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Journal of Catalysis 221 (2004) 347–353

JOURNAL OF CATALYSIS

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A comparison between conventional and ultrasound-mediated heterogeneous catalysis: hydrogenation of 3-buten-1-ol aqueous solutions

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Received 25 June 2003; revised 4 August 2003; accepted 4 August 2003

Abstract

A power flow scheme applicable to probe-type ultrasound reactors is presented, that has been deduced from both theoretical estimates and experimental measurements employing a thermal insulated vessel. Under typical conditions for water at 1 atm pressure, 77% of the electrical power is converted into mechanical motion of the probe, that in turn is dissipated to both acoustic power ($\sim 12\%$) and cavitational heating ($\sim 88\%$). Approximately 92% of the mechanical power of the probe was converted into heat, with the remaining power presumably converted into audible acoustic and/or mechanical motion. In a second type of experiment performed here, heterogeneous catalysis experiments have been performed at 298 K in an isothermal (i.e., jacketed) reaction vessel comparing chemistry in conventional (e.g., thermal) versus ultrasound-assisted systems. Both product state distribution and reaction rate measurements have been performed for the hydrogenation (using hydrogen gas) of aqueous 3-buten-1-ol solutions employing Pd-black powder. Products from the heterogeneous catalysis include isomerization to *cis*- and *trans*-2-buten-1-ol, as well as hydrogenation to 1-butanol. A reaction scheme involving surface-bound alkyl-radical species, consistent with previous published work, is proposed to explain product formation. Based on the observed differences in *cis*- to *trans*-2-buten-1-ol ratios in conventional versus ultrasound experiments, employing untreated and prereduced catalysts, it has been determined that ultrasound creates catalyst site(s) enhancing the *cis*-to-*trans* 2-buten-1-ol ratio from 0.25 to 0.55. In addition, comparing the total isomerization to hydrogenation ratio (*cis*- plus *trans*-2-buten-1-ol to 1-butanol ratio), for ultrasound-assisted and conventional catalysis, reveal a ~ 5-fold enhancement in isomerization relative to the more energetically favored hydrogenation due to the application of ultrasound. Finally, the product formation rates for 1-butanol, as well as isomerization plus hydrogenation, revealed that conventional and ultrasound experiments showed both a nonlinear dependence with applied ultrasound power and no differences between untreated and prereduced catalysts. The observed reaction rate enhancements were 1:36:183 for the conventional, 90 W ultrasound, and 190 W ultrasound experiments, respectively.

Keywords: Sonochemistry; Ultrasound; Heterogeneous catalysis; Product state distribution; Kinetics

1. Introduction

In recent years, the chemical effects of ultrasound have been applied to heterogeneous catalysis [1–5], as well as related phenomena of crystallization [6], nanoparticle formation [7], catalyst production [8], and reagent (e.g., pollutant) remediation [9,10]. Pioneering work by Lauterborn and co-workers [11,12] and Blake and Gibson [13] has shown that during cavitation near an extended interface, impingement of liquid "jets" into the surface can occur. This result was obtained from high-speed microcinemagraphic observation that during cavitation bubble implosion often occurs in the vicinity of a solid–liquid interface. These liquid jets are thought to possess speeds of $> 100\ \mathrm{m/s}$ that, in principle, can yield heterogeneous chemistries different from conventional (bulk thermal) techniques. Furthermore, SEM/TEM imaging studies of powders dispersed in liquids before and after sonication suggest that during cavitation high-speed interparticle collisions occur, that can lead to catalyst activation and eventually sintering into larger structures [1]. These combined phenomena, in part, serve as motivation for our work here.

Sonochemically activated heterogeneous catalysis is increasing in popularity [14], unfortunately much of the research activity is not easily accessible in the West [15]. Catalysts employed in previous studies have been primarily nickel (either activated powder or Raney type) [16,17] with

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doi:10.1016/j.jcat.2003.08.008

some investigations using Pd/C [18]. Of particular interest in the Pd/C investigations is the ability of both methanol [14] and formic acid [19] to act as hydrogenation species to alkene or ester compounds. Extending the scope of this prior work, here we examine the hydrogenation of aqueous 3-buten-1-ol solutions employing Pd-black powder. In particular, the branching ratio of isomerization relative to hydrogenation is examined.

