Journal of Catalysis 315 (2014) 48–58

Contents lists available at ScienceDirect

Journal of Catalysis

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

Acid strength and bifunctional catalytic behavior of alloys comprised of noble metals and oxophilic metal promoters

David Hibbitts [a,1], Qiaohua Tan [a], Matthew Neurock [a,b,*]

[a] Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, United States
[b] Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States

ARTICLE INFO

Article history:
Received 6 September 2013
Revised 12 March 2014
Accepted 31 March 2014
Available online 21 May 2014

Keywords:
Hydrogenolysis
Ring opening cyclic ethers
DFT, bifunctional catalysis
Hydrodeoxygenation
Oxophilic metal promoters
Deprotonation energies
Hydroxymethyl tetrahydrofuran

ABSTRACT

The promotion of metal catalysts with partially oxidized oxophilic MO_x species, such as ReO_x-promoted Rh, has been demonstrated to produce Brønsted acid sites that can promote hydrogenolysis of oxygenate intermediates such as those found in biomass-derived species. A wide variety of alloy compositions and structures are examined in this work to investigate strongly acidic promoters by using DFT-calculated deprotonation energies (DPE) as a measure of acid strength. Sites with the highest acid strength had DPE less than 1100 kJ mol^{-1}, similar to DPE values of heteropolyacids or acid-containing zeolites, and were found on alloys composed of an oxophilic metal (such as Re or W) with a noble metal (such as Rh or Pt). NH_3 adsorbs more strongly to sites with increasing acid strength and the activation barriers for acid-catalyzed ring opening of a furan ring decrease with increasing acid strength, which was also shown to be stronger for OH acid sites bound to multiple oxophilic metal atoms in a three-fold configuration rather than OH sites adsorbed in an atop configuration on one oxophilic metal, indicating that small MO_x clusters may yield sites with the highest acid strength.

© 2014 Published by Elsevier Inc.

1. Introduction

Biomass, which is comprised of carbohydrates that can be hydrolyzed to form C_5–C_6 sugars rich in oxygen, provides a sustainable alternative to petroleum for the production of fuels and chemicals but requires efficient strategies to selectively remove oxygen. Various heterogeneous-catalyzed paths, which include decarboxylation, decarbonylation, and hydrogenolysis, have been proposed and used to selectively produce value-added chemicals as well as intermediates with higher H/C ratios for fuel production [1–3]. Among these paths, hydrogenolysis has the distinct advantage of maintaining the chain length of the hydrocarbon substrate, thus avoiding the unnecessary production of CO or CO_2 by-products and providing a carbon neutral process.

Hydrogenolysis of various polyols, including glycerol, a by-product of biodiesel production [1], has been targeted in the literature for synthesis of valuable chemical intermediates or fuel precursors. Glycerol hydrogenolysis is active over various supported metal catalysts, including Ru [4–7], Pd [4,8], Pt [4,6,9], Rh [8,10], and PtRu and AuRu [6] alloys at temperatures near 473 K under moderate pressures of hydrogen (14–100 bar). Carbon-supported Pt, Pd, and Rh catalysts predominantly convert glycerol via C–O hydrogenolysis to *1,2-propanediol (1,2-PrDO)* with ~80% initial selectivity [4,6,8,9], which undergoes further C–O hydrogenolysis to form propanol; these catalysts, however, also show activity for C–C hydrogenolysis, leading to undesired C_2 products. Chia et al. recently examined the hydrogenolysis of glycerol on Rh/C catalysts at a lower temperature (393 K) and found that C–C hydrogenolysis was suppressed resulting in a product distribution of 18% *1,2-PrDO*, 5% *1,3-PrDO*, 8% 1-propanol (*1-PrOH*), and 69% 2-propanol (*2-PrOH*) [11]. These product selectivities indicate that the C–O hydrogenolysis of glycerol primarily occurs at the less-substituted (terminal) carbon center on these metal catalysts.

Cyclic ethers derived from biomass [3,12] such as 2-(hydroxymethyl)tetrahydrofuran (*HMTHF*) can also undergo C–O hydrogenolysis, opening their ring to form linear or branched products. The ability to selectively activate specific C–O bonds in the ring could result in sustainable routes to valuable chemical intermediates. Work on Rh/SiO_2 has indicated that C–O hydrogenolysis occurs more selectively at the unsubstituted carbon of the ring-ether, forming *1,2-pentanediol* (*1,2-PeDO*) at >60% selectivity [13].

