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Synthesis of diesel range alkanes with 2-methylfuran and mesityl oxide from lignocellulose

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ABSTRACT

For the first time, the alkylation of 2-methylfuran with mesityl oxide was carried out over a series of solid acid catalysts. Among the investigated candidates, Nafion-212 resin exhibited the highest catalytic efficiency and good stability, which can be rationalized by the higher acid strength of this catalyst. The hydrodeoxygenation (HDO) of the alkylation products of 2-methylfuran with mesityl oxide was also studied. Ni–Mo_2C/SiO_2 and Ni–W_2C/SiO_2 were firstly used for the HDO of biomass derived oxygenates and demonstrated excellent catalytic performance for the conversion of the alkylation products to alkanes. Compared with Ni–W_2C/SiO_2, Ni–Mo_2C/SiO_2 exhibited higher selectivity to diesel range alkanes. Over the Ni–Mo_2C/SiO_2 catalyst, high carbon yield of diesel range alkanes (77%) could be achieved by the HDO of the alkylation products of 2-methylfuran and mesityl oxide at 573 K and 6.0 MPa H_2. This value is evidently higher than those obtained over noble metal catalysts and Ni–W_xC/AC under the same reaction conditions.

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1. Introduction

Energy and environment are two mostly concerned problems, nowadays. As one of the solutions, the catalytic conversion of renewable biomass to fuels [1–3] and chemicals [4–8] becomes a very popular research area. Lignocellulose is the main component of agriculture wastes or forest residues. Following the pioneering works of Dumesic's group [9,10] and Huber and co-workers [11,12], the synthesis of renewable diesel or jet fuel by the C–C coupling reactions of the lignocellulose derived platform chemicals followed by hydrodeoxygenation (HDO) has drawn wide attention [13–19].

2-Methylfuran (2-MF) is the selective hydrogenation product of furfural which is available on an industrial scale by the hydrolysis–dehydration of the hemicellulose part of agriculture wastes and forest residues [20–22]. Mesityl oxide is the self aldol condensation product of acetone which can be produced by the Acetone–*n*-Butanol–Ethanol (ABE) fermentation of lignocellulose [16]. In the recent work of Corma's group [23], it was found that a C_{11} oxygenate (i.e. 4-methyl-4-(5-methylfuran-2-yl)pentan-2-one) can be produced by the alkylation of 2-MF with mesityl oxide under the catalysis of mineral acids (H_2SO_4 and HCl), or *para*-toluenesulfonic acid. This compound can be further hydrodeoxygenated to diesel or jet fuel alkanes over noble metal catalyst. In practical application, solid acids are more preferable because they can be easily sperated and reused. However, to our knowledge, there is no report on the application of solid acid as the catalyst for the alkylation of 2-MF with mesityl oxide.

Hydrodeoxygenation (HDO) is a key step for the conversion of alkylation product of 2-MF and mesityl oxide to diesel or jet fuel range alkanes. In the past years, most of works about the HDO of biomass derived oxygenates were carried out over noble metal catalysts. Due to the high cost and limited reserve of non-noble metals, the exploration of non-noble HDO catalyst is of great significance. In our recent work, the nickel-promoted tungsten carbide (Ni–W_xC/C) catalyst was found to be highly active in conversion of cellulose to ethylene glycol [6] and the HDO of the HAA products of 2-MF [24]. Molybdenum is cheaper and more available than tungsten. So far, there is no report about the HDO of biomass derived oxygenates over nickel-promoted molybdenum carbide (Ni–Mo_2C) catalyst.

In this work, the alkylation of 2-MF with mesityl oxide was carried out for the first time over a series of solid acid catalysts. Among the investigated candidates, Nafion-212 resin exhibited the highest catalytic efficiency and stability. The influences of reaction conditions on the catalytic performance of Nafion-212 resin were investigated. Finally, the HDO of the alkylation products of 2-MF and mesityl oxide was also carried out over a series of catalysts.

