ACS Catalysis
VIEWPOINT
pubs.acs.org/acscatalysis

Hydrogen Storage and Energy Recovery Using Aldehydes and Ketones: A Key Role for Catalysis

Robert J. Angelici*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, United States

1. INTRODUCTION

Global warming and its impact on the environment and society are driving governments around the world to mandate reductions in carbon dioxide emissions. The European Union has implemented the EU Emissions Trading System which is intended to reduce carbon dioxide emissions through a cap and trade mechanism.[1−3] In the U.S., the EPA is requiring fossil-fuel-fired electric utilities and refineries to reduce their greenhouse gas emissions beginning in mid 2012.[4] These regulations will force industries to replace fossil fuels with other sources of energy that do not produce carbon dioxide. Among the energy sources that are carbon-free are solar, wind, and ocean waves. All of them produce electricity, but they do so at times that do not consistently match the daily or seasonal variations in energy needs of society. While these forms of energy have the potential to offset much of our dependence on fossil fuels, it is the storage of this energy at off-peak demand times that is required to make these nonpolluting forms of energy viable.

One approach to storing off-peak electricity is to convert it into a nonpolluting chemical fuel such as hydrogen (dihydrogen). While H_2 has the great advantage of producing only water when it reacts with oxygen in air (eq 1), it has a very low boiling point and is highly flammable which makes it

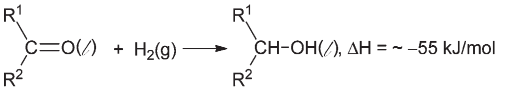
$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\ell), \quad \Delta H = -285\ \text{kJ/mol} \quad (1)$$

very difficult to store and to be transported. A variety of materials have been proposed as storage media (SM) for hydrogen[5−11] (eq 2) including metal hydrides,[5−11] metal-organic frameworks,[12,13]

$$\mathrm{SM} + \frac{x}{2}H_2(g) \rightleftharpoons \mathrm{SM}\cdot x\mathrm{H} \quad (2)$$

carbon,[14−16] organic materials,[17,18] CO_2/formic acid,[19−22] boron−nitrogen compounds,[23] and other solids and liquids.[5−11,24] All of them have shortcomings related to the conditions required for hydrogen uptake or release, selectivity of the reactions, stability of the absorbent, and the energy required to provide low and high pressures and temperatures needed to drive reaction 2.[5−11]

In this Viewpoint, I am proposing that aldehydes and ketones be considered for storage of H_2 that is generated by the electrolysis of water[25,26] using off-peak demand electricity. The hydrogen storage reaction (HSR) would be accomplished by the hydrogenation of an aldehyde/ketone according to eq 3. This is an exothermic reaction with a ΔH of approximately −55 kJ/mol for

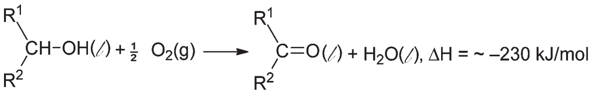


$$\mathrm{R^1R^2C{=}O}(\ell) + H_2(g) \longrightarrow \mathrm{R^1R^2CH{-}OH}(\ell),\ \Delta H = \sim -55\ \text{kJ/mol} \quad (3)$$

R^1 = aryl or alkyl
R^2 = H, aryl or alkyl

aldehydes/ketones such as benzaldehyde and acetone.[27] Thermodynamics are favorable for this hydrogenation, and a variety of catalysts are known to facilitate these reactions as described in the following sections.

Energy from the hydrogen stored in the product alcohol (in eq 3) can be recovered in the catalyzed reaction of the alcohol with oxygen/air to give water and the original aldehyde/ketone (eq 4). The sum of the hydrogen storage reaction (HSR, eq 3) and the energy recovery



$$\mathrm{R^1R^2CH{-}OH}(\ell) + \tfrac{1}{2}O_2(g) \longrightarrow \mathrm{R^1R^2C{=}O}(\ell) + H_2O(\ell),\ \Delta H = \sim -230\ \text{kJ/mol} \quad (4)$$

