SynOpen R. Ballesteros-Garrido, R. Adam THIEME OPEN ACCESS Spotlight

Zinc Oxide (ZnO): an Amphoteric Metal Oxide with Dehydrogenating Activity

Rafael Ballesteros-Garrido*
Rosa Adam*

Departament de Química Orgànica, Universitat de València,
Av. Vicent Andrés Estellés s/n, Burjassot 46100, Spain
Rafael.Ballesteros-Garrido@uv.es
rosa.adam@uv.es

Received: 27.12.2022
Accepted after revision: 28.03.2023
Published online: 28.03.2023 (Accepted Manuscript),
20.04.2023 (Version of Record)
DOI: 10.1055/a-2063-4007; Art ID: SO-2022-12-0082-SPOT

Crowd-Reviewed

Key words catalysis, hydrogen transfer, heterogeneous catalysis, heterocycles, acceptorless dehydrogenative condensation

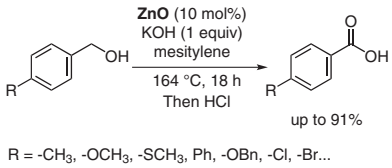
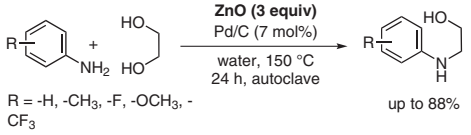
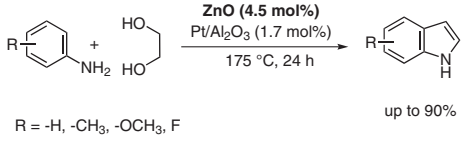
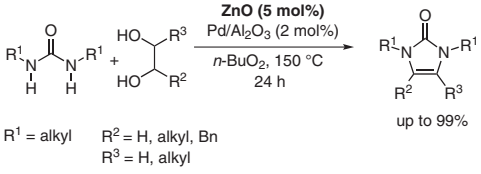
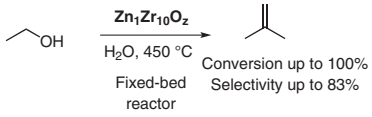
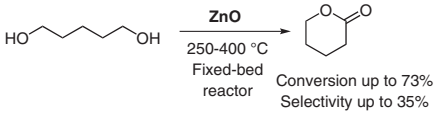
Zinc oxide (ZnO) is an available, affordable, and nontoxic compound with significant applications in various transformations.[1] Its major use is found in rubber industry as vulcanizing activator,[2] however, is also employed as pigment, food additive, and as a component of consumer goods such as ceramics, plastics, or cosmetics.[3] This last application is explained because it is a broad-spectrum UV absorber and presents antibacterial properties.[1] Moreover, ZnO has interesting electrical properties as it is, indeed, a wide band gap semiconductor. Hence, many reports have described the utility of ZnO in electrochemical devices or solar cells.[4] Due to its multiple uses, many syntheses have been described for ZnO.[5] In a small laboratory scale, ZnO can be easily obtained upon heating any Zn^{2+} salt in the presence of water, while in the industry is synthesized by well-known pyrometallurgical or hydrometallurgical processes. Ultimately, ZnO as a 99% powder can be purchased below 100 €/kg from different suppliers and also as nanoparticle dispersion in water.

In catalysis, ZnO is a well-known support for other metal or metal oxides nanoparticles exhibiting interesting properties such as its amphoteric nature. However, its simple use as a catalyst for organic transformations is rare. Remarkably, in 1970 Müller and Steinbach reported on the photodecomposition of isopropanol into acetone by this material, which is indeed an oxidation releasing molecular hydrogen.[6] More recently, many other research confirmed this particular dehydrogenative reactivity employing similar systems such as propanol or butanol.[7–11] This goes beyond the classic acid–base catalysis that may be expected for such transition-metal oxide. Dehydrogenation reactions present a high interest in organic chemistry as they can be applied for the simplification of complex synthesis applying hydrogen borrowing[12] or acceptorless dehydrogenation[13] strategies. In Table 1 a series of recent reactions in which ZnO acts as catalyst in dehydrogenation-type processes are summarized. Of course, the acid–base behavior of this compound has also been explored.[14–17]

Rafael Ballesteros-Garrido graduated in chemistry from the Universitat de València in 2006 and in Chemical Engineering from the École Européenne de Chimie, Polymères et Matériaux de Strasbourg in 2006 (ECPM, France), obtained his PhD from the University of Strasbourg under the direction of Dr. Leroux and Prof. Colobert. Currently he is a senior lecturer at the Universitat de València. His research interests focus on catalysis and materials.

Rosa Adam received her PhD degree with honors in 2013 under the supervision of Prof. Abarca and Prof. Ballesteros at the Universitat de València. Currently she is Ramón y Cajal researcher at Universitat de València. Her research interests are focused on catalysis applied to organic chemistry.