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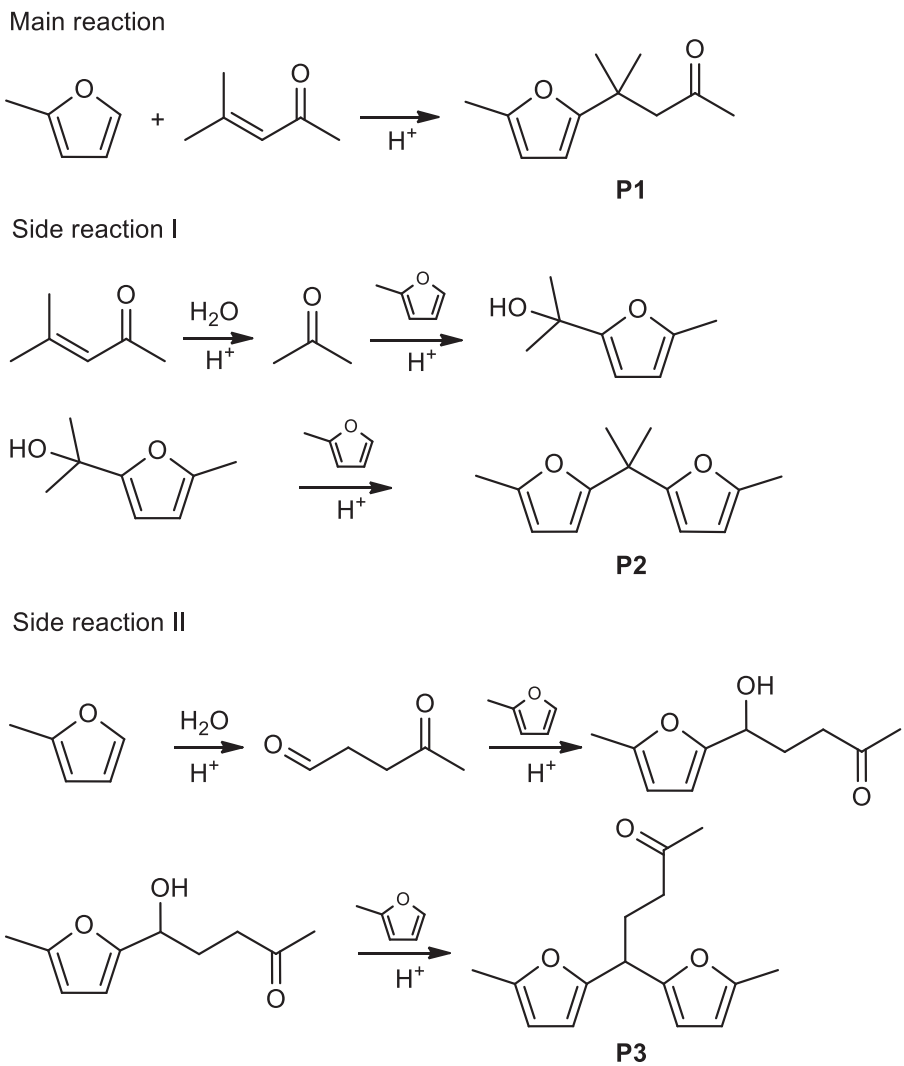

Scheme 1. Reaction pathways for the different products during the alkylation of 2-MF with mesityl oxide.

Among them, Ni–Mo_2C/SiO_2 demonstrated the highest activity and selectivity to diesel or jet fuel range alkanes. To understand the excellent catalytic performance of this catalyst, the fresh and used Ni–Mo_2C/SiO_2 catalysts were characterized by XRD, TEM and XPS.

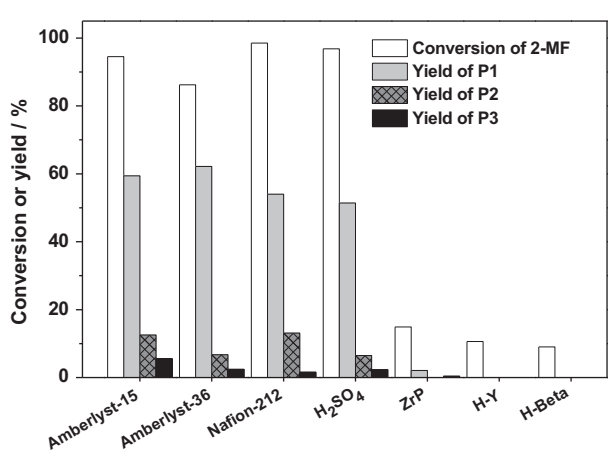

Fig. 1. Conversions of 2-MF and yields of **P1**, **P2**, **P3** over different catalysts; reaction conditions: 333 K, 2 h; 1.64 g (20 mmol) 2-MF, 1.96 g (20 mmol) mesityl oxide, 0.15 g catalyst.

2. Materials and methods

2.1. Preparation of catalysts

Nafion-212 resin (average pore size about 4 nm, 51 μm thick) was supplied by Dupont Company. It was cut into small pieces (about 2 mm × 2 mm) before use. Amberlyst-15 and Amberlyst-36 resins were purchased from Sigma–Aldrich (with average pore diameters of 29 nm and 24 nm, respectively). H-Y (SiO_2/Al_2O_3 = 4) and H-Beta (SiO_2/Al_2O_3 = 394) zeolites were provided by Nankai University. Zirconium phosphate (ZrP) was prepared by the co-precipitation method described in Ref. [25]. In the typical synthesis, 1 mol L^{-1} $ZrCl_2O{\cdot}8H_2O$ and 1 mol L^{-1} $(NH_4)H_2PO_4$ aqueous solution were mixed at a molar ratio of P/Zr = 2.0. The as-obtained precipitate was filtered, washed with deionized water, dried at 333 K for 12 h and then calcined in static air at 673 K for 4 h.

The Pd/SiO_2, Pt/SiO_2, Pd/AC and Pt/AC catalysts used in the HDO step were prepared by the incipient wetness impregnation of the SiO_2 (200 mesh, Qingdao Ocean Chemical Plant, S_{BET} = 391 $m^2\,g^{-1}$) or active carbon (AC, supplied by NORIT Company) with the aqueous solutions of $PdCl_2$ and $H_2PtCl_6{\cdot}6H_2O$. The precursors as obtained were put at room temperature overnight, and then dried at 393 K for 12 h. To facilitate the comparison, the metal contents in the Pd/SiO_2, Pt/SiO_2, Pd/AC and Pt/AC catalysts were controlled as 5 wt.%. These catalysts were reduced *in-situ* by hydrogen at

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