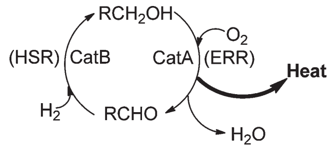
reaction (ERR, eq 4) is simply the combustion of H_2 (eq 1), and the sum of the ΔH values for eqs 3 and 4 is the ΔH for eq 1. The energy recovery reaction (ERR, eq 4) produces heat (~230 kJ/mol), which is 55 kJ/mol less than that (285 kJ/mol) for the direct combustion of H_2 (eq 1). Thus, the cost of storing hydrogen in the form of an alcohol is ~55 kJ/mol, although some of this energy (eq 3) is, in principle, usable. However, the storage of hydrogen in the form of a liquid alcohol is much more practical than storing neat H_2. The heat energy produced in the ERR (eq 4) could be used to heat buildings and in industrial processes. Heat from this reaction has been used to drive the endothermic dehydrogenation of alcohols ($R_2CHOH \rightarrow R_2C{=}O + H_2$) as well as a variety of other hydrogen-containing organic compounds, which are proposed as hydrogen storage media, as described recently in a patent.[28]

The overall process for hydrogen storage in an aldehyde and energy recovery from its alcohol is shown in Scheme 1. For an aldehyde/ketone to be a viable hydrogen storage medium, the ERR must be highly selective for the generation of the aldehyde; this requires finding or choosing a catalyst (CatA) that is specific for this reaction. The HSR must also make use of a catalyst

Special Issue: Victor S. Y. Lin Memorial Issue

Received: April 5, 2011
Published: May 13, 2011

Scheme 1. Overall Process for H_2 Storage (HSR) and Energy Recovery (ERR) Using an Aldehyde/Alcohol System



(CatB) that is selective for the formation of the alcohol. In the next two sections are described known catalysts for both the HSR and ERR reactions. The availability of promising catalysts for these reactions suggests that aldehydes/ketones could be key components in a realistic energy storage/energy recovery system. In the next section, the HSR and ERR reactions for the benzaldehyde/benzyl alcohol hydrogen storage system are analyzed. In the subsequent section, the use of several ketones/alcohols in hydrogen storage systems (Scheme 1) are discussed briefly.

2. HYDROGEN STORAGE AND ENERGY RECOVERY SYSTEMS

2.1. Benzaldehyde/Benzyl Alcohol in a Hydrogen Storage/Energy Recovery System (Scheme 1). The benzaldehyde/benzyl alcohol system has been chosen to illustrate the possibilities for aldehydes/ketones in hydrogen storage and energy recovery because these compounds have several favorable properties. As described in their MSDS's, both benzaldehyde (mp −26 °C, bp 179 °C) and benzyl alcohol (mp −15 °C, bp 205 °C) are liquids which means that they can be interconverted in the HSR and ERR reactions without using an added solvent, and they can be transported by pipeline and tankers. Both benzaldehyde and benzyl alcohol are flammable, but they have relatively high autoignition temperatures (192 and 436 °C, respectively) and are much less flammable than gasoline. Being FDA-sanctioned and generally recognized as safe for foods,[29] they pose a low toxicity hazard. Benzaldehyde is described as having an "aromatic (slight)" odor, and benzaldehyde is described as having a "pleasant almond-like odor" and is used as a flavoring agent and odorant. Benzaldehyde is "very slightly soluble in cold water", which will make it easily separable from the water byproduct in the ERR (eq 4). Both benzaldehyde and benzyl alcohol are currently produced on a large scale.

A key component in a successful hydrogen storage/energy recovery system (Scheme 1) based on benzaldehyde/benzyl alcohol is CatA for the ERR (eq 5). The ΔH for this reaction is the difference between ΔH (−285 kJ/mol) for eq 1 and ΔH for the hydrogenation of benzaldehyde (−53.9 kJ/mol, eq 3).[30] Numerous heterogeneous catalysts have been demonstrated for this reaction. They are summarized in several reviews.[31−34] In Table 1 are listed examples of these catalysts and the conditions under which they catalyze reaction 5. Relatively inexpensive metals (Mn, K, Cu, Mo, and V) comprise the catalysts in entries 1−5.[35−39] Although the conditions for these reactions were not necessarily chosen to optimize the conversions of benzyl alcohol, the aldehyde yields are generally very high. Selectivities for benzaldehyde are especially important so as to minimize losses of the alcohol to byproduct; the selectivities for benzaldehyde are all greater than 97%. Most of the reactions use 1 atm of O_2 pressure, but entry 1 uses air.

