

 HYDROGEN STORAGE

## A reformed approach

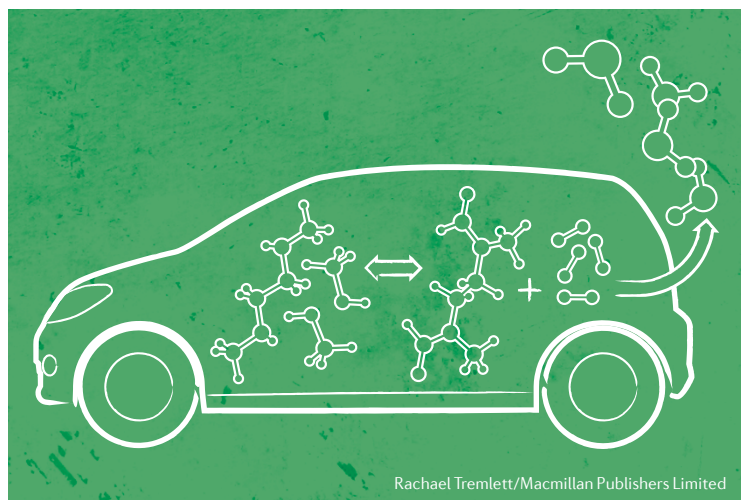


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The intermittency of renewable energy sources means that we need efficient technologies to store energy. One way to accomplish this is to use this energy to drive a reaction that affords a fuel such as  $\text{H}_2$ . As this energy carrier is difficult to store at room temperature, researchers turn to latent  $\text{H}_2$  sources, such as methanol ( $\text{CH}_3\text{OH}$ ). Although  $\text{CH}_3\text{OH}$  reacts with  $\text{H}_2\text{O}$  to afford  $\text{CO}_2$  and the desired  $\text{H}_2$ , this steam-reforming process requires high temperatures. By contrast, the reversible conversion of  $\text{CH}_3\text{OH}$  and an amine to a formamide and  $\text{H}_2$  — termed ‘amine reforming’ — is a mild and practical means of  $\text{H}_2$  storage according to the group of Surya Prakash, who report their findings in the *Journal of the American Chemical Society*.

Reversing steam reforming is problematic because the oxidized and dehydrogenated product of  $\text{CH}_3\text{OH}$  (namely,  $\text{CO}_2$ ) is volatile and requires separation from  $\text{H}_2$ . “An attractive alternative is to avoid the release of  $\text{CO}_2$  altogether,” states Prakash, a goal well met by their amine reforming reaction, in which a ruthenium catalyst dehydrogenates  $\text{CH}_3\text{OH}$  to formaldehyde ( $\text{CH}_2\text{O}$ ), which then condenses with a secondary amine to form a carbinolamine. Subsequent dehydrogenation of this product affords a formamide — a non-volatile store of  $\text{CH}_3\text{OH}$ -derived  $\text{CO}$ . The secondary diamine  $N,N'$ -dimethylethylenediamine reacts reversibly with two equivalents of  $\text{CH}_3\text{OH}$  to liberate a bis(formamide) and four equivalents of  $\text{H}_2$ ; the weight of  $\text{H}_2$  is 5.3% of the total. The conversion of ethylenediamine to the corresponding cyclic urea and  $\text{H}_2$  would seem a better choice (6.6 wt%  $\text{H}_2$ ), but the primary amines tested were found to react sluggishly.



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Just as crucial as the choice of substrate is the type of catalyst used. The dehydrogenative coupling of  $\text{CH}_3\text{OH}$  with  $N,N'$ -dimethylethylenediamine proceeds smoothly (toluene, 5 mol%  $\text{K}_3\text{PO}_4$ , 120 °C, 90% yield) with the secondary amine complex  $[\text{Ru}\{\text{HN}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2\}\text{H}(\text{CO})\text{Cl}]$ . The catalyst is bidirectional as it also hydrogenates the bis(formamide) back to the precursors (>95% yield). The mechanism involves interconversion of a hydridoruthenium amine with a ruthenium amide and  $\text{H}_2$ ; the complex of the methylated amine analogue,  $\text{MeN}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$ , is inactive. Other catalysts mediate deleterious dehydrogenation of  $\text{CH}_2\text{O}$  to  $\text{CO}$ , and the presence of the latter in the  $\text{H}_2$  produced — even in trace quantities — poisons  $\text{H}_2$  oxidation catalysts in fuel cells.

It is promising that a commercially available catalyst can reversibly dehydrocouple  $\text{CH}_3\text{OH}$  and amines to give  $\text{CO}$ - and  $\text{CO}_2$ -free  $\text{H}_2$ . This study compares favourably with work in which elaborate catalysts mediated a similar reaction with  $\text{CH}_3\text{CH}_2\text{OH}$ , a heavier  $\text{H}_2$  carrier with a  $\text{CH}_3$  group that is inert

under the reaction conditions. However, although Prakash's team can drive  $\text{CH}_3\text{OH}$  dehydrocoupling in either direction by controlling  $\text{H}_2$  pressure, it needs heat and is slow in the absence of solvent, the weight of which (not to mention that of the catalyst) makes the total  $\text{H}_2$  weight percentage much lower than the US Department of Energy target (5.5 wt%  $\text{H}_2$  by 2020). Acknowledging this, Prakash is also looking for bidirectional catalysts for steam reforming under mild conditions. “Potentially,  $\text{CH}_3\text{OH}/\text{NH}_3$  mixtures could reversibly store up to 9.5 wt%  $\text{H}_2$  while trapping carbon in the form of urea,” notes Prakash. Once developed, these technologies would boost the utility of a methanol economy, something that our environment will no doubt welcome.

David Schilter

**ORIGINAL ARTICLE** Kothandaraman, J. *et al.* Efficient reversible hydrogen carrier system based on amine reforming of methanol. *J. Am. Chem. Soc.* **139**, 2549–2552 (2017)

**WEB SITE**

US Department of Energy Office of Energy Efficiency & Renewable Energy: <https://energy.gov/eere/fuelcells/materials-based-hydrogen-storage>