

Surface diffusion of cyclic hydrocarbons on nickel

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ABSTRACT

Surface diffusion of adsorbates is difficult to measure on realistic systems, yet it is of fundamental interest in catalysis and coating reactions. quasielastic neutron scattering (QENS) was used to investigate the diffusion of cyclohexane and benzene adsorbed on a nickel metal sponge catalyst. Molecular dynamics simulations of benzene on a model (111) nickel surface showed localised motion with diffusion by intermittent jumps. The experimental data was therefore fitted to the Singwi–Sjölander model and activation energies for diffusion of 4.0 kJ mol^{-1} for benzene and 4.3 kJ mol^{-1} for cyclohexane were calculated for the two dimensional model. Limited motion out-of plane was seen in the dynamics simulations and is discussed, although the resolution of the scattering experiment is insufficient to quantify this. Good agreement is seen between the use of a perfect crystal as a model for a disordered system over short time scales, suggesting that simple models are adequate to describe diffusion over polycrystalline metal surfaces on the timescale of QENS measurement.

1. Introduction

Surfaces have higher energy than the bulk which leads to phenomena such as altered structure (relaxation, reconstruction), differing reactivity (catalysis, passivation) and the accumulation of species (adsorption). The investigation of surfaces and interfaces is therefore well established, although this does not mean that direct measurements at a surface are experimentally simple. Surface selective techniques often use probes that are incompatible with a gas atmosphere such as low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS) and ion scattering [1]. Reflection techniques e.g. reflection absorption infrared spectroscopy (RAIRS) [2] and sum frequency generation (SFG) [3] demand an almost perfectly flat surface, but have more flexibility in atmospheric control. Surface selective techniques therefore often place such extreme demands on the sample preparation and morphology that they do not accurately represent the systems they aim to model. Consequently there is much ongoing work aiming to bridge the “pressure and materials gap” [4] that exists between model systems and the subjects of interest.

In many situations investigators are interested in the form of adsorbed materials upon a bulk substrate, where the dominant properties of the bulk overwhelm the minority adsorbate. Although it may be possible to overcome this through careful background subtraction, highly absorbing materials, such as carbon or finely divided metals frustrate the use of optical spectroscopy as an interrogative tool [5]. To distinguish the adsorbate from the substrate in these situations,

alternatives that provide strong contrast between adsorbent and adsorbate must be used. Neutrons provide a unique probe in this context, as they interact with the atomic nucleus, rather than the electronic cloud experienced by photons and electrons. Hydrogen has a uniquely high incoherent neutron scattering cross section, so the incoherent scattering from an organic adsorbate on an inorganic material will be dominated by the hydrogen signal.

For catalytic research, the most common use of neutrons has been to measure the vibrational modes in adsorbed organic molecules with energy transfer values around 1–600 meV ($8\text{--}4840 \text{ cm}^{-1}$) [6]. At lower energies, it is possible to probe the diffusive motions of molecules, provided a neutron spectrometer with sufficiently high energy resolution. The technique of using the very low energy transfer region around the elastic peak is referred to as quasielastic neutron scattering (QENS). Catalytically relevant diffusion measurements with QENS have primarily investigated motion of guest molecules in zeolite hosts, often with the support of molecular dynamics (MD) simulations, as they access similar timescales [7].

When neutrons are scattered by static atoms, there is no energy exchange and the collision is elastic. Where the atoms are mobile, inelastic collisions may occur, and the measured quasielastic peak becomes broadened. Spectrometers therefore have a dynamic window defined by their resolution, at the slow motion limit, and the dynamic range/noise, for the faster motions at the other extreme. Quantification of this broadening and how it varies with the momentum scattering vector, Q , can provide insight into the quantity and variety of atomic

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motion. The quasielastic peak centred at zero energy transfer can be represented as a convolution of the elastic component with quasielastic components for each motion present. The elastic component is represented as the convolution of a delta function and the measured resolution function. For a three dimensional diffusion process, a Lorentzian peak is convolved. In the two dimensional case, the peak shape is considerably more complex. Under realistic circumstances however, the peak shape is often acceptably approximated by a Lorentzian at higher Q , due to limits in spectrometer resolution [8].

Surface diffusion measurement with QENS has been limited to small molecules on metals [9] or metal oxides [10] and more diverse sorbates on carbon [11,12]. Work by Calvo-Almazán et al. has thoroughly investigated the motion of aromatic hydrocarbons across the planes of exfoliated graphite [13,14]. From this it has been shown that it is possible to extract the friction parameters that determine the motion of adsorbates across a well-defined potential energy surface.

Raney nickel is a high surface area, commercially available catalyst formed by leaching the aluminium from a Ni-Al alloy to leave a spongy, skeletal nickel structure. Originally developed for the hydrogenation of vegetable oils, [15] it has found application in numerous organic transformations, including the hydrogenation of benzene to cyclohexane [16]. The structure of a frozen monolayer of each adsorbate has been determined previously by LEED [2,17] This material is an amorphous metal catalyst that presents primarily the (111) surface [18,19] and thus is an excellent choice to measure QENS spectra of adsorbates moving across a metal substrate. The high symmetry and planar geometry of the benzene molecule makes for an ideal system to model. Simulations of the diffusion of benzene on nickel were therefore carried out to provide confidence in our interpretation of the experimental data.