$$\mathrm{PhCH_2OH}(\ell) + \frac{1}{2}\mathrm{O_2(g)} \xrightarrow{\mathrm{CatA}} \mathrm{PhCHO}(\ell) + \mathrm{H_2O}(\ell),$$

$$\Delta H = -231\ \mathrm{kJ/mol} \qquad (5)$$

Entries 6−8 make use of supported ruthenium hydroxide/oxide.[40−42] The temperature and O_2 pressure conditions are mild, and selectivities are very high (>99%). Other catalysts consisting of ruthenium hydroxide/oxide supported on various solids have also been reported.[32,43]

Nanogold on solid supports catalyzes the oxidation of benzyl alcohol to benzaldehyde often with very high selectivities, as shown in entry 9.[44] Nanogold on other supports has also been reported to catalyze this reaction.[32,45−47] The mixed metal nanoparticles, Au−Pd/SBA-15, supported on mesoporous SBA-15, are very active and are more resistant to agglomeration because the metal particles are located in the mesopores of SBA-15 (entry 10).[48] The gas-phase oxidation of benzyl alcohol is catalyzed by Ag supported on CaO, as well as MgO and SiO_2, to give benzaldehyde with very high selectivities (entry 11).[49] A few supported Pd catalysts have been reported,[32] such as Pd metal supported on a clay which catalyzes reaction 5 with high selectivity (96%).[50]

The catalyst systems summarized in Table 1 clearly indicate that there are several promising catalysts for the recovery of energy from the hydrogen in benzyl alcohol (eq 5). Which catalytic system is optimal for this reaction depends upon the cost of the catalyst, its lifetime, the temperature, pressure, equipment requirements, among many other factors.

Even more firmly established than catalysts for the ERR (eq 5) are catalysts for the hydrogen storage reaction (HSR) for benzaldehyde (eq 6). A variety of catalysts are known for this reaction.[51] A supported Ni/SiO_2 catalyst gives very high selectivities (∼99%) for benzyl alcohol at 120° under 1 atm of H_2 in a flow reactor.[52] Copper supported on SiO_2, ZrO_2, and carbon gives the alcohol at a relatively low temperature (100 °C) and 1 atm of H_2.[53,54] Supported Pd catalysts, such as Pd/bentonite, are also effective for the hydrogenation of benzaldehyde to benzyl alcohol with 100% selectivity under mild conditions (100 °C, 5 atm H_2).[55] Ruthenium supported on mesopolymers are also highly active for benzaldehyde hydrogenation to benzyl alcohol (99% selectivity) at room temperature under 40 atm H_2 pressure.[56] In addition to the specific catalysts mentioned above for reaction 6, many more are reported in the literature. It is therefore very likely that an efficient catalyst can be chosen for this reaction.

$$\mathrm{PhCHO}(\ell) + \mathrm{H_2(g)} \xrightarrow{\mathrm{CatB}} \mathrm{PhCH_2OH}(\ell),$$

$$\Delta H = -53.9\ \mathrm{kJ/mol} \qquad (6)$$

While there are many advantages to the use of benzaldehyde/benzyl alcohol in the HSR and ERR system described in Scheme 1, this system would be suitable for use only in stationary (nontransportation) applications because the amount of combustible hydrogen (2H in $C_6H_5CH_2OH$) is only 1.9% by weight, which is short of the U.S. Department of Energy target value of 6.5% for use in transportation fuels.[9] Even the inclusion of two or three hydroxymethyl groups in the molecule, as in $C_6(CH_2OH)_xH_{6-x}$, where x = 2 or 3, would increase the combustible hydrogen to only 2.9% and 3.6% for n = 2 and 3, respectively.