In the present work two types of studies are discussed. First, the power flow scheme in probe-type ultrasonic reactors is mapped out relevant to our investigations. The purpose of this measurement is to address issues pertaining to the required power necessary to achieve a given product formation rate. Second, hydrogenation experiments employing a simple water-soluble alkene compound (3-buten-1-ol) are performed so as to examine reaction pathways (i.e., product state distribution) leading to isomerization and hydrogenation. Furthermore, rates of reaction differences in conventional versus ultrasound-assisted catalysis are determined. Finally, one criteria often utilized by industry for evaluating a new synthetic approach is based on the atom economy and the E-factor [20]. The atom economy means the number of atoms in the starting materials that are found in the product. The E-factor is based on the amount of waste (in kg per kg) of product. This factor can also be correlated with the toxicity of waste. Since the atom economy of ultrasound-assisted heterogeneous catalysis in prior studies has often not been identified, in the work here an effort is made to report these values.

2. Experimental

2.1. Materials

Palladium black of 99.9% purity (metals basis; Alfa Aesar), having a nominal BET specific surface area of 20 m^2/g, was used either without prior reduction or prereduced by sonication in a procedure discussed below. Aqueous solutions were prepared using deionized water (18 MΩ-cm) using 3-buten-1-ol (98+% purity; Aldrich Chemical Company) as a reactant. All reagent solutions contained 1.0 wt% 3-buten-1-ol and 50 mg Pd-black powder. The hydrogenations employed hydrogen gas from A&L specialty gas (99.99% purity) at a pressure of 6.8 atm.

2.2. Reaction apparatus and procedure

Commercially available sonication equipment was used to perform the studies described here. A Branson Ultrasonics Model 450 Sonifier II unit, capable of delivering up to 400 W (20 kHz), was used. In addition, both unjacketed (Branson Model 101-021-003) and jacketed (Branson Model 101-021-006) reaction cells were used for studies of either the power flow scheme in our piezoelectric stack on resonant horn (i.e., probe type) reactor or the isothermal heterogeneous catalysis studies at 298 ± 3 K, respectively.

A brief summary of the experimental procedure for experiments employing untreated Pd catalyst material is as follows. First, the catalyst and aqueous reagents were weighed and a (prerun) sampling vial was filled for subsequent analysis. Second, the catalyst/aqueous solution was introduced into the jacketed reaction vessel, manually stirred, and attached to the ultrasonic probe assembly. Third, a NesLab RTE-140 bath circulation unit used to maintain constant temperature throughout an experiment. Temperature was maintained at 298 ± 3 K by setting the bath circulation temperature to account for the temperature difference between the inside of the reactor and the bath temperature during sonication. For example, a linear relationship was observed for this temperature differential as a function of applied electrical power such that a 4.0 K differential existed when 100 W of electrical power was supplied to the system. Fourth, ∼ 10 pressure/vent cycles of the closed reactor cell with hydrogen gas was performed prior to filling with a static pressure of 6.8 atm of hydrogen gas. Fifth, ultrasound was applied for a specified time and electrical power supplied by the sonifier was noted. No mechanical stirring of the solution was performed during sonication. Sixth, the hydrogen gas was vented and the reactor assembly was disassembled. Seventh, the solution was again mechanically stirred and a sample was collected for subsequent analysis by filtering (0.45-µm hydrophilic Millipore filter). Eighth, the reaction vessel was reassembled and the process repeated.

