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Studies of Bimetallic (Pt, Ru) Catalysts with Aberration-Corrected STEM and Theory

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Aberration-corrected Z-contrast (HAADF) STEM offers significant advantages for materials research due to its superior resolution and sensitivity, which allows observation of atomic-scale phenomena with unprecedented detail. ORNL's 300 kV VG Microscopes' HB603U STEM with Nion aberration corrector has a subAngstrom probe size [1] and routinely allows us to image single heavy atoms inside the materials and on their surfaces, providing the ideal experimental input for the concurrent first-principles calculations. These abilities proved necessary for elucidating the mechanism of stabilization of La-doped γ-Al_2O_3 by dopant single atoms [2]. Combination of STEM and simultaneously acquired EELS assisted in the explanation of the drastic difference in stability between Cr/ γ-Al_2O_3 and Cr/η-Al_2O_3 catalytic systems, which was traced back to minor differences in vacancies' distribution in the bulk of the support [3]. Another promising avenue of research lies in the field of bimetallic catalysts. Z-contrast STEM is invaluable as the atomic structure and ultimately distribution of different metal atoms within catalytic particles can be revealed.

We conducted a systematic STEM study of the prospective catalyst system (Pt, Ru)/MgO prepared from bimetallic cluster precursors of different stoichiometries [4]. For all cases, we observe regular monolayer-like metal particles on the surface, which have similar structure but varying sizes (Fig.1 (a), (b)). On the MgO (110) surface, the particles are aligned closely with support lattice (Fig. 1(c)). Away from step defects, particles are not fixed rigidly to the surface, but travel easily under the beam, changing the outline and shedding and absorbing single atoms; however, the structural pattern stays the same.

Density functional theory calculations have been used to determine the structure of possible particles on MgO (110). We find that regular monolayer-like structures can be formed by Pt, with metal atoms bonded to surface oxygen, from small isolated clusters (Fig 2(a)) to continuous (Fig 2(b)) or semicontinuous (Fig. 2(c))layers. The binding energy of the particles to the flat surface of the substrate is fairly low, in full agreement with experimentally observed mobility. We analyze the dependence of binding energy on cluster composition (addition of Ru), as well as the influence of surface defects such as steps and vacancies on cluster structure and mobility. Implications for the catalytic activity of the (Pt, Ru)/MgO system will also be discussed

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[6] We are grateful to Profs. R. D. Adams and M.A. Amiridis (University of South Carolina) for the provision of bimetallic catalyst samples. This work was supported by USDOE under contract DE-AC05-00OR22725 managed by UT-Battelle, LLC

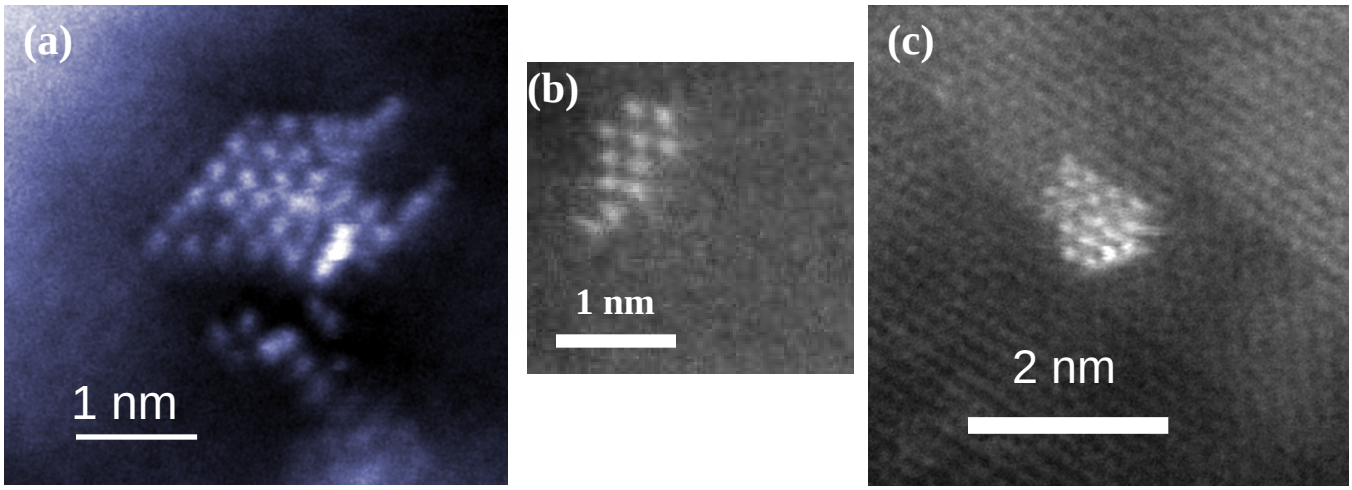

Fig.1 Monolayer-like metal structures on MgO surface: (a), (b) – particles of different sizes, (c) – particle on MgO (110) surface aligned with the substrate lattice.