In addition to these unpromoted catalysts, a number of studies over supported noble metal catalysts such as Rh, Pt, and Ir promoted by acidic species or substrates such as amberlyst [14–16],

---

[*] Corresponding author at: Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, United States. Fax: +1 434 982 2658.
E-mail address: mn4n@virginia.edu (M. Neurock).

[1] Present address: Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States.

http://dx.doi.org/10.1016/j.jcat.2014.03.016
0021-9517/© 2014 Published by Elsevier Inc.

H_2SO_4 [17,18], H_2WO_4 [8,15], and $H_4SiW_{12}O_{40}$ [19] or alloyed with partially reduced oxides such as MoO_x [10,11,20,21], WO_x [10,20], or ReO_x [10,13,18,20–23] have demonstrated distinctly different trends in selectivity as C–O hydrogenolysis predominantly proceeds at the *more* substituted C–O bonds. *HMTHF* preferentially opens at the more substituted C–O bond to form 1,5-pentanediol with greater than 95% selectivity in the presence of these promoters, and similar results were observed for C_6 cyclic ethers [11,13,20,21]. For glycerol, these promoters result in significant increases in the selectivity to *1,3-PrDO* [9–11,18,23] which is only observed in small quantities on the unpromoted catalysts and at higher temperatures. ReO_x on Pt, for example, was shown to significantly increase the rate of glycerol reforming compared to that on unpromoted Pt [24,25]. Chia et al. studied hydrogenolysis of a wide range of polyols in addition to glycerol and *HMTHF* over ReO_x-promoted Rh/C and observed that hydrogenolysis selectively occurs at secondary alcohol groups [11]. Koso et al. later reported similar results for hydrogenolysis of many of the same polyols over ReO_x and MoO_x-promoted Rh/SiO_2 [21]. We showed previously that rates and selectivities for hydrogenolysis of a wide range of linear polyols and C_5 and C_6 ethers could be linearly related to their gas-phase carbenium ion reaction energies [11], thus indicating that ReO_x, WO_x, and MoO_x promoters result in the formation of acid sites which are likely M-OH groups at the metal–solution interface.

Although the specific nature of the active acid site is unknown, these sites are thought to be either embedded into or strongly bound to the promoted metal as the presence of acids in solution such as H_2SO_4 or HCl is far less active and selective and cannot maintain the sustained operational times (>120 h) demonstrated for ReO_x-Rh/SiO_2 [11]. NH_3 TPD offers experimental evidence of acid sites on ReO_x-promoted Pt/C and that the acid site density, but not strength, increases with Re loading [25]. The ratio of acid to metal sites is 0.28 for a Re:Rh loading of 1:2 with an NH_3 adsorption energy on the acid site of -100 kJ/mol, indicating moderate acid strength [11]. EXAFS has been performed on a number of these alloys, including Rh-ReO_x [10,13,21,26], Rh-MoO_x [21], Pt-ReO_x [9,27], and most recently, Ir-ReO_x [18] and curve-fitting results from these studies offer insights into the nature of the alloy and therefore the acid site, however, large uncertainties weaken the conclusions one can draw.

First-principle density functional theory (DFT) calculations can be used to examine and test acid strength of possible sites for a wide range of alloy materials as previously reported [11]. The deprotonation energy (DPE) provides a direct measure of acid site strength [28] and was used to examine acid strength of hydroxylated Re in the surface of 201-atom cubo-octahedral Rh and Pt nanoparticles as well as other alloys. The results indicate that materials such as ReO_x-promoted Rh have DPE values that are similar to those for heteropolyacids (HPAs) such as $H_4SiW_{12}O_{40}$ [19,28]. We extend these preliminary ideas in this work by systematically examining a wider range of acid sites that can form in different alloys and evaluating the role of O–H bond strength and EA of the resulting conjugate base. Furthermore, we seek to determine how DPE compares with experimentally-relevant measurements such as the NH_3 adsorption energy as well as ring-opening reactivity.