Table 1. Examples of Catalysts for the Energy Recovery Reaction (ERR, eq 5) Using Benzyl Alcohol

entry	CatA	conditions[a]	yield	selectivity	ref
1	$KMn_8O_{16} \cdot nH_2O$	110 °C, 0.2 atm (air), toluene, 4 h, batch	95%	100%	35
2	γ-MnO_2	110 °C, 1 atm, toluene, 2 h, batch	75%	>99%	36
3	K−Cu−TiO_2	210 °C, 1 atm, none, flow	72%	>98%	37
4	CuMn/Al_2O_3	100 °C, 1 atm, toluene, 4 h, batch	91%	>99%	38
5	$(NH_4)_4PMo_{11}VO_{40}$	250 °C, 1 atm, none, flow	62%	97%	39
6	$Ru(OH)_x/Al_2O_3$	80 °C, 1 atm, toluene, 0.5 h, batch	45%	>99%	40,41
7	$Ru(OH)_x/TiO_2$	80 °C, 1 atm, toluene, 0.5 h, batch	62%	>99%	40,41
8	$Ru(OH)_x$/CaO−ZrO_2	90 °C, 1 atm, *o*-xylene, 0.75 h, batch	100%	100%	42
9	Au/Cu−Mg−Al oxides	90 °C, 1 atm, $C_6H_3Me_3$, 3 h, batch	98%	>99%	44
10	Au−Pd/SBA-15	80 °C, 0.2 atm (air), H_2O, 8 h, batch	39.2%	97%	48
11	Ag/CaO	240 °C, <1 atm, none, flow	22%	>99.5%	49

[a] Reaction temperature, O_2 pressure, solvent, reaction time, batch or flow reactor.

These latter compounds also have the disadvantage that they are solids at room temperature, and their syntheses are much more expensive than benzyl alcohol.

2.2. Ketones and Their Alcohols in Hydrogen Storage/Energy Recovery Systems (Scheme 1). Although the benzaldehyde/benzyl alcohol system has many positive features, it is worth considering ketone/alcohol systems that may have advantages under certain circumstances. Acetophenone (mp 20 °C, bp. 202 °C) may have an advantage if conditions for the ERR (eq 4) lead to overoxidation of benzaldehyde to benzoic acid (although it is not an issue under the conditions discussed above, Table 1). Hydrogenation of acetophenone to 1-phenylethanol (mp 21 °C, bp 204 °C) is catalyzed by a variety of heterogeneous catalysts including Cu−Cr oxide, Ni,[57] Pd, Pt,[51] and Co.[58] The ERR reaction (eq 4) of 1-phenylethanol is catalyzed by several of the same catalysts used for the oxidative-dehydrogenation of benzyl alcohol: $Ru(OH)_x$/CaO−ZrO_2,[42] $Ru(OH)_x/TiO_2$,[40] Au/Cu−Mg−Al oxides,[44] Bi−Pd/Al_2O_3,[59] and others.[32,33] Selectivities of these oxidations to acetophenone are typically higher than 98%. One disadvantage of the acetophenone/1-phenylethanol system is the lower mass of combustible hydrogen (2H in $C_6H_5CH(OH)CH_3$), 1.6%.

In the acetone/*i*-propanol system, combustible hydrogen in *i*-propanol is 3.3%. The higher hydrogen density in *i*-propanol, as compared with benzyl alcohol, has the advantage of reduced storage volume. However, the lower boiling points for acetone (56 °C) and *i*-propanol (82 °C), and therefore higher volatilities, may pose more safety issues, although these liquids are currently produced and shipped on a very large scale.[60] Both the hydrogenation of acetone and oxidative-dehydrogenation of *i*-propanol are performed industrially.[60]

Like acetone and *i*-propanol, methyl ethyl ketone (mp −87 °C, bp 80 °C) and 2-butanol (mp −115 °C, bp 100 °C) are produced commercially and are interconverted by hydrogenation of methyl ethyl ketone and oxidative-dehydrogenation of 2-butanol. Recently, new catalysts for the oxidative-dehydrogenation of 2-butanol have been reported. One of these, $KMn_8O_{16} \cdot nH_2O$, catalyzes the ERR (eq 4) of 2-butanol to give methyl ethyl ketone with 100% selectivity in refluxing toluene (110 °C) under 1 atm of O_2.[35] The oxidative-dehydrogenation of 2-octanol, a homologue of 2-butanol, is catalyzed by $Ru(OH)_x/TiO_2$ in toluene at 80° under 1 atm of O_2 to give an 84% yield of 2-octanone with >99% selectivity.[40]

Other ketones worth considering for hydrogen storage are cyclohexanone and possibly cyclopentanone. Both can be hydrogenated to the corresponding alcohol.[51] Cyclohexanol undergoes oxidative-dehydrogenation in the presence of 1 atm of O_2 and the $KMn_8O_{16} \cdot nH_2O$ catalyst to give cyclohexanone in 60% yield with 100% selectivity at 110 °C.[35] Cyclopentanol conversion to cyclopentanone in 76% yield with >99% selectivity at 80 °C is catalyzed by $Ru(OH)_x/TiO_2$ under 1 atm of O_2.[40] The ketones discussed in this section, acetophenone, acetone, methyl ethyl ketone, and cyclohexanone, represent a range of properties that offer options for hydrogen storage, and catalysts are known for their HSR and ERR reactions.