The experimental procedure for experiments employing prereduced Pd catalyst material was identical to that given above except for the following. First Pd catalyst powder, water, and hydrogen gas (6.8 atm) were introduced as described above to the reaction vessel and sonicated for 5 min at 200 W (electrical) power prior to each experiment. Next, the 3BEN reagent was added to the prereduced catalyst solution and mechanically stirred, and the first sample collected nominally 1 min after 3BEN addition. The catalyst prereduction experiments yielded product formation immediately after 3BEN addition, thus the first sample collected at 1 min had measurable products present.

2.3. Reactant and product sample analyses

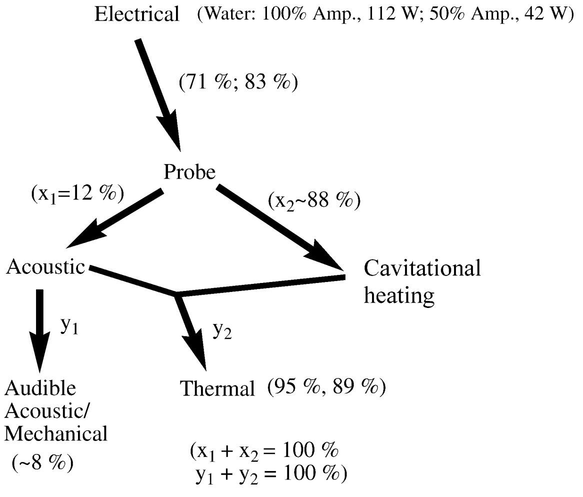
Qualitative identification and quantitative analyses were performed using an Hewlett-Packard GC/MS (5890 Series II GC and 5972 MSD) equipped with a DB-5 column (30 m, 0.2 mm i.d., 1.00-µm film). Manual sample injections (1.0 µL) in triplicate were performed as part of the routine data reduction. A statistical analysis revealed that relative concentrations were accurate to within ±7.0% of the stated percentage concentration, whereas the accuracy among manual injections was ±15%. Analyses of the liquid samples both prior to sonication and after reactions allowed an estimate of the mass conservation to be performed. Of particular interest is whether the application of ultrasound results in degradation of the reactant 3-buten-1-ol into (undesirable) products such as carbon dioxide, hydrogen, and water, as has been observed for other aqueous organic solutions [21,22]. Such analyses allow the atom economy to be determined [20].

3. Results

3.1. Power dissipation scheme

An important aspect of understanding ultrasound-assisted heterogeneous catalysis is to map out the ultrasound power flow scheme. The nature of this investigation is to understand power flow in a probe-type ultrasonic reactor. The pertinent question that arises is: For a given electrical power output (W) from the power supply of the sonifier unit, what power flow pathways exist and what are their relative importance leading to the eventual conversion into heat? Our analysis of the power dissipation scheme closely follows the approach taken by Loning et al. [23].

The ultrasonic unit is composed of three primary parts: 1, power supply; 2, convertor consisting of piezo-ceramic elements; and 3, probe assembly. Put simply, electrical power from the power supply is sent to the convertor where a minor fraction is converted into heat and a major fraction is converted into mechanical motion of the probe. The power flow scheme as outlined above for deionized, air-saturated, water at 1 atm pressure, at both 100 and 50% amplitude settings, is illustrated in Scheme 1. For a particular amplitude, the electrical power delivered by the power supply depends on the nature of the coupling between the titanium probe and the fluid being sonicated. It is interesting to note that for the hydrogenation experiments employing 6.8 atm hydrogen gas, 190 W electrical power at 60% amplitude was delivered. This value can be compared to 112 W of power at 100% amplitude under atmospheric conditions (e.g., only 1.0 atm pressure). Therefore, pressurization with hydrogen is seen to significantly enhance coupling between the probe and the fluid.



Scheme 1. A schematic illustration of the power dissipation scheme for our probe-type ultrasonic reactor is presented. Percentages have been arrived at using both experimental and theoretical estimates (see text) using deionized (air saturated) water as the fluid at 1 atm pressure.