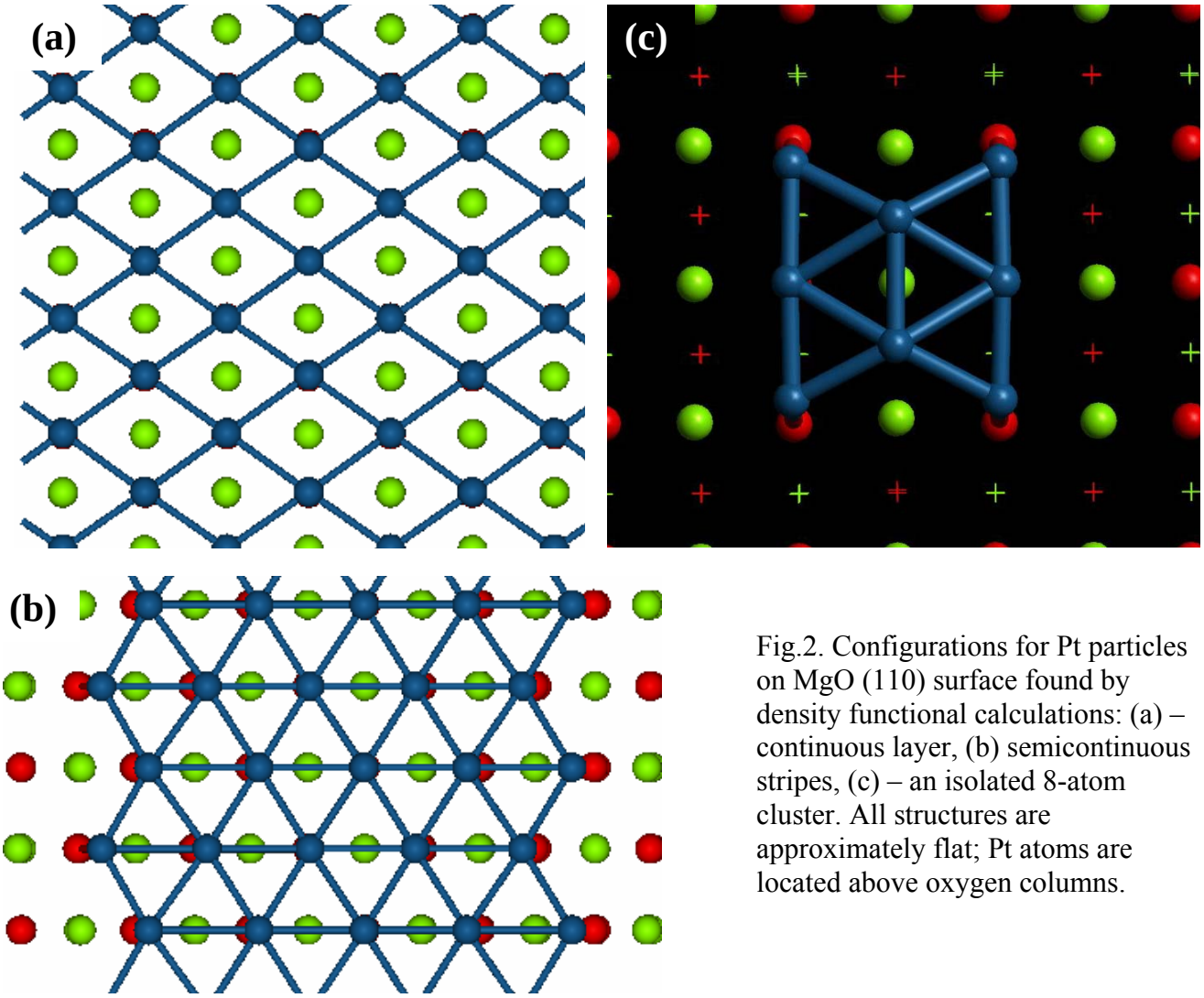

Fig.2. Configurations for Pt particles on MgO (110) surface found by density functional calculations: (a) – continuous layer, (b) semicontinuous stripes, (c) – an isolated 8-atom cluster. All structures are approximately flat; Pt atoms are located above oxygen columns.

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