3. CONCLUSIONS

Recognizing the importance of reducing carbon dioxide emissions, many research efforts and resources have been devoted to energy systems based on the reaction of H_2 with O_2 to form H_2O. Such systems require the generation of H_2 from nonfossil sources such as the electrolysis of water[25,26] using wind or solar energy or from biomass.[61] Because of the nature of H_2 production by these methods, it is necessary to find ways to store H_2 that is generated in excess of that required by industry and society. Despite the many attempted approaches to hydrogen storage, as noted in the Introduction, no system is yet up to the challenge. One of the difficulties faced in designing such a system is the thermodynamics of eq 2,[8,11,62] which precludes both the forward and reverse reactions from being highly favorable without using energy-consuming methods of changing the H_2 gas pressure or the temperature. In addition, the kinetics and selectivity of this reaction are often not suitable for practical hydrogen storage and release. Of course, the handling of gaseous H_2 poses major challenges for any hydrogen-gas-based energy system.

In the system (Scheme 1) that is proposed herein, hydrogen is reacted (HSR) with an aldehyde or ketone to give a liquid alcohol. This is a thermodynamically favorable reaction for which numerous heterogeneous catalysts are known. Rather than liberating H_2 from the alcohol,[63−66,] as is characteristic of most hydrogen storage systems (eq 2), the proposed recovery of energy from the alcohol involves its selective combustion to the original aldehyde/ketone and water. This reaction (eq 4) is also highly favorable thermodynamically and yields about 230 kJ of heat energy per mol of alcohol. Numerous catalysts, many quite recently reported, selectively facilitate this reaction.

The major goal of this Viewpoint is to suggest that aldehydes and ketones be considered as hydrogen storage media for a system that converts excess electric energy to a storable heat source. Much of the fundamental catalysis research on the hydrogen storage (HSR) and energy recovery (ERR) reactions has been accomplished. Evaluation of the best aldehydes/ketones and best catalysts is yet to be done; optimizing reaction conditions to achieve high yields and selectivities, along with long catalyst lifetime, is necessary. This system is most suitable for stationary applications, such as organizations/communities that require both electricity and heat that could be provided by wind and solar installations. The aldehyde/ketone approach is a reasonable first step in the direction of storing off-peak electric energy for later use in heating applications.

AUTHOR INFORMATION

Corresponding Author

*E-mail: angelici@iastate.edu.

REFERENCES

(1) Ellerman, A. D.; Joskow, P. L. 2008, http://www.pewclimate.org/docUploads/EU-ETS-In-Perspective-Report.pdf.

(2) Tietenberg, T. . In *The Encyclopedia of Earth*; Environmental Information Coalition: Washington, DC, 2009; http://eoearth.org/article/European_Union_Emissions_Trading_Scheme_%28EU_ETS%29.

(3) EU Action Against Climate Change, http://ec.europa.eu/environment/climat/pdf/emission_trading2_en.pdf (accessed 04/01/11).

(4) Johnson, J. W. *Chem. Eng. News* **2011**, *89* (1), 10.

(5) Barbaro, P.; Bianchini, C. *Catalysis for Sustainable Energy Production*; Wiley-VCH: Weinheim, Germany, 2009.

(6) Crabtree, R. H. *Energy Production and Storage: Inorganic Chemical Strategies for a Warming World*; Wiley-VCH: Weinheim, Germany, 2010.

(7) de Jongh, P. E.; Adelhelm, P. *ChemSusChem* **2010**, *3*, 1332–1348.

(8) Züttel, A. In *Catalysis for Sustainable Energy Production*; Wiley-VCH: Weinheim, Germany, 2009; pp 109−169.

