

## Catalysts for Hydrogen Storage

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Hydrogen is a form of storable chemical energy that can supplement intermittent renewable energy conversion. Effective processing and storage methods are the key factors that need to be resolved to achieve hydrogen economy.

### Application of Catalysts in Hydrogen Storage

- **Catalysts for Compound chemical hydrogen compound material**  
Such materials are mainly composed of light alkali metals and alkaline earth metals (such as Li, Na, K, Al, etc.) and non-metallic elements such as B and N. Among them, due to its high hydrogen capacity, large amount of availability and low cost, the lightweight composite hydride NaAlH<sub>4</sub> is a potential solid hydrogen storage material. Studies have found that the introduction of catalysts can improve the dehydrogenation performance of NaAlH<sub>4</sub>, lower the decomposition temperature, improve the kinetics and reduce the activation energy.

Addition	Rate (wt% h <sup>-1</sup> )		Addition	Rate (wt% h <sup>-1</sup> )		Addition
	5 min	1 h		5 min	1 h	
AgCl	0.26	0.09	GeCl <sub>4</sub>	0.50	0.10	TiCl <sub>2</sub>
CdCl	0.26	0.08	HfCl <sub>4</sub>	1.44	0.30	TiCl <sub>3</sub>
CeCl <sub>3</sub>	1.89	0.62	MnCl <sub>2</sub>	0.73	0.23	TiCl <sub>4</sub>
CoF <sub>3</sub>	1.06	0.27	MoCl <sub>3</sub>	0.87	0.24	TiF <sub>3</sub>
CrCl <sub>2</sub>	0.59	0.21	NbCl <sub>4</sub>	0.93	0.30	VCl <sub>2</sub>
CrCl <sub>3</sub>	0.25	0.15	PdCl <sub>2</sub>	0.34	0.15	VCl <sub>3</sub>
CuCl	0.39	0.11	PtCl <sub>4</sub>	0.33	0.13	VCl <sub>4</sub>
FeCl <sub>2</sub>	0.50	0.26	RhCl <sub>3</sub>	0.38	0.22	YbCl <sub>3</sub>
FeCl <sub>3</sub>	0.59	0.21	RuCl <sub>3</sub>	1.68	0.51	ZnCl <sub>2</sub>
GaCl <sub>3</sub>	0.22	0.07	SrCl <sub>2</sub>	0.34	0.07	ZrCl <sub>4</sub>
GdCl <sub>3</sub>	0.79	0.26				

Figure 1. Catalyst addition and resultant dehydrogenation rate [1]

- **Catalysts for Liquid organic hydrogen storage material**

Such materials usually use the unsaturated bonds of the molecules themselves to undergo catalytic hydrogenation reaction with hydrogen, and use the reverse process to achieve catalytic dehydrogenation. N-ethylcarbazole is an organic liquid hydrogen storage material found to be completely hydrogenated/dehydrogenated with a dehydrogenation temperature below 200 °C.

Since the hydrogenation of polyaromatic compounds is a thermodynamically exothermic process, it is relatively easy to fully catalyze the hydrogenation reaction. Therefore, the research on catalysts mainly focuses on the dehydrogenation step. The catalytic processes are divided into homogeneous or heterogeneous (such as Ru, Pd nanoparticles supported by oxides or carbon materials). For example, a high-efficiency N-ethylcarbazole dehydrogenation catalyst can be prepared by using a metal heterogeneous catalyst supported by carbon-nitrogen materials.

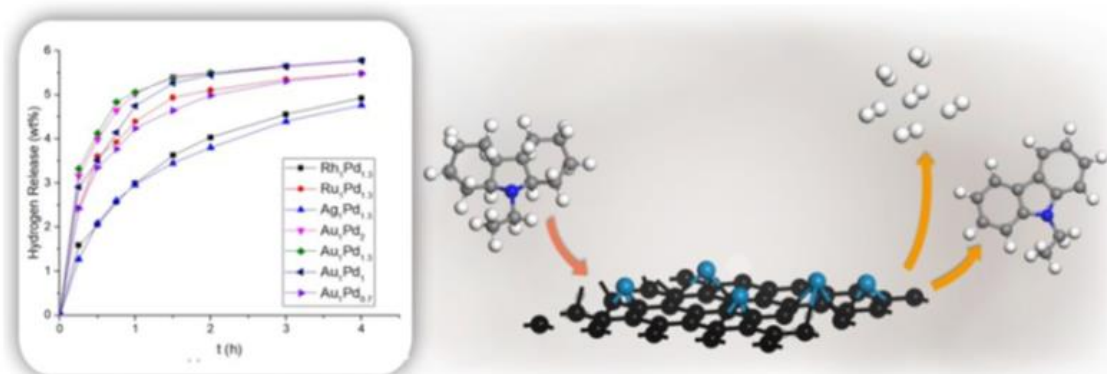


Figure 2. Hydrogen release amount for 12H-NEC on different catalysts [2]

- **Catalysts for Methanol/formic acid hydrogen storage**

Storage systems based on formic acid and alcohol are very attractive hydrogen carriers because they can be made from CO<sub>2</sub> or other renewable materials, can be used in stationary energy storage devices such as hydrogen refueling stations, and can also be used directly as transportation fuels. In order to efficiently release hydrogen from these molecules and regenerate these molecules from CO<sub>2</sub> and hydrogen, catalysts play an important role in these processes. The types of catalysts involved include noble metal catalysts, non-noble metal catalysts, and catalysts that are active under alkali-free conditions.

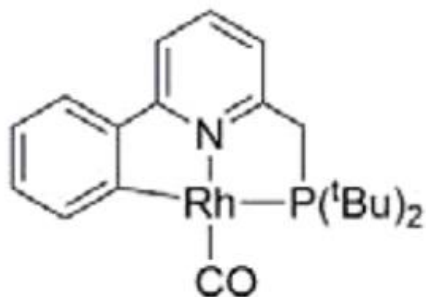


Figure 3. Structures of rhodium pincer complexes that are active in base-free formic acid dehydrogenation [3]

## References

1. D.L. Anton. (2003). "Hydrogen desorption kinetics in transition metal modified NaAlH<sub>4</sub>", *Journal of Alloys and Compounds* 356–357: 400-404.
2. Bin Wang. (2019). "One-Pot Synthesis of Au/Pd Core/Shell Nanoparticles Supported on Reduced Graphene Oxide with Enhanced Dehydrogenation Performance for Dodecahydro-N-ethylcarbazole", *ACS Sustainable Chemistry & Engineering* 7(1): 1760–1768.
3. Katerina Sordakis. (2018). "Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols", *Chemical Reviews* 118(2): 372–433.

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