Scheme 1 can be understood by considering the following. From the discussion above, electrical power is sent to a convertor that generates mechanical motion from electrical energy, the degree of total power dissipation set by the coupling between the solution and the titanium probe, as well as the percentage full-scale amplitude setting of the sonifier unit. By operating the probe in both water and air, where the latter yields only dielectric losses in the convertor, the percentage power transfer to the 1.27-cm-diameter probe can be determined. Hence, the 71 and 83% conversions of electrical power into mechanical power should be applied to the 112 and 42 W electrical powers, respectively. Next, mechanical motion of the probe can generate the following effects: (1) acoustic power; (2) nonlinear cavitational heating; and (3) noncavitating mechanical mixing such as acoustic streaming and radiation pressure [24]. The former has been estimated from the power transmission coefficient from titanium to water using appropriate acoustic impedances [25]. Finally, a calorimetric measurement of the temperature rise of water (employing the unjacketed insulated reactor) was used to compute the pathway percentage into heat with the remainder assigned to audible acoustic/mechanical power dissipated to the surroundings. As the complete conversion of acoustic power into heat cannot account for the observed (calorimetric) heating of water, a combination of cavitational heating and/or fluid mixing effects must also be important.

The ultrasound-assisted and conventional heterogeneous catalysis experiments were all performed at 298 ± 3 K using a jacketed (water-cooled) reactor. It is unclear to what degree both purely acoustic power and cavitational heating power gives rise to enhancements in heterogeneous reaction rates and selectivity (vide infra). An attempt was made here utilizing the isothermal reactor to exclude bulk-heating effects as the principle cause of differences in these types of chemistry. In principle, transient effects such as cavitational heating include effects such as bubble formation and collapse near an interface, perhaps causing liquid jets incident upon the catalyst surface and inducing chemistry [11–14].

3.2. Hydrogenation and isomerization

A primary objective of this study is to perform a direct comparison between conventional versus ultrasound-mediated heterogeneous catalysis. We have chosen 3-buten-1-ol (3BEN) for this comparison for the following reasons: (1) It is a relatively simple, water-soluble, alkene compound. (2) Hydrogenation employing a standard catalyst and hydrogen gas can be investigated. (3) The relative conversion to 1-butanol (hydrogenation) versus *cis*- and *trans*-2-buten-1-ol (C2BEN and T2BEN) (isomerization) can be studied. (4) A comparison between product formation rates yielding enhancements arising from the application of ultrasound can

Table 1
Product distribution as a function of reaction time for ultrasound and conventional experiments

Time (min)	3BEN	1BUT	T2BEN	C2BEN
Ultrasound UT1: (190 W)				
0	100	0	0	0
1	75.43	8.85	10.07	5.65
2	66.31	12.71	13.47	7.51
3	57.85	15.94	17.15	9.06
4	29.13	29.38	28.98	12.51
5	4.81	44.34	40.72	10.13
Ultrasound UT2: (92 W)				
0	100	0	0	0
4	89.7	3.88	4.1	2.32
8	67.85	10.39	13.5	8.26
12	53.38	14.77	20.63	11.22
16	37.91	22.01	27.47	12.61
20	20.25	28.79	36.77	14.19
Conventional UT3 (no ultrasound)				
0	100	0	0	0
50	95.36	3.66	0.98	0
100	89.83	7.67	2.09	0.41
150	85.23	10.98	3.1	0.69
200	79.03	15.37	4.37	1.23
250	73.6	18.81	5.86	1.73
Conventional PR1 (prereduced; 90 W ultrasound)				
1[a]	86.11	5.36	5.94	2.58
4	74.97	9.04	10.64	5.35
8	65.13	13.22	14.51	7.14
12	33.07	24.99	29.62	12.32
16	4.33	41.85	44.5	9.32
Conventional PR2 (prereduced; no ultrasound)				
1[a]	87.1	5	5.38	2.52
50	80.76	8.2	7.48	3.56
100	77.11	10.52	8.63	3.74
150	73.14	13.01	9.74	4.11
200	68.71	15.55	11.27	4.47
250	65.65	17.6	11.86	4.89

[a] After Pd prereduction 3BEN was added to solution, the solution was mechanically mixed, and the first sample was collected. Approximate mixing time for this first sample was 1 min.

be examined. The third item above could have commercial significance as ultrasound may provide an effective means of converting a terminal alkene to internal *cis*- and *trans*-alkenes.

