



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



Heterogeneous catalysis in complex, condensed reaction media

David C. Cantu, Yang-Gang Wang, Yeohoon Yoon, Vassiliki-Alexandra Glezakou, Roger Rousseau*, Robert S. Weber*

Pacific Northwest National Laboratory, Institute for Integrated Catalysis, PO Box 999 MS-IN K2-12, Richland, WA 99352, United States

ARTICLE INFO

Article history:

Received 20 May 2016
Received in revised form 29 July 2016
Accepted 19 August 2016
Available online xxx

Keywords:

Bio-oil
Upgrading
Solvophilicity
Epiphilicity
Cybotactic region

ABSTRACT

Many reactions required for the upgrading of biomass into fuels and chemicals—hydrogenation, hydrodeoxygenation, hydrocracking—are ostensibly similar to those practiced in the upgrading of petroleum into fuels. But, repurposing hydroprocessing catalysts from refinery operations to treat bio-oil has proved to be unsatisfactory. New *catalysts* are needed because the composition of the biogenic reactants differs from that of petroleum-derived feedstocks (e.g. the low concentration of sulfur in cellulose-derived biomass precludes use of metal sulfide catalysts unless sulfur is added to the reaction stream). New *processes* are needed because bio-oils oligomerize rapidly, forming intractable coke and “gunk”, at temperatures so low that the desired upgrading reactions are impractically slow, and so low that the bio-oil upgrading must be handled as a condensed fluid. Ideally, the new catalysts and processes would exploit the properties of the multiple phases present in condensed bio-oil, notably the polarizability and structure of the fluid near a catalyst’s surface in the cybotactic region. Molecular simulation results of the cybotactic region adjacent to different catalyst surfaces in the hydrogenation of phenol suggest that Pd catalysts supported on hydrophilic surfaces are more active than catalysts based on lipophilic supports because the former serve to enhance the concentration of the phenol in the vicinity of the Pd. The effect stems from thermodynamics, not the rate of mass transport.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The molecules in a gaseous reaction medium in the vicinity of a supported catalyst maintain a substantially random organization unless they adsorb or are oriented by a strong potential field. In contrast, the molecules in a liquid reaction medium can exhibit an organization that is appreciably different from their bulk structure whenever they approach an interface [1–3]. The near-surface portion of the fluid may be called the cybotactic region, a term borrowed from solution chemistry [4].

In supported catalysts the area fraction of exposed support is typically much larger than the area fraction of the exposed catalyst domains. For example [5] when 1.5 wt% Pd is supported on a typical alumina (~240 m²/g) at 50% exposure, the area fraction of metal is only about 1 area%. Therefore, the structure of the cybotactic region can be expected to be dominated by solvent interactions with the support, rather than with the metal, because solvent reorganization in the cybotactic region can extend over distances of nanometers.

In such cases, it should be possible to influence the catalytic rates in liquid reaction media by varying the solvophilicity of the support, an infrequently studied property. Studies of solvent effects in heterogeneous catalysis [6–9] usually compare kinetics in reaction media composed of different solvents while keeping the catalyst constant. The complementary experiment, keeping the solution composition constant while varying the solvophilicity of the support [5,10], is less common. Studies of both types are needed to complete our understanding of the fluid-solid interface in the catalytic upgrading of bio-oils, where the reaction medium varies from amphiphilic to a combination of lipophilic and hydrophilic phases as a function of conversion. To identify and simulate the composition and structure of the cybotactic region near heterogeneous catalysts operating in the liquid phase requires new experimental [11] and modeling methods [12–15]. Identifying the composition of the cybotactic region is relevant for catalysis because the concentrations in the cybotactic region are those that enter a microkinetic formulation of the rate equation.

Here, we report the use of preliminary molecular dynamics models of the cybotactic region of the reaction medium associated with the aqueous phase hydrogenation of phenol in the vicinity hydrophilic and lipophilic surfaces. In particular, we have studied the role of entropy and binding energy in determining

* Corresponding authors.

E-mail addresses: Roger.Rousseau@pnnl.gov (R. Rousseau), Robert.Weber@pnnl.gov, rweber221@gmail.com (R.S. Weber).

<http://dx.doi.org/10.1016/j.cattod.2016.08.025>

0920-5861/© 2016 Elsevier B.V. All rights reserved.

speciation at the solid/liquid interface. Our results augment a hypothesis advanced by Pérez and Corma [5] that the reaction involves adlineation between metal-activated hydrogen and the phenol adsorbed on the support.

2. Methods

In catalysts supported on high surface area carriers, the curvature of pore walls may play an important role in structuring the fluid phase. Here, as a first step, we report our work only with planar surfaces. We ask two questions: (1) what species are present at the solid/liquid interface, and (2) what drives them to be there. Our analysis focused on a solvent mixture containing 2 mol% phenol in water and its adsorption at 50, 100 and 250 °C, which are relevant to the low and high temperate stages in the hydrotreating process. We chose the following support materials as models of idealized lipophilic and hydrophilic supports with slightly different binding properties (Fig. 1):

- Graphene, lipophilic but preferentially adsorbs aromatics due to π - π stacking.
- Hydrogen terminated diamond, lipophilic with weak sticking to all organics.
- Lewis acidic alumina, hydrophilic.
- Hydroxy-terminated alumina, hydrophilic but able to bind both phenol and water via hydrogen bonds.