2. Computational methodology

First-principle DFT calculations were carried out to determine all of adsorption, reaction, and activation energies reported herein over both ideal single crystal (1 1 1) surfaces and 201-atom cubo-octahedral metal clusters using the Vienna ab initio simulation package (VASP) [29–31]. Planewaves were constructed with an energy cutoff of 396 eV and Vanderbilt ultrasoft pseudopotentials with real space projection operators defining the features of the core region. The correlation and exchange energies were obtained using the Perdew–Wang 91 (PW91) form of the generalized gradient approximation (GGA) [32].

Vacuum-phase calculations were performed spin-polarized using an $18 \times 18 \times 18$ Å unit cell. Ideal single crystal surfaces were modeled as two-dimensional slabs with a 3×3 unit cell and 4 metal layers in the *z*-direction. Slabs were separated by 10 Å and the bottom two layers were held fixed in their bulk atomic positions while the top two layers were allowed to fully relax. Calculations on surfaces were carried out non-spin-polarized until the maximum force upon any atom was less than 0.05 eV/Å; forces were obtained using a fast Fourier transform (FFT) grid with a cutoff of twice the planewave cutoff; wavefunctions were converged to within 10^{-6} eV with a $3 \times 3 \times 1$ *k*-point mesh. Once the geometry was converged, a single-point calculation is performed at a $6 \times 6 \times 1$ *k*-point mesh.

Transition state calculations for ring opening of *HMTHF* were carried out by first determining the minimum energy path (MEP) using the NEB method [33,34] with 8–16 images converged to 0.3 eV/Å to generate initial structures for simulations that use the Dimer method [35] and are run with the same level of accuracy as the optimizations described above. The transition states were verified on a selected number of systems by carrying out a full normal mode analyses. The work function of the metal surfaces was calculated as the difference between the Fermi energy and the maximum *xy*-averaged potential, which is within the vacuum region separating the periodic slabs.

Metal particles were modeled using 201-atom cubo-octahedral particles shown in Fig. 1. Calculations on metal particles were carried non-spin-polarized in a cubic unit cell with a minimum of 12 Å of vacuum separating particles between periodic cells. All structure optimizations reported were carried out until the maximum force upon any atom was less than 0.05 eV/Å; forces were obtained using a fast Fourier transform (FFT) grid with a cutoff of twice the planewave cutoff; wavefunctions were converged to within 10^{-6} eV. These calculations were performed using the γ-point version of VASP. Monopole and dipole moments of the cell were calculated and used to correct the energy; for charged calculations, quadrupole corrections were also applied. The effect of tighter convergence criteria was negligible on the quantities calculated below, as shown in Table S1. The work function was calculated as the difference between the Fermi energy and the *xy*-averaged potential at the point $z = 0$, which is within the vacuum region separating the periodic clusters.

Deprotonation energy (DPE) is defined as the energy difference between the MOH of the cluster/surface and the separated anionic cluster/surface and the H + species (Eq. (1)). Dehydrogenation energy (DHE) is defined as the energy difference between homolytically dissociated ($MO^{\cdot} + H^{\cdot}$) and initial MOH states (Eq. (2)). Electron affinity of the conjugate base (EA) is defined as the negative of the change in energy upon charging the neutral MO site for an extra electron (Eq. (3)). Eqs. (1)–(3) can be rearranged in order to show the direct relationship between DPE, DHE, and EA (Eq. (4)). Alternatively, rather than explicitly calculating charged systems, the work function (WF) of the $MO\cdot$ system can be used to compute the DPE (DPE^{WF}, Eq. (5)); for bulk metals, the WF is essentially equivalent to the negative of electron affinity (EA); however, as discussed below, this is not the case for small 201-atom particles as a result of the small band gaps for finite-sized metal clusters. NH_3 adsorption energies (NH_3 AE) were calculated as the energy difference between the bound state and the MOH cluster plus the energy of NH_3 in a vacuum cell (Eq. (6)). Binding energies (BE) of O^* and OH^* were calculated as the energy differences between the bound state and the metal cluster plus the energy of the $O^{\cdot}$ or $OH^{\cdot}$ in a vacuum cell (Eqs. (7) and (8)). Eq. (9) shows

Download English Version:

https://daneshyari.com/en/article/61085

Download Persian Version:

https://daneshyari.com/article/61085

Daneshyari.com