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Review

Recent progress for direct synthesis of dimethyl ether from syngas on the heterogeneous bifunctional hybrid catalysts

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ABSTRACT

The recent rising demand of renewable energies and climate changes has been driving intensive academic researches into new chemical routes to sustainable and clean fuel productions in order to meet the demands of industrial evolution by solving energy crisis due to limited fossil fuel reservoirs and increasing environmental pollutants. Dimethyl ether (DME) is a multi-purpose synthetic fuel and chemical that can be used as an excellent alternative to diesel fuel and liquefied petroleum gas (LPG). The present review paper briefly provides an overview of the recent developments for a direct synthesis of DME from synthesis gas (syngas, $CO + H_2$) over some hybridized bifunctional heterogeneous catalysts composed of copper-based hydrogenation catalysts with solid acid components such as alumina or zeolites mainly, where the catalytic activities significantly depend on its properties influenced by synthesis protocols, porosities, surface areas, interactions of active metals with supports, distributions of metal particles on the supports and so on. We have also briefly covered the hydrogenation of CO_2, a model reaction for the utilization of CO_2 containing in syngas, to produce DME and thereby significantly mitigate its environmental impacts. Furthermore, the catalytic performances of the direct synthesis of DME by hydrogenation of carbon oxides were explained in terms of the acid sites of the solid acid catalysts and surface area of metallic copper nanoparticles in the hybridized bifunctional catalysts with their preparation protocols.

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1. Introduction

The energy utilization cycle generally consists of three stages such as an energy generation, distribution and consumption, all of which must be closely balanced for an ideal energy infrastructure [1]. Meanwhile, the world energy consumption is steadily increasing, and thus rapidly depleting energy resources owing to an industrial evolution by generating significant environmental pollutants from an increasing population and globalization [2]. The conventional fossil resources such as crude oil, coal and natural (or shale) gases are the major sources of world's primary energies (Fig. 1a) that are used mostly as fuels (Fig. 1b) [3]. However, when fossil fuels are burnt they predominantly produce CO_2 that has been identified as a major source contributing to climate changes. Besides they generate other harmful gases such as SOx and NOx which need to be removed to meet the environmentally acceptable fuel requirements. To limit these unwanted harmful gas increases, some supplements of fossil fuels are prerequisite for a sustainable society [1,4]. Furthermore, the present use of natural resources does not secure the ability of future generations to meet their own energy needs. Although the exploitation of unconventional fossil fuel resources such as shale oil and shale gas could significantly increase the availability of affordable fossil fuels, the impacts of their production on the environment are also raising numerous concerns [5]. The utilization of these fossil and unconventional resources also impair the problems associated with the greenhouse gas emissions (especially, CO_2) and thus it is vital for mankind to find renewable, sustainable and environmentally friendly alternative chemicals for heat, power and transportation and so on.

A great deal of researches has been conducted to meet the rising demands for energy and to mitigate CO_2 emission by developing more sustainable technologies that use the available raw materials like coal, natural gas and biomass [4,6]. Synthesis gas (syngas, mainly $CO + H_2$ mixtures), the raw materials for clean fuels and platform chemicals, can be produced from coal, natural gas, biomass and other waste resources. Although, for economic reasons, syngas is now exclusively produced from natural gas and coal, it could be made from any carbon containing feedstock including biomass. Biomass, CO_2 neutral resource, extensively distributed in the world and it is considered as one of the alternative feedstock for the production of fuels and chemicals [7,8].

Two main chemical transformation routes were reported in the literatures for the conversion of syngas into fuels. (1) The production of linear aliphatic hydrocarbons including methane by methanation has been well known by Fischer-Tropsch synthesis (FTS) reaction which can be catalyzed by the supported transition metals such as Ru, Fe and Co. (2) Syngas to methanol which gives dimethyl ether (DME) by dehydration. Both the above routes have been successfully implemented in industry for the production of synthetic fuels [9]. However the former method should require CO_2-free syngas, whereas methanol/DME synthesis route can be conducted in the presence of CO_2-rich syngas and thus it has been considered as a promising method to get synthetic clean fuels and to mitigate CO_2 emission. Both methanol and DME can be used as synthetic fuels. Nevertheless, DME provides a high H/C ratio with relatively harmless. Therefore, DME is more preferable and often plays an alternative role to methanol [10]. DME, also called as methoxymethane (CH_3OCH_3), the smallest aliphatic ether, is a non-toxic, non-carcinogenic and non-corrosive compound. DME can be used as an excellent alternative to diesel fuel due to its high cetane number (55–60) and a low emission of CO, NOx in the exhaust gases from a diesel engine as it has no C—C bond structures. It also has similar physical properties as that of liquefied petroleum gas (LPG) and hence can be used as an alternative fuel for cooking and heating [11a]. Furthermore, the well-developed infrastructures of LPG can be adapted for DME and this makes DME outstanding for practical uses [10]. As multisource, multi-purpose clean fuels, it is also projected as a chemical feedstock of the 21st century for the production of hydrocarbon, oxygenates and higher ethers [7]. For instance, there is a huge market value for acetic acid, gasoline and olefins which can be possibly derived from DME (Fig. 2). Since DME having a high H/C ratio and intense energy density, it can be used

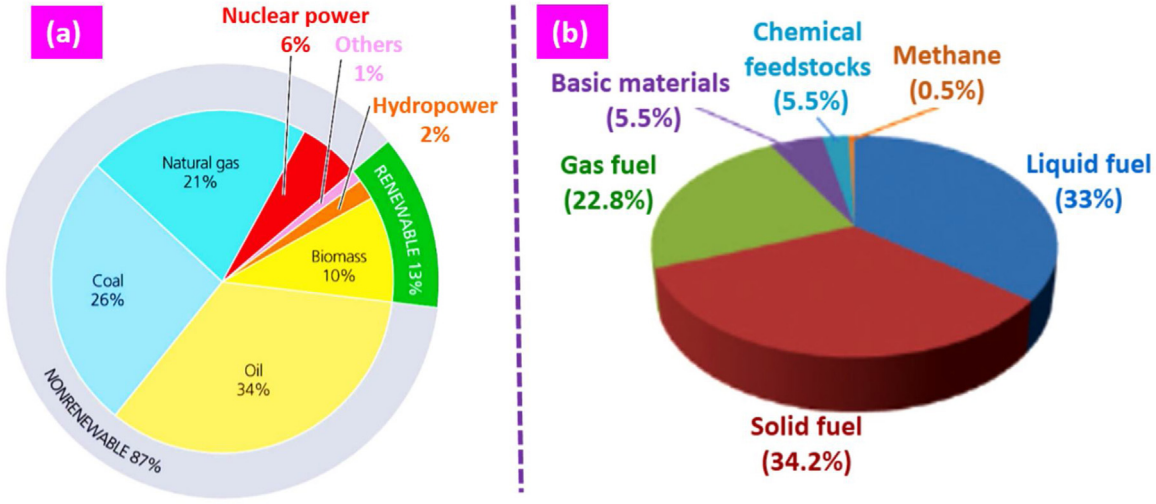

Fig. 1. (a) World's primary energy resources and (b) their uses [modified form of Ref. [3]].