In addition, we modeled the interaction of the fluid phase with a Pd(111) surface, which binds phenol strongly.

Density functional theory (DFT) calculations of phenol at metal aqueous interfaces have been described previously [16]. In brief, optimized surface geometries were obtained with *ab initio* molecular dynamics simulations using the CP2K package [17,18]. These simulations can provide accurate estimates of surface adsorption and reactivity, but are limited by system size and simulation time.

Table 1
Gas phase phenol binding energies (in kJ/mol) from density functional theory, from classical force fields and their difference (FF-DFT).

	Density Functional Theory	Classical Force Field	Difference
Graphene	-52.9	-47.2	5.7
Diamond	-42.3	-51.0	-8.8
Al ₂ O ₃	-15.2	-34.0	-18.8
Hydroxy-terminated Al ₂ O ₃	-12.3	-20.4	-8.1
Pd(111)	-199.3	-191.5	7.8

The detailed statistical mechanical sampling of solids in contact with multicomponent liquids requires large length (~10 nm) or large-time (~ns) scale simulations that cannot be routinely performed for such complex systems. To overcome this limitation, data from these simulations (surface coordinates, atomic charges, binding energies) were used to construct and parameterize larger-scale liquid simulations. Classical molecular dynamics (MD) was used to simulate the surface-solvent mixture systems, using Gromacs [19] software. The OPLS all atom force field [20] was used for organic atoms (C,H,O) except for water molecules, which were modeled with TIP3P [21]. The CLAYFF [22] force field parameters were employed for alumina. For Pd atoms, the well depth of the non-bonded interactions was changed to match the phenol binding energies, and the equilibrium distance was taken from the Universal Force Field [23]. Table 1 shows gas phase phenol binding energies with DFT and the classical force field, showing agreement within <10 kJ/mol, except for alumina at ~18 kJ/mol.

To obtain free energies, gas phase entropies for phenol binding were calculated with the vibrational, rotational, and translational partition functions using frequencies obtained with density functional theory calculations of gas phase phenol and bound state phenol. We obtain liquid phase free energies from the classical MD simulations by compiling a probability distribution of species, $\rho(z)$, as a function of distance to the surface (Fig. 2). The free energy of

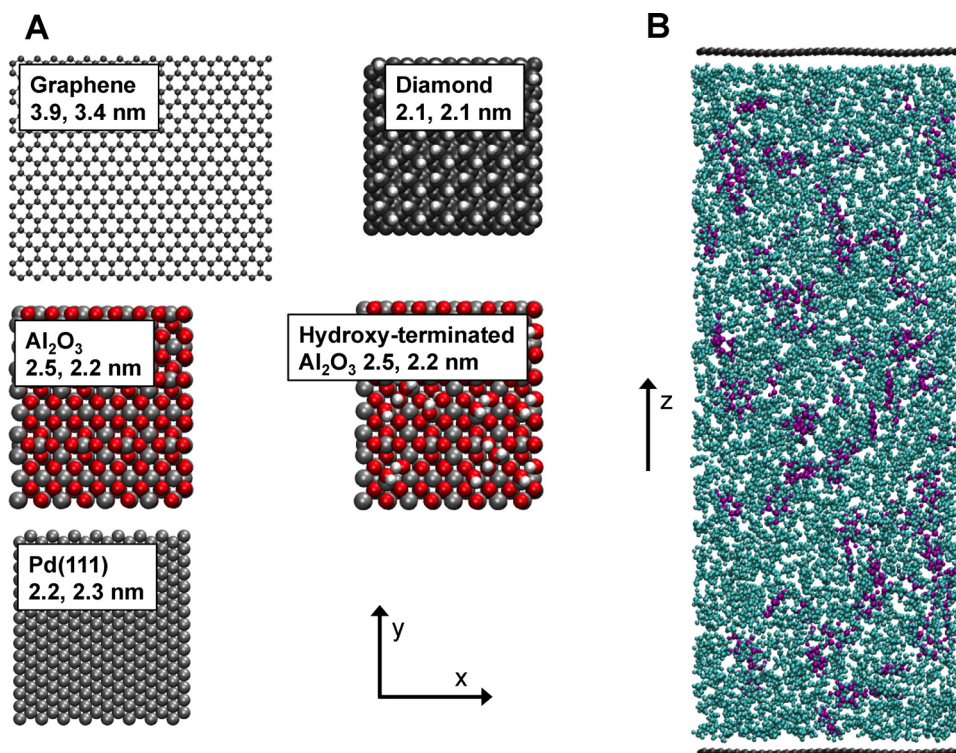


Fig. 1. (A) Surface models employed in this study graphene, hydrogen-terminated diamond, Lewis acidic alumina, hydroxyl-terminated alumina, and Pd(111). Numbers below names denote x and y surface dimensions. (B): Representation of the solution phenol (purple) and water (cyan) in contact with the graphene (gray) surface.

Download English Version:

<https://daneshyari.com/en/article/4757039>

Download Persian Version:

<https://daneshyari.com/article/4757039>

[Daneshyari.com](https://daneshyari.com)