(9) *Hydrogen Fuel: Production, Transport, and Storage*; Gupta, R. B., Ed.; CRC Press: Boca Raton, FL, 2009.

(10) Mandal, T. K.; Gregory, D. H. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2009**, *105*, 21–54.

(11) Eberle, U.; Felderhoff, M.; Schüth, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6608–6630.

(12) Hirscher, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 381–382.

(13) Ma, S.; Zhou, H.-C. *Chem. Commun.* **2010**, *46*, 44–53.

(14) Yürüm, Y.; Taralp, A.; Veziroglu, T. N. *Int. J. Hydrogen Energy* **2009**, *34*, 3784–3798.

(15) Wang, L.; Yang, R. T. *Catal. Rev. — Sci. Eng.* **2010**, *52*, 411–461.

(16) Collins, D. J.; Zhou, H.-C. In *Encyclopedia of Inorganic Chemistry*; Wiley: New York, 2009.

(17) Makowski, P.; Thomas, A.; Kuhn, P.; Goettmann, F. *Energy Environ. Sci.* **2009**, *2*, 480–490.

(18) Crabtree, R. H. *Energy Environ. Sci.* **2008**, *1*, 134–138.

(19) Loges, B.; Boddien, A.; Gärtner, F.; Junge, H.; Beller, M. *Top. Catal.* **2010**, *53*, 902–914.

(20) Johnson, T. C.; Morris, D. J.; Wills, M. *Chem. Soc. Rev.* **2010**, *39*, 81–88.

(21) Enthaler, S.; von Langermann, J.; Schmidt, T. *Energy Environ. Sci.* **2010**, *3*, 1207–1217.

(22) Fukuzumi, S. *Eur. J. Inorg. Chem.* **2008**, 1351–1362.

(23) Campbell, P. G.; Zakharov, L. N.; Grant, D. J.; Dixon, D. A.; Liu, S.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 3289−3291 and references therein.

(24) Cheng, H.; Chen, L.; Cooper, A. C.; Sha, X.; Pez, G. P. *Energy Environ. Sci.* **2008**, *1*, 338–354.

(25) Guerri, E.; Trasatti, S. In *Catalysis for Sustainable Energy Production*: Wiley-VCH: Weinheim, Germany, 2009; pp 235−269.

(26) Hauch, A.; Ebbesen, S. D.; Jensen, S. H.; Mogensen, M. *J. Mater. Chem.* **2008**, *18*, 2331–2340.

(27) Rogers, D. W. *Heats of Hydrogenation*; World Scientific Publishing: Singapore, 2006.

(28) Pez, G. P.; Cooper, A. C.; Scott, A. R. U.S. Patent US0260630 A1, 2008.

(29) http://www.inchem.org/ (accessed 03/10/11).

(30) Cubberley, A. H.; Mueller, M. B. *J. Am. Chem. Soc.* **1946**, *68*, 1149–1151.

(31) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037–3058.

(32) Matsumoto, T.; Ueno, M.; Wang., N.; Kobayashi, N. *Chem. Asian J.* **2008**, *3*, 196–214.

(33) Vinod, C. P.; Wilson, K.; Lee, A. F. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 161–171.

(34) Hayashi, M.; Kawabata. H. Gerard, F. L., Eds.; In *Advances in Chemistry Research*; Nova Science Publishers: New York, 2006; Vol. 1, pp 45−62.

(35) Makwana, V. D.; Garces, L. J.; Liu, J.; Cai, J.; Son, Y.-C.; Suib, S. L. *Catal. Today* **2003**, *85*, 225–233.

(36) Fu, X.; Feng, J.; Wang, H.; Ng, K. M. *Nanotechnology* **2009**, *20*, 375601–375609.

(37) Fan, J.; Dai, Y.; Li, Y.; Zheng, N.; Guo, J.; Yan, X.; Stucky, G. D. *J. Am. Chem. Soc.* **2009**, *131*, 15568–15569.

(38) Tang, Q.; Gong, X.; Zhao, P.; Chen, Y.; Yang, Y. *Appl. Catal., A* **2010**, *389*, 101–107.

(39) Lingaiah, N.; Reddy, K. M.; Babu, N. S.; Rao, K. N.; Suryanarayana, I.; Prasad, P. S. S. *Catal. Commun.* **2006**, *7*, 245–250.