Experimental data for untreated catalyst experiments (UT1, UT2, UT3 runs) and two prereduced catalyst experiments (PR1, PR2 runs) are presented in Table 1. Listed are the mass percentages for the 3BEN, 1BUT, T2BEN, and C2BEN species as a function of time. The average mass conservation for the three ultrasound experiments was computed to be 104 ± 10%, indicating that cavitational effects, should they be present to an appreciable extent, do not effectively degrade the reagent 3BEN into products other that those desired. Thus a very favorable atom economy exists (~ 100%) for these experiments.

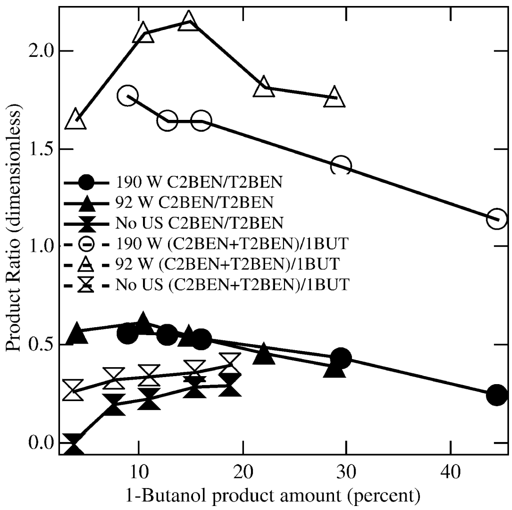


Fig. 1. A plot of the *cis*- to *trans*-2-buten-1-ol ratio (C2BEN/T2BEN) is given for the 190 W ultrasound, 92 W ultrasound, and conventional experiments, as a function of percentage 1-butanol product formed. Also presented is the total isomerization to hydrogenation ratio, (T2BEN + C2BEN)/1BUT. No prior reduction of the catalyst was performed.

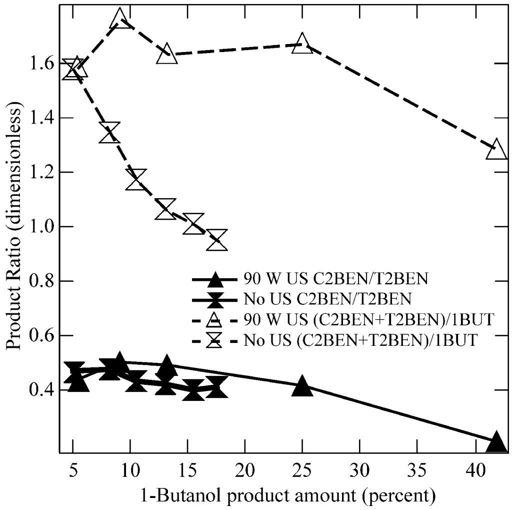


Fig. 2. A plot of the *cis*- to *trans*-2-buten-1-ol ratio (C2BEN/T2BEN) is given for the 92 W ultrasound and conventional experiments, as a function of percentage 1-butanol product formed. Also presented is the total isomerization to hydrogenation ratio, (T2BEN + C2BEN)/1BUT, similar to Fig. 2. Prereduction of the catalyst was performed using hydrogen gas and the application of ultrasound (see text).

