) <=> O2 + 2S

iii) NOx release from BaO/Al2O3 (following an exotherm)
NO2(PT) + NO3(S) <=> NO2NO3(S) + PT

iv) NOx reduction to N2.

The files here (in a CHEMKIN format) provide the reaction mechanisms for the first 3 steps in the cycle.

Features of the mechanisms:
i) All reaction are reversible.

ii) All reactions have kinetic rates in the form of Arrhenius type expressions.

iii) Some reactions can have coverage dependent activation energies.

Effectivess of Pt to oxidize NO is found to reduce in the presence of BaO. For the specific catalyst formulation (Pt and BaO particle loadings and their distributions) used in the experiments, effectiveness of Pt was reduced by 15 times. For lack of a sufficient

explanation or model equations, this "masking" effect, for now, has to handled by multiplying the Pt loading with a effectivess factor when BaO is present. The effectiveness factor would depend on BaO loading and some measure of the proximity between Pt and BaO sites. For catalyst loading comparable to those used in the experiments by Olsson et al., an effectivess factor of 15 can be used.