

Energy Harvesting & Storage

Room Lehua - Session EH-MoM

Surfaces & Interfaces for Environmental Processes

Moderator: Jun Yoshinobu, ISSP, Univ. of Tokyo, Japan

8:20am EH-MoM2 In-situ FTIR Spectroscopy of Water Adsorption on Alkali-free Glass Surfaces, *Nicholas J. Smith, G.P. Agnello*, CORNING Incorporated

The adsorption of water on glass surfaces is believed to be critical in mediating a number of surface properties, and is particularly relevant for alkali-free multicomponent glasses used as display substrates when considering attributes like coating adhesion or electrostatic charging. Prior observations on similar glasses, as well as silica, have yielded intriguing observations about the capacity, the kinetics, and especially the structure of water that chemically or physically adsorbs on glass surfaces. In this work, we report on application of in-situ FTIR spectroscopy methods to experimentally investigate the nature of water adsorbed on planar alkali-free glass surfaces as a function of humidity and vacuum pre-treatment, shedding light on the content and structure of adsorbed water.

8:40am EH-MoM3 Nuclear-spin State Filtering and Conversion of H₂ with Solid Surfaces for Efficient Hydrogen Liquefaction, *G. Nakamura, K. Takeyasu, S. Ohno, D. Ivanov, S. Ogura, Katsuyuki Fukutani*, University of Tokyo, Japan

Hydrogen is a clean energy source, and storing hydrogen in a liquid form is a high-density storage method. Molecular hydrogen exists in nuclear-spin isomers of ortho and para species according to the total nuclear spin [1]. Since these species are correlated to the rotational states with even and odd rotational quantum numbers (J) because of the symmetry of the total wavefunction with respect to the permutation of the two nuclei, the stable state at the liquid hydrogen temperature is the para state. Although the ortho-para conversion in an isolated state is strictly forbidden, the conversion is promoted at solid surfaces [1], which has been used for efficient hydrogen liquefaction. Due to the symmetry of the H₂ molecule, on the other hand, the molecule-surface interaction is anisotropic depending on the molecular orientation, which can be analyzed with the J -state selective temperature-programmed desorption (TPD) [2]. In the present work, we have investigated the potential anisotropy of H₂ on a Pd(210) surface with resonance-enhanced multiphoton ionization (REMPI). With the anisotropic potential, furthermore, we propose that the ortho and para species can be separated by surface scattering, which is potentially used for efficient hydrogen liquefaction. We demonstrate such nuclear-spin state filtering on a TiO₂(110) surface.

When the Pd(210) surface is exposed to H₂ at ~30 K, H₂ is molecularly chemisorbed on a H-covered surface, which is revealed by a TPD peak at ~70 K [3]. When this desorption is J -state selectively detected, the $J=0$ para H₂ is desorbed at 74 K, while the $J=1$ ortho H₂ is desorbed at a higher temperature of 78 K. This indicates that the adsorption energy of the ortho species is larger than that of the para species. This is due to the lifting of the degeneracy of the ortho state induced by the potential anisotropy. From the population ratio of the ortho and para states, the ortho-para conversion time in this adsorption state is found to be shorter than ~10 s, which is much faster than Ag surfaces [1]. By applying a pulsed supersonic H₂ beam, the angular distribution of H₂ scattered from TiO₂(110) is state-selectively measured. Whereas the $J=1$ ortho H₂ reveals a broad distribution in the near-specular direction, the $J=0$ para H₂ shows a slightly shifted distribution. We discuss the scattering of H₂ via an anisotropic potential and resultant nuclear spin-state filtering.

References

- [1] K. Fukutani, T. Sugimoto, Prog. Surf. Sci. 88, 279 (2013).
- [2] T. Sugimoto, K. Fukutani, Phys. Rev. Lett. 112, 146101 (2014).
- [3] P. K. Schmidt et al., Phys. Rev. Lett. 24 87, 096103 (2001).