Table 1 Recent Applications of ZnO as Catalyst or Cocatalyst in Dehydrogenation Reactions

Borrowing hydrogen reactions, as well as acceptorless dehydrogenative condensations, require an initial dehydrogenation step triggering the whole catalytic cycle. In 2018, Madsen and coworkers reported how ZnO in the presence of KOH at 164 °C was able to dehydrogenate alcohols into carboxylic acids.[18] In this transformation, ZnO and KOH were heated at 170 °C for 1 h prior to solvent and alcohol addition. A wide range of alcohols was employed, including benzylic alcohols, but also allyl and alkyl derivatives. Yields vary from 42% up to 91%. To note, molecular hydrogen was detected (and monitored) and reactions were performed under nitrogen atmosphere proving this to be a neat dehydrogenation without any presence of molecular oxygen.	
Ballesteros-Garrido *et al.* reported on a combination of Pd/C and ZnO to synthesize β-amino alcohols from anilines and ethylene glycol, using a water/ethylene glycol 50:50 mixture as solvent.[19] The catalytic system was able to activate the challenging ethylene glycol dehydrogenation and mediate a hydrogen borrowing reaction, affording the desired products in yields up to 88%. β-Amino alcohols are difficult to obtain, and their synthesis normally requires the use of halo alcohols as starting materials. Further studies expanded this protocol to other diols obtaining the corresponding amino alcohols in lower yields.[20]	
Intimately related with the previous result, Ballesteros-Garrido *et al.* described a different catalyst combination (Pt/Al_2O_3 and ZnO) for an acceptorless dehydrogenative coupling.[21] The combination of anilines and ethylene glycol, employed also as solvent, allowed the preparation of indoles in yields up to 90%. Interestingly, molecular hydrogen was measured in this reaction confirming a dehydrogenation mechanism. This method was further improved reducing the amount of ethylene glycol to 2 equiv. and employing *N*-methyl-2-pyrrolidine (NMP) as solvent. Other alcohols such as 2,3-butane diol or 1,2-cyclohexane diol have been also successfully employed in the presence of additional PTSA catalysis and increasing the temperature up to 195 °C.[22] This approach have been also extended to the synthesis of polycyclic aromatic N-heterocycles.[23]	
Cabrero-Antonino, Adam *et al.* reported the synthesis of a variety of imidazolones through the acceptorless dehydrogenative condensation of ureas and diols.[24] This reaction was catalyzed by the combination of Pd/Al_2O_3 and ZnO, able to mediate the diol dehydrogenation. Moreover, the catalytic mixture proved to be reusable in two catalytic cycles. The protocol could be applied to the synthesis of up to 13 imidazolones using unactivated diols such as ethylene glycol. It is worth mentioning that for allyl alcohols ZnO is not required, indicating the important role of ZnO in the activation of the less reactive diols. Molecular hydrogen was also detected in these experiences.	
This kind of reaction has also recently been employed for the transformation of bioethanol into isobutene employing this time nanosized $Zn_xZr_yO_z$ mixed oxides.[25] Indeed, in this approach, neat ZnO was able to produce neat acetone starting form ethanol up to 60%. Older reports indicate that ZnO–CaO and $ZnO–Fe_2O_3$ were able to catalyze this reaction. Surprisingly, neat ZrO yielded ethylene almost quantitively.[26–28] These reactions were carried out under molecular nitrogen/water atmosphere and again enhance the evidence of ZnO as essential for dehydrogenations.	
An application combining the acid/base behavior together with the dehydrogenating activity of ZnO was reported by Gnanamani *et al.*[29] in 2019. In this work, the dehydration and dehydrogenation of 1,5-pentanediol to 4-penten-1-ol, tetrahydropyran and, more important, tetrahydropyran-2-one was studied employing ZnO and a ZrO_2–ZnO mixed oxide materials as catalysts at temperatures from 250 °C to 400 °C in a fixed-bed reactor. In this study it was shown how reaction selectivity can be tuned changing the acid/base properties and oxygen vacancies at different Zr/Zn proportions. Among all products that can be obtained, tetrahydropyran-2-one requires a double dehydrogenation.	
More recently, Jiang, Jiao, Kondratenko, and coworkers reported a relevant application of ZnO dehydrogenating activity.[30] The authors showed that a mixture of ZnO with nonacidic SiO_2 materials was an active catalytic system for the propane dehydrogenation to propene at 550 °C in a fixed-bed reactor. The authors elucidate the in situ formation of an active material constituted by supported ZnO_x species. It is important to remark that the developed catalyst shows three times higher propene productivity at similar selectivity when compared with a commercially available catalyst for this process.	

Conflict of Interest

The authors declare no conflict of interest.

