Towards A Sustainable and Near Ambient DeNOx Under Lean Burn Conditions: A Revisit to NO Reduction on Virgin and Modified Pd(111) Surfaces

Kanak Roy,[#] Ruchi Jain,[#] Chinnakonda S. Gopinath[,#,♦]*

[#]Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India.
[♦]Center of Excellence on Surface Science, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India
Email: cs.gopinath@ncl.res.in

Supporting Information (SI)

SI-1 – MBI Experimental Setup

All kinetic and TPD experiments reported in this manuscript were performed using an extension of the so-called King and Wells collimated beam method. The home-built molecular beam instrument (MBI) used consists a 12 L capacity stainless steel ultra high vacuum (UHV) chamber evacuated with a 210 L/s turbo-molecular drag pump (Pfeiffer, TMU261) to a base pressure of about 3 x 10^{-10} Torr. The MBI is equipped with a molecular beam doser setup (Figure S1), a quadrupole mass spectrometer (Pfeiffer, Prisma QMS 200 M3), a sputter ion gun (AG5000, VG Scientific), and sample preparation facilities. The mass spectrometer is kept out of the line-of-sight of the sample to avoid any angular desorption effects. The molecular beam doser consists of a 10 mm disc multi-channel array made up of micro-capillary glass tubes of 1mm in length and 10 μm in diameter each (Collimated Holes Inc, USA). The gas-flux in the molecular beam is determined and controlled by the precision leak-valve opening and the backing gas pressure in the gas-manifold. A laterally movable stainless steel shutter, which is manually operated, was placed between the micro-capillary doser and the Pd(111) crystal in order to interrupt the beam when desired (Figure S1). The Pd single crystal (8 mm dia. and 1 mm thick, from Metal crystals and Oxides Ltd., Cambridge) was cut in the (111) direction and polished using standard procedures. It was mounted by spot-welding a 0.5 mm thick tantalum wire on the periphery of the crystal and connected to a pair of copper rods, which in turn were connected to a power-thermocouple feed-through. A K-type thermocouple was welded on the backside of the crystal and to the thermocouple leads of the feed-through. The above feed-through is connected to liquid nitrogen reservoir. The crystal can be cooled to about 100 K with liquid nitrogen or resistively heated to 1373 K. For the present experiments, the distance between the crystal and the beam doser is set to 5 mm. 45 % of the molecular beam is intercepted at a distance of 5 mm between the molecular beam doser and Pd(111) surface under the experimental conditions reported. Due to high flux conditions on the sample surface, re-adsorption of gas molecules from the gas-phase (after adsorption from direct molecular beam) is small and well within the experimental error limit of 5 %.

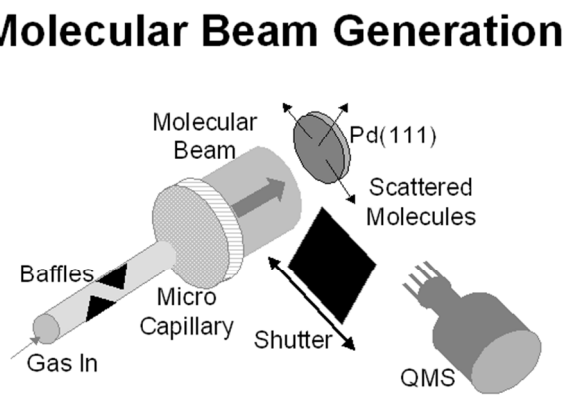

Figure S1. Schematic representation of molecular beam generation.

SI-2

Highlights of the results are as follows: (a) First and foremost is the demonstration of NO dissociation at lower temperatures under net oxidizing conditions, at least up to 325 K, against 450 K for the same on virgin Pd(111) surfaces. Md-Pd(111) shows high rate of N_2 production than virgin Pd(111) surfaces at any given temperatures between 325 and 700 K. (b) Sustainability of NO + H_2 + O_2 reaction on Md-Pd(111) surfaces is evident from the formation of reduced (N_2) and oxidized (H_2O) products at lower temperatures, indicating the Md-Pd(111) surfaces are not prone to poisoning. (c) Although SS rate of N_2 production decreases gradually at lower temperatures, increasingly selective N_2 formation is observed on Md-Pd(111) surfaces. The above observation validates NO dissociation closer to room temperatures, without any NH_3 formation and in the presence of excess oxygen (z = 3). NO molecules compete strongly with oxygen for adsorption sites and the surface may be dominated by NO + H_2 reaction. (d) 1:1:1, 1:1:2 and 1:1:3 reactants exhibit N_2 production up to 375, 350 and 325 K, respectively though NO-content decreases with increasing O_2-content in the compositions. (e) NH_3 production shows an intricate trend. Oxygen rich composition shows the maximum NH_3 at temperatures >425 K; however, 1:1:2 shows a minimum amount of NH_3 production. Pd(111) and Md-Pd(111) surfaces shows a similar trend in NH_3 production, except for a shift to lower temperatures with the latter. N_2O production shows similar trend as that of N_2.