9:20am EH-MoM5 Chemical Gradients Formation on Polymer Surfaces for Directed Molecular Transport, *Hyung-Jun Koo*, Seoul National University of Science and Technology, Republic of Korea; *P.V. Braun*, University of Illinois at Urbana-Champaign, USA; *K.V. Waynant*, University of Idaho, USA; *C. Zhang*, University of Illinois at Urbana-Champaign, USA

Surfaces containing defined microscale chemical gradients are important for various applications including a sample library with an extremely dense variable set and a smart platform to direct 2D-molecular transport. In this

regard, reliable methods to form milli- to micron-scale chemical gradients are required. We present two facile microfluidic methods to form narrow surface chemical gradients in a tertiary amine functionalized polymer brush via a selective quaternization. Two methods are on the basis of different physical mechanisms: permeation into porous media vs. diffusion at liquid/liquid laminar interface. Concentration and separation as well as directional transport driven by surface-gradient on highly hydrated polymer films will be also demonstrated. Such a new concept to control 2D transport of molecules could generally be applied for signal enhancement in chemical sensors to detect tiny amount of harmful molecules, e.g., pollutants, toxins, etc..

References:

1. *H.-J. Koo*, K. V. Waynant, C. Zhang, R. T. Haasch, P. V. Braun, "General Method for Forming Micrometer-Scale Lateral Chemical Gradients in Polymer Brushes", *Chemistry of Materials*, 26, 2678 (2014).
2. *H.-J. Koo*, K. V. Waynant, C. Zhang, P. V. Braun, "Polymer Brushes Patterned with Micrometer-Scale Chemical Gradients using Laminar Co-Flow", *ACS Applied Materials & Interfaces*, 6, 14320 (2014).
3. C. Zhang, A. Sitt, *H.-J. Koo*, K. V. Waynant, H. Hess, B. D. Pate and P. V. Braun, "Autonomic molecular transport using hydrogel films containing programmed chemical potential gradients", *Journal of the American Chemical Society*, 137, 5066 (2015)

10:20am EH-MoM8 Activation of CO₂ using Heterogeneous Catalysts, *Junji Nakamura*, Tsukuba University, Japan

INVITED

Methanol synthesis by hydrogenation of CO₂ using Cu catalysts is one of the promising reactions to convert CO₂ into useful chemicals. Formate species is the pivotal intermediates formed as the initial step of CO₂ hydrogenation (CO₂ + H₂ → HCOO_a). The reaction rate of formate synthesis is very low and the reaction probabilities are about 10⁻¹² at 340K. The formate synthesis must be accelerated in order to convert CO₂ to methanol efficiently. Our previous kinetic measurements have suggested that formate is synthesized via Eley-Rideal typed mechanism, in which CO₂ molecules directly attack adsorbed hydrogen atoms on Cu surfaces. The structure insensitivity observed for formate synthesis experiments on Cu(111), Cu(100), and Cu(110) were well explained by the Eley-Rideal mechanism based on DFT calculations. In addition, sharp angular desorptions of CO₂ have been observed for formate decomposition as the reverse reaction of formate synthesis, indicating thermal non-equilibrium reaction. We thus performed molecular beam experiments to prove the Eley-Rideal typed mechanism, in which CO₂ molecules with controlling vibrational and translational energies were reacted with adsorbed hydrogen on cold Cu(111) and Cu(110) surfaces (TS =150-215 K). The formation of formate was found by infrared spectroscopy and temperature programmed desorption measurements of CO₂ and H₂ from decomposition of formate. We confirmed the formation of formate species on Cu(111) and Cu(110) with reaction probabilities of 10⁻⁵ by heating nozzle above 1000 K, while no formate is formed at nozzle temperatures below 1000 K. The results indicate the Eley-Rideal typed mechanism with thermal non-equilibrium character. DFT calculations also reproduce the Eley-Rideal typed mechanism, in which translational and vibrational excitations of CO₂ are required to overcome the barrier of formate synthesis, 0.6-0.7 eV. The understanding on dynamics of CO₂ activation is expected to apply for the state-to state chemistry of methanol synthesis. That is, selective energy supply for an energy-efficient methanol synthesis process.

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