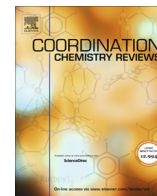




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Review

Recent progress for reversible homogeneous catalytic hydrogen storage in formic acid and in methanol

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ABSTRACT

Development of technologies using hydrogen as an energy carrier instead of fossil fuels is strongly required today. Especially, new, reversible, sustainable hydrogen storage technologies have received increasing attention. Formic acid (FA) and methanol (CH₃OH) are considered as effective liquid chemicals for hydrogen storage as being easier to handle than solid or gas materials. This review summarizes the recent progress of research on the development of homogeneous catalysts mainly focusing on FA and CH₃OH and the reports on the complexes based on both precious and non-precious metals which are rapidly increasing in the past few years.

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Abbreviations: 4DHBP, 4,4'-dihydroxy-2,2'-bipyridine; 6DHBP, 6,6'-dihydroxy-2,2'-bipyridine; Acac, acetylacetonate; Acriphos, 4,5-bis(diphenylphosphino)acridine; Bpy, 2,2'-bipyridine; Cp, cyclopentadienyl; Cp', pentamethyl cyclopentadienyl; DMOA, *N,N*-dimethyloctylamine; Dmpe, 1,2-bis(dimethylphosphino)ethane; DHPT, 4,7-dihydroxy-1,10-phenanthroline; DBU, 1,8-diazabicyclo(5.4.0)undec-7-ene; FA, formic acid; FADH, formic acid dehydrogenation; mTPPMS, *meta*-triphenylphosphine monosulfonate; NHC, *N*-heterocyclic carbene; PC, propylene carbonate; PEHA, pentaethylenhexamine; PTA, 1,3,5-triaza-7-phosphaadamantane; PP₃, tris[(2-diphenylphosphino)ethyl]phosphine; *t*BuPNP, 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine; Tetrphos, 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane; Tf, trifluoromethanesulfonyl; TON, turnover number; TOF, turnover frequency; Triphos, 1,1,1-tris(diphenylphosphinomethyl)ethane.

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1. Introduction

Today, most of the energy consumption on the earth depends on fossil fuels, causing the global warming as a result of the large release of CO₂ into the air. To avoid depletion of natural resource and environmental pollution, developing the effective, low-cost and environmentally-friendly energy storage systems is strongly demanded. Hydrogen can be considered as an ideal candidate for this purpose, because its combustion releases only energy and water without other by-products. Despite of many advantages, the difficulty to storage and transport hydrogen remains as a serious bottleneck for its practical use. Therefore, considerable efforts have been made to develop new materials to enhance capability of hydrogen storage.

Although many solid chemical materials such as ammonia borane [1] and sodium borohydride [2] have been studied, their solution stability, by-product emission, recyclability and cost did not reach the level of practical use. On the other hand, liquid organic hydrogen carriers are considered to be more beneficial, because they can be handled and transported more easily than solid materials. Many studies on these carriers such as formic acid (FA) [3], methanol (CH₃OH), and methyl cyclohexane [4,5], have been reported so far. FA, known as a main product of biomass treatment, has been studied as one of the most promising and safest materials for hydrogen storage with its high hydrogen content (4.4 wt%) in liquid state at room temperature. In a similar way, CH₃OH is also considered as a useful material which contains 12.6 wt% of H₂. To apply these chemical compounds into the technology of hydrogen storage, it is necessary to develop the sustainable methods to synthesize them and release H₂ from them. A possible effective method is direct hydrogenation of CO₂. In particular, the development of environmentally-friendly and sustainable catalysts for H₂ production will lead to the establishment of large scale production of FA and CH₃OH. In addition, CO₂ seems to have economic and environmental advantages as a raw material because it is a nontoxic, readily available and inexpensive carbon source.

In this review, we report recent progress of researches on the hydrogen production from FA/CH₃OH and the reversible reaction for these compound production by using homogeneous catalysts. Recent achievements from 2015 until mid of 2017 are summarized in this report. Reports published before 2015 are listed in the previous reviews [3,6–10].

2. Hydrogen storage utilized by formic acid

This section makes a survey of recent developments of homogeneous catalysts for the reaction of hydrogen storage utilized by FA.

2.1. Dehydrogenation of formic acid to H₂ evolution

There are two possible pathways for the catalytic FA decomposition (Eqs. (1) and (2)): One is the hydrogen evolution from formic acid dehydrogenation (FADH) (Eq. (1)), and the other is the CO generation from FA dehydration (Eq. (2)). To avoid the undesirable CO generation, the function of catalysts are required to be capable to generate hydrogen exclusively (Eq. (1)). In 1967, Coffey et al.

reported a pioneering work on this issue, describing the active Ir catalysts with phosphine ligands with a TOF of 1187 h⁻¹ [11]. After this report, a number of papers on FADH catalysts started to be published, but these reported reactions still needed elevated reaction temperature and organic additives, furthermore, sometimes CO was detected in the generated gases from FA. In 2008, the two excellent results of FADH using Ru catalysts were independently reported by Beller [12] and Laurenczy [13]. Their catalysts could effectively produce H₂ without any CO contamination in relatively low temperature in aqueous solutions. Especially, Beller's report was very significant from the viewpoint of practical use, because they demonstrated the fuel cells driven by H₂ from FA [12]. Additionally, generating H₂ with a robust Ru catalyst in a large-scale and for a long time was achieved by continuous adding FA via a pump [14]. Following these results, FA as a hydrogen storage became to gather renewed attention.



Recently, the reports on catalysts based on non-precious metals for FADH are increasing. Although performances of these catalysts were unsatisfied compared with those of precious metals such as Ru and Ir, they have still advantages, because these metals are earth-abundant and low cost. In this section, we report recent researches on the FADH catalyzed by non-precious metals as well as precious metals (Fig. 1, Table 1).

2.1.1. Non-precious metals

In 2011, Beller and Laurenczy et al. showed the first results of Fe catalysts for FADH, that Fe salts such as Fe(BF₄)₂·6H₂O with a combination of PP₃ as a tetradentate ligand could catalyze FADH with high activity [35]. After publishing this result, various catalyst systems composed of Fe have started to be studied. Recently, Laurenczy et al. published Fe(BF₄)₂ with water-soluble m-trisulfonated-tris[2-(diphenylphosphino)ethyl]phosphine sodium salt as a PP₃ derivative (**Fe-1**) for FADH (Entry 1) at 80 °C [15]. This catalyst system could be employed in water as a green solvent. H₂ was generated with no CO (less than 5 ppm contamination) and the initial turnover frequency (TOF) of 200 h⁻¹ was obtained. In addition, it was confirmed that the reaction activity of a catalyst using PP₃ decreased in the closed system, but no inactivation was observed in **Fe-1**. These effects were investigated in an aqueous solution, using a medium pressure sapphire NMR tube as a reaction vessel. The generation of pressure at 80 °C was monitored at 25 mM pre-catalyst with a metal to ligand ratio of 1:1 and with an initial FA concentration of 2.2 M. After reaching the maximum pressure (≈50 bar), the tube was carefully vented and refilled with 0.2 g FA. This process was repeated several times (Fig. 2). Especially, this system was not deactivated even in oxygen exposure.

Li et al. reported an isolated Fe–H complex (**Fe-2**) with a C^N-cyclometalated ligand for FADH (Entry 2) [16]. At first, the generation of a formate complex considered as a key intermediate in FADH was detected by the reaction of CO₂. Following this result, investigation on the effect of additives in the catalytic FADH by **Fe-2** has started and found that adding NEt₃ and LiBF₄ activated

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