2. Material and methods

2.1. Experimental

Activated Raney nickel with a declared surface area of 80–100 m²/g was obtained from Aldrich as a slurry in water. Caution is necessary in preparation of the active material, as it is pyrophoric in air when dry. Approximately 50 g was crudely dried using a Büchner funnel and transferred while still moist to a copper-sealed inconel reactor system that has been previously described [20,21]. This was dried overnight at 423 K in a helium flow of 400 sccm. 100 sccm H₂ was then added to the flowing gases and the reactor heated to 500 K for 80 min to ensure removal of any metal oxide. The nickel was then cooled in 400 sccm of helium.

The clean nickel sample was then separated into three portions in an argon-filled glovebox. One was prepared for measurement by sealing into an annular aluminium sample holder with 2 mm annular gap, with the other two retained in sealed inconel reactors for further treatment. These were loaded with either cyclohexane or benzene (99.5 and 99.9% respectively, both Sigma-Aldrich) by flowing argon over the metal after passing through a Dreschel bottle filled with the solvent. After 1 h of gas flow, the reactors were purged with pure argon for 10 min to remove any excess organic. These samples were then transferred in the glovebox to similar aluminium sample holders. Each clean nickel sample was approximately 11.5 g. The sample loaded with benzene showed a 0.28 g mass increase, and the cyclohexane 0.22 g. This can be estimated to provide an approximate coverage of between 0.4 and 1.5 monolayers of the adsorbate, assuming the range of surface area quoted by the manufacturer and the packing geometries from LEED measurements in references 2 and 17.

Quasielastic neutron spectra were recorded with the (002) pyrolytic graphite reflection on the IRIS spectrometer at the ISIS neutron and muon source. Temperature was controlled from 6 to 302 K using a helium closed cycle refrigerator. Data reduction used the Mantid [22] software, with peak fitting carried out in DAVE [23]. All gases used

were supplied by BOC, with 99.99% purity or better.

2.2. Molecular dynamics simulation

A rigid nickel face centred cubic slab 30 × 34.5 × 16.258 Å in dimensions with d-spacing 2.49 Å was used as the catalyst. A 136.262 Å region of vacuum is present in the z -axis between each face of the nickel slab. The benzene-benzene interactions are that of the commonly used OPLS force-field; however we have devised our own parametrisation of the Ni-Benzene interactions via a fitting of the simulation data at 302 K to that of the QENS results. In particular a Lennard–Jones interaction is used for both the H–Ni and C–Ni interactions, with a constant sigma which is based on commonly used metal-C interactions ($\sigma = 2 \text{ \AA}$). The interaction strength (ϵ) however is a free parameter which has been varied over a series of simulations in order to match the hydrogen QENS signal from experiment. As previously mentioned, the parametrisation was only performed at 302 K, therefore the results of simulations at lower T show the transferability of the parametrisation across the studied temperature range. All simulations were performed in the Molecular dynamics package LAMMPS. Thirty-two benzene molecules are used in each simulation, corresponding to the approximate experimental coverage. Simulations were run with a time-step of 1 fs with benzene molecules as rigid bodies within the NVT ensemble using the Nosé–Hoover thermostat. Simulations were allowed to equilibrate for 3 ns before statistics were accumulated. Electrostatics were handled using the particle-particle-mesh approach. The trajectory was saved every pico-second over the course of a 5 ns trajectory, which was used as the source for all reported data.

3. Results

3.1. Experimental

Q resolved QENS data were recorded at five temperatures for each sample, as displayed in Fig. 1. For the bare nickel sample very little broadening is apparent as the temperature increases, indicating that the individual atoms are rigidly held in the metallic lattice. This behaviour also suggests that there is no residual mobile hydrogen on the Ni surface which might cause the hydrogenation reaction to occur with benzene. For the samples containing organic materials, broadening is clearly evident as the temperature is increased and diffusion across the surface occurs. There is little variation in the elastic peak intensity with Q for all samples, which indicates low Bragg scattering and hence low long range order in both the metal and the adsorbate layer.

The Q -resolved data for the organic-loaded samples were fitted using three components. The instrumental resolution was represented

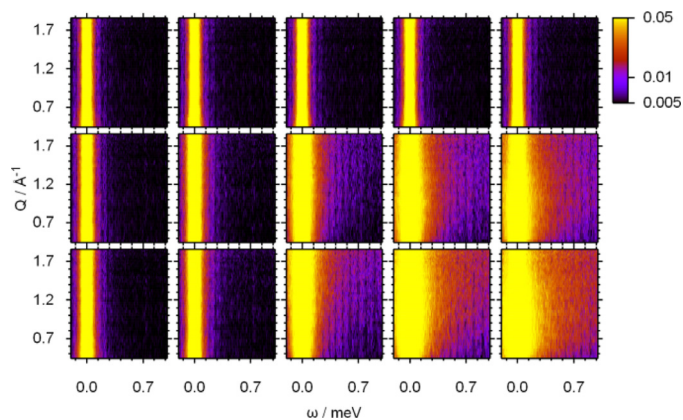


Fig. 1. Experimental QENS spectra for nickel (top), nickel + Benzene (centre) and nickel + cyclohexane (bottom) at base temperature, 77, 152, 227 and 302 K increasing from left to right.

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