Fig. 1 presents a reduced form of the data presented in Table 1 for the untreated catalyst experiments (UT1, UT2, and UT3). In particular, the C2BEN/T2BEN isomer ratio is illustrated, as is the total isomerization to hydrogenation ratio, given as (C2BEN + T2BEN)/1BUT, as a function of percentage 1BUT product formed. In a similar fashion, Fig. 2 presents the same product ratios except that the prereduced (PR1 and PR2) experimental data have been used. It is important to note that additional experiments revealed that no product formation was observed in the absence of catalyst

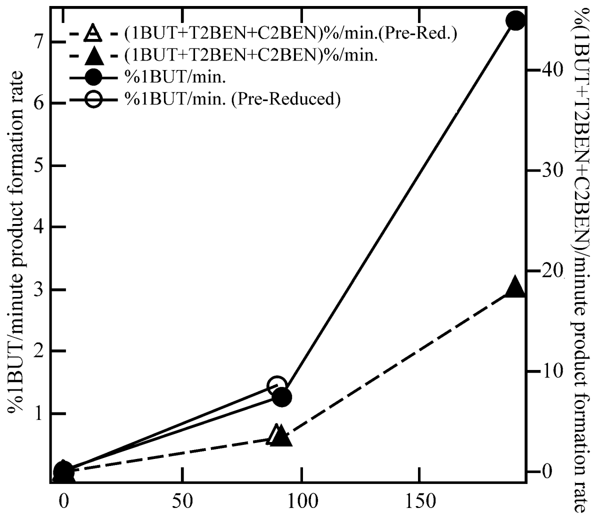


Fig. 3. Product formation rates are presented for 1BUT and 1BUT + T2BEN + C2BEN (hydrogenation plus isomerization), for both untreated Pd catalysts and prereduced Pd catalysts. Note the nonlinear dependence in product formation rate with applied ultrasonic power, and the nearly identical product formation rates between untreated and prereduced catalysts.

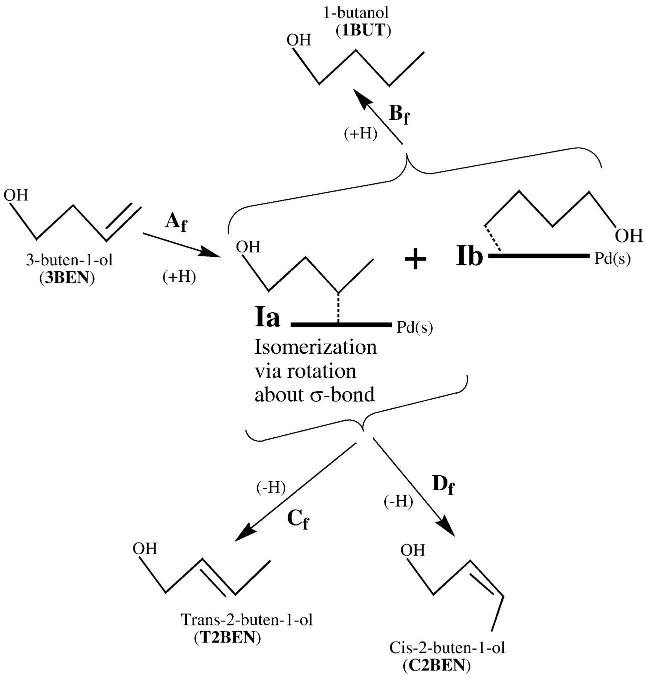
and/or hydrogen gas. Thus 3BEN plus catalyst and hydrogen are needed for chemistry to proceed.

3.3. Rate of reaction

Another important parameter to characterize is the rates of product formation in conventional and ultrasound-assisted systems, for both untreated and prereduced Pd catalyst experiments. Fig. 3 presents the percentage mass of product formed per minute, for 1BUT, as well as 1BUT + T2BEN + C2BEN (total product), as a function of applied ultrasound electrical powers. Here zero ultrasound power corresponds to the conventional catalysis results. Several points are worth noting about Fig. 3. First, the 1BUT + T2BEN + C2BEN and 1BUT formation rates are strongly correlated with one another. The relation between these two rates are such that for the ultrasound experiments only the 1BUT production rate is lower by a factor of 2.5 compared to the 1BUT + T2BEN + C2BEN product formation rate. Second, a nonlinear relationship exists between product formation rates and applied ultrasound power. In particular, the 1BUT product formation rates for the conventional, 90/92 W ultrasound, and 190 W ultrasound experiments were observed to have a ratio of 1:36:183, respectively. Third, and perhaps most importantly, within experimental error, the product formation rates are equal for the untreated and prereduced Pd catalyst experiments.