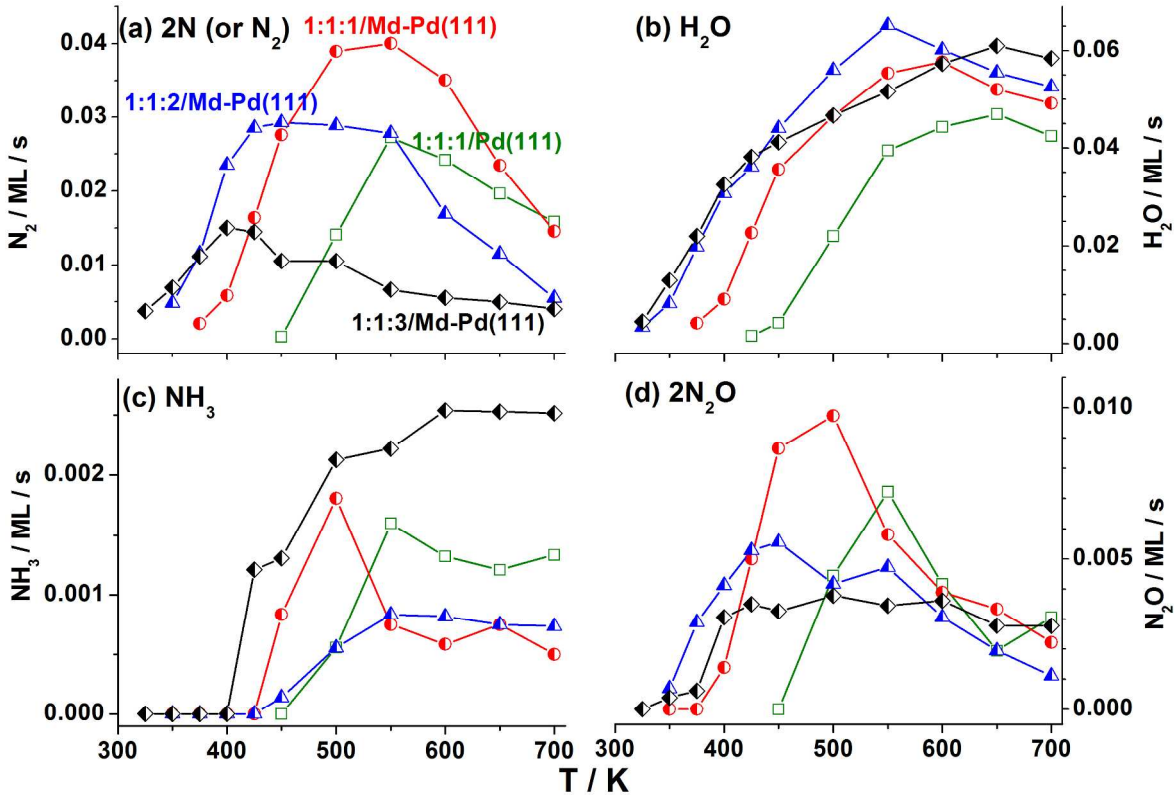

Figure S2: Steady state rate measured from NO + H_2 + O_2 reaction on Md-Pd(111) surfaces carried out with 1:1:z (z = 1-3) compositions between 325 and 700 K for the products (a) N_2, (b) H_2O, (c) NH_3, and (d) N_2O. Steady state rate measured on virgin Pd(111) surface with

1:1:1 composition is given for reference. Rate values higher (lower) than 0.005 ML/s was reproduced within 5% (20%) error limit.