(40) Yamaguchi, K.; Kim, J. W.; He, J.; Mizuno, N. *J. Catal.* **2009**, *268*, 343–349.

(41) Mizuno, N.; Kamata., K.; Yamaguchi, K. *Top. Catal.* **2010**, *53*, 876–893.

(42) Yasu-eda, T.; Kitamura, S.; Ikenaga, N.; Miyake, T.; Suzuki, T. *J. Mol. Catal. A: Chem.* **2010**, *323*, 7–15.

(43) Zotova, N.; Hellgardt, K.; Kelsall, G. H.; Jessiman, A. S.; Hii, K. K. *Green Chem.* **2010**, *12*, 2157–2163.

(44) Haider, P.; Baiker, A. *J. Catal.* **2007**, *248*, 175–187.

(45) Enache, D. I.; Knight, D. W.; Hutchings, G. J. *Catal. Lett.* **2005**, *103*, 43–52.

(46) Hou, W.; Dehm, N. A.; Scott, R. W. J. *J. Catal.* **2008**, *253*, 22–27.

(47) Pina, C. D.; Falletta, E.; Prati, L.; Rossi, M. *Chem. Soc. Rev.* **2008**, *37*, 2077–2095.

(48) Ma, C. Y.; Dou, B. J.; Li, J. J.; Cheng, J.; Hu, Q.; Hao, Z. P.; Qiao, S. Z. *Appl. Catal., B* **2009**, *92*, 202–208.

(49) Yamamoto, R.; Sawayama, Y.; Shibahara, H.; Ichihashi, Y.; Nishiyama, S.; Tsuruya, S. *J. Catal.* **2005**, *234*, 308–317.

(50) Wang, H.; Deng, S.-X.; Shen, Z.-R.; Wang, J.-G.; Ding, D.-T.; Chen, T. H. *Green Chem.* **2009**, *11*, 1499–1502.

(51) Nishimura, S. *Handbook of heterogeneous catalytic hydrogenation for organic synthesis*; Wiley-Interscience: New York, 2001; pp 171, 176−178.

(52) Keane, M. A. *J. Mol. Catal. A: Chem.* **1997**, *118*, 261–269.

(53) Lanasri, K.; Saadi, A.; Bachari, K.; Halliche, D.; Cherifi, O. *Stud. Surf. Sci. Catal.* **2008**, *174B*, 1279–1282.

(54) Merabti, R.; Bachari, K.; Halliche, D.; Rassoul, Z.; Saadi, A. *React. Kinet. Mech. Catal.* **2010**, *101*, 195–208.

(55) Divakar, D.; Manikandan, D.; Kalidoss, G.; Sivakumar, T. *Catal. Lett.* **2008**, *125*, 277–282.

(56) Song, L.; Li, X.; Wang, H.; Wu, H.; Wu, P. *Catal. Lett.* **2009**, *133*, 63–69.

(57) Bertero, N. M.; Trasarti, A. F.; Apesteguía, C. R.; Marchi, A. J. *Appl. Catal., A* **2011**, *394*, 228–238.

(58) Zhang, X. B. *React. Kinet. Mech. Catal.* **2011**, *102*, 417–424.

(59) Keresszegi, C.; Grunwaldt, J.-D.; Mallat, T.; Baiker, A. *J. Catal.* **2004**, *222*, 268–280.

(60) Weissermel, K.; Arpe, H.-J. In *Industrial Organic Chemistry*; Wiley-VCH: Weinheim, Germany, 2003.

(61) Balat, H.; Kirtay, E. *Int. J. Hydrogen Energy* **2010**, *35*, 7416–7426.

(62) Dietrich, B. L.; Goldberg, K. I.; Heinekey, D. M.; Autrey, T.; Linehan, J. C. *Inorg. Chem.* **2008**, *47*, 8583–8585.

(63) H_2 has been liberated from several alcohols. See refs 64−66.

(64) Shimizu, K.; Sugino, K.; Sawabe, K.; Satsuma., A. *Chem.—Eur. J.* **2009**, *15*, 2341–2351.

(65) Mitsudome, T.; Mikami, Y.; Ebata, K.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. Commun.* **2008**, 4804–4806.

(66) Kim, W.-H.; Park, I. S.; Park, J. *Org. Lett.* **2006**, *8*, 2543–2545.