4. Discussion

In this section two main issues are discussed. First, a reaction scheme is presented that draws on similarities between hydrogenation (using Pd) of the aqueous 3-buten-1-ol and gaseous 1-butene systems, where the latter has been extensively studied previously. Second, the type of catalyst active site(s) responsible for chemistry in the ultrasound-irradiated and no ultrasound (blank) experiments will be approximately accounted for, despite there being insufficient knowledge for an absolute determination of their properties.



Scheme 2. A reaction scheme illustrating a proposed mechanism for isomerization and hydrogenation is given. Rate coefficients for the various forward reaction pathways are given as A, B, C, and D. Important reaction intermediates proposed to exist, from which products are formed, are labeled Ia and Ib.

A reaction scheme that accounts for product formation in our experiments, and more importantly is consistent with previously published studies, is presented in Scheme 2. This scheme can be interpreted as follows. Hydrogen atom addition, with rate coefficient A, generates both Ia (C4 H-atom addition) and Ib (C3 H-atom addition). The addition of a second surface-adsorbed H atom to Ia or Ib, with rate coefficient B, generates the hydrogenated product 1BUT. Owing to the fact that the isopropyl radical is more stable than the ethyl radical by 2.5 kJ/mol [26], and the bonding of each to the Pd surface is assumed identical, the Boltzman distribution of states expression suggests that the Ia/Ib ratio at 298 K is 2.7. This two-step alkene hydrogenation scheme where the intermediate is a relatively stable surface bound alkyl-radical species was originally proposed by Horuiti and Polayni nearly 70 years ago [27]. Prior literature support for this mechanism (process A and B) comes from identical products being obtained in both equilibrated and nonequilibrated hydrogen/deuterium mixtures [28–30]. Furthermore, recent experimental work that determined hydrogen gas reaction orders (~ 0.5) suggests that either process A or B can be rate limiting [31,32]. Also taken from prior published mechanisms [30] is the C2 hydrogen atom elimination reactions yielding T2BEN and C2BEN, each proceeding with rate coefficients C and D, respectively. It is clear that only species Ia can yield T2BEN and C2BEN, as H elimination from C3 of species Ib would yield the reagent 3BEN. This mechanism is consistent with our data as in principle efficient rotation about the C2–C3 σ-bond prior to H-atom elimination can occur for the surface-bound alkyl radical species yielding the isomerized product.

An examination of Figs. 1 and 2 can yield insight into the type of catalyst active site(s) responsible for the observed chemistry. For example, Fig. 1 (non prereduced catalyst) shows that the C2BEN/T2BEN ratios for the ultrasound and no ultrasound (blank) experiments are 0.55 and 0.25, respectively. However, for the prereduced catalyst experiments of Fig. 2 the ultrasound and no ultrasound ratios are both ~ 0.50. It can be proposed therefore that ultrasound either applied as part of the catalyst prereduction process, or during the course of an experiment, acts to create catalyst active site(s) that increase the C2BEN/T2BEN ratio, and that even after ultrasound is not applied to the system a persistent high C2BEN/T2BEN ratio exists.

A somewhat more interesting situation arises for the isomerization relative to hydrogenation ratio, (C2BEN + T2BEN)/1BUT (which we will denote I/H). For this ratio, Fig. 2 shows that the ultrasound and blank values of ~ 1.7 and 0.3, respectively, differ by a large amount. It can be proposed that ultrasound prepares actives site(s) greatly favoring a large I/H ratio. Furthermore, from the pre-reduced catalyst results of Fig. 2 it is seen that the blank experiment has the I/H ratio monotonically decreasing with increasing percentage 1BUT formation. This suggests that the catalyst site(s) responsible for the I/H ratio are less stable during the course of an experiment and hence change over time, unlike the site(s) controlling the C2BEN/T2BEN ratio. Examining the proposed mechanism of Scheme 2, since Ia is a precursor to product formation, it can be concluded that the ratio of rate coefficients $(C + D)/B$ is enhanced by the application of ultrasound.