References

(1) Li, J.; Ma, S.; Liu, X.; Zhou, Z.; Sun, C. Q. *Chem. Rev.* **2012**, *112*, 2833.
(2) Moezzi, A.; McDonagh, A. M.; Cortie, M. B. *Chem. Eng. J.* **2012**, *1*, 185.
(3) Sharma, D. K. M Shukla S.; Sharma, K. K.; Kumar, V. *Mater. Today: Proc.* **2022**, *49*, 3028.
(4) Kołodziejczak-Radzimska, A.; Jesionowski, T. *Materials* **2014**, *7*, 2833.
(5) Vittal, R.; Kuo-Chuan, H. *Renewable Sustainable Energy Rev.* **2017**, *70*, 920.
(6) Müller, H. D. M.; Steinbach, F. *Nature* **1970**, *225*, 728.
(7) Kolboe, S. *J. Catal.* **1972**, *27*, 379.
(8) Klingshirn, C. *Phys. Status Solidi B* **2007**, *244*, 3027.
(9) Saad, L.; Riad, M. *J. Serb. Chem. Soc.* **2008**, *73*, 997.
(10) Gliński, M.; Gadomska, A. *React. Kinet. Catal. Lett.* **1998**, *64*, 275.
(11) Raizada, V. K.; Tripathi, V. S.; Darshan, Lal.; Singh, G. S.; Dwivedi, C. D.; Sen, A. K. *J. Chem. Technol. Biotechnol.* **1993**, *56*, 265.
(12) Watson, A. J. A.; Williams, J. M. J. *Science* **2010**, *329*, 635.
(13) Gunanathan, C.; Milstein, D. *Science* **2013**, *341*, 1229712.
(14) Hosseini-Sarvari, M.; Sharghi, H. *J. Org. Chem.* **2006**, *71*, 6652.
(15) Chhattise, P.; Saleh, S.; Pandit, V.; Arbuj, S.; Chabukswar, V. *Mater. Adv.* **2020**, *1*, 2339.
(16) Saha, M.; Das, A. R. *Curr. Green Chem.* **2020**, *7*, 53.
(17) Ban, L.; Zhang, H. Li Y.; Wu, R.; Huang, X.; Zhao, J.; Zhao, Y. *J. Phys. Chem. C* **2021**, *125*, 16536.
(18) Monda, F.; Madsen, R. *Chem. Eur. J.* **2018**, *24*, 17832.
(19) Llabres-Campaner, P. J.; Ballesteros-Garrido, R.; Ballesteros, R.; Abarca, B. *Tetrahedron* **2017**, *73*, 5552.
(20) Llabres-Campaner, P. J.; Woodbridge-Ortega, P.; Ballesteros-Garrido, R.; Ballesteros, R.; Abarca, B. *Tetrahedron Lett.* **2017**, *58*, 4880.
(21) Llabres-Campaner, P. J.; Ballesteros-Garrido, R.; Ballesteros, R.; Abarca, B. *J. Org. Chem.* **2018**, *83*, 521.
(22) Belleza, D.; Zaragozá, R. J.; Aurell, M. J.; Ballesteros, R.; Ballesteros-Garrido, R. *Org. Biomol. Chem.* **2021**, *19*, 677.
(23) Gonzalez-Sanchis, N.; Perez-Quilez, P.; Bellezza, D.; Flor-Sanchez, A.; Ballesteros, R.; Ballesteros-Garrido, R. *Synthesis* **2022**, *54*, 5226.
(24) Arango-Daza, J. C.; Lluna-Galán, C.; Izquierdo-Aranda, L.; Cabrero-Antonino, J. R.; Adam, R. *ACS Catal.* **2022**, *12*, 6906.
(25) Sun, J.; Zhu, K.; Gao, F.; Wang, C.; Liu, J.; Peden, C. H. F.; Wang, Y. *J. Am. Chem. Soc.* **2011**, *133*, 11096.
(26) Murthy, R. S.; Patnaik, P.; Sidheswaran, P.; Jayami, M. *J. Catal.* **1988**, *109*, 298.
(27) Nakajima, T.; Yamaguchi, T.; Tanabe, K. *J. Chem Soc., Chem. Commun.* **1987**, 394.
(28) Nakajima, T.; Nameta, H.; Mishima, S.; Matsuzaki, I.; Tanabe, K. *J. Mater Chem.* **1994**, *4*, 853.
(29) Beasley, C.; Gnanamani, M. K.; Martinelli, M.; Góra-Marek, K.; Hamano, K.; Shafer, W. D.; Wanninayake, N.; Kim, D. Y. *ChemistrySelect* **2019**, *4*, 3123.
(30) Zhao, D.; Tian, X.; Doronkin, D. E.; Han, S.; Kondratenko, V. A.; Grunwaldt, J.-D.; Perechodjuk, A.; Vuong, T. H.; Rabeah, J.; Eckelt, R.; Rodemerck, U.; Linke, D.; Jiang, G.; Jiao, H.; Kondratenko, E. V. *Nature* **2021**, *234*, 23.