As a point to note, despite there being differences in product state distribution according to Figs. 1 and 2, the overall rate of product formation for the no ultrasound and 92 W ultrasound experiment of Fig. 3 shows that there is little difference in the rate of product formation between the prereduced and reduced experiments. Also, since the rate of product formation is nonlinear in applied ultrasound power, it is most cost effective (% product/W is greater) to operate at the higher ultrasound powers.

The role that the OH group in 3BEN plays in the isomerization and hydrogenation reactions cannot be deduced from our data employing water as a solvent. As no isomerization was observed without the presence of hydrogen gas, the OH group likely does not bond to the surface and hence play a role in isomerization. To test this hypothesis, we employed methanol as a solvent and performed two experiments for the non-prereduced 3BEN hydrogenation—one at 40 W and the other at 185 W (electrical) ultrasound powers. These experiments showed an identical *cis*/*trans* ratio with percentage 1BUT formation and comparable rates of reaction compared to the aqueous experiments. Thus OH group adsorption to the surface (from methanol, 3BEN, T2BEN, or C2BEN) does not appear to control product state distribution. Furthermore, as our mass conservation was $\sim 100\%$ and little butanal was detected (less than 2%), 3BEN apparently did not act as a hydrogenation species. This result differs somewhat from prior published work [14].

5. Conclusions

For the 3BEN molecule studied here, the conversion of a terminal alkene into an internal one forming both *cis* and *trans* isomers with an enrichment ~ 5-fold compared to conventional catalysis was noted. In addition, a comparison between untreated and prereduced catalysts for conventional experiments has shown that intrinsically different catalyst site(s) exist, as reflected in the product state distributions. The ability of ultrasound to enhance the production of less energetically favorable products has the potential of being useful in commercial synthesis. Mechanistically, based on prior work, the C3 surface-adsorbed alkyl radical intermediate (Ia) bound to the Pd surface can undergo C3 H-atom addition to 1-butanol, or C2 H-atom elimination to *cis*- and *trans*-2-buten-1-ol. One goal of future work proposed here will be to find experimental conditions (catalyst type, ultrasound power, hydrogen gas pressure, etc.) that maximize differences between ultrasound and conventional catalytic processing methods. Consistent with this goal is to monitor energy expenditure resulting in product formation. The power flow scheme presented here is the first task undertaken to accomplish this goal. This information is likely crucial in assessing energy savings for a process. For example, if enrichment in, say, *cis*-to-*trans* isomers for a synthetic process can be obtained with ultrasound, a cost analysis must consider ultrasound-expended energy compared to conventional (thermally) generated products plus the cost associated with sample purification (e.g., distillation).

The experimental data presented here have shown that differences in product state distribution and reaction rate exist between conventional and ultrasound-assisted heterogeneous catalytic systems. Much work is needed to map out these differences as a function of temperature, reagent concentration (hydrogen gas pressure and liquid phase concentrations), reaction time (extent of reaction), catalyst type, and ultrasound/static reactor operating conditions (i.e., power).

Acknowledgments

We note many fruitful discussions of this work with James White and John Holladay of Pacific Northwest National Laboratory (PNNL). The encouragement, and yet critique, of this work by them is particularly noted. In addition, the advice of Dr. Ajit Mal of UCLA pertaining to the ultrasonic power dissipation scheme is greatly appreciated. Financial support was obtained through a Laboratory Directed Research and Development (LDRD) grant administrated by PNNL. PNNL is operated by Battelle for the US Department of Energy.

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