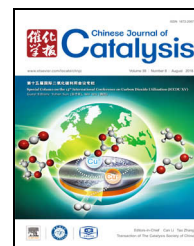


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## Article

# Fabrication of Pd-based metal-acid-alkali multifunctional catalysts for one-pot synthesis of MIBK



Rui Ma <sup>a,b</sup>, Yunpeng Li <sup>a,b</sup>, Guandong Wu <sup>a,b</sup>, Yufei He <sup>a,b,\*</sup>, Junting Feng <sup>a,b</sup>, Yingying Zhao <sup>a,b,\*</sup>, Dianqing Li <sup>a,b</sup>

<sup>a</sup> State Key Laboratory of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup> Beijing Engineering Center for Hierarchical Catalysts, Beijing University of Chemical Technology, Beijing 100029, China

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## ABSTRACT

The one-pot synthesis of methyl isobutyl ketone (MIBK) from acetone using multifunctional catalysts is an important sustainable organic synthesis method with high atom and energy efficiency. Herein, we report a series of Pd supported on mixed metal oxide (MMO) catalysts with controllable acidic/basic/metallic sites on the surface. We study the relationship between the nature, synergy, and proximity of active sites and the catalytic performance of the multifunctional catalyst in the tandem reaction, in detail. In the existence of Lewis acid and base sites, the catalysts with medium-strength acidic/basic sites show preferred activity and/or MIBK selectivity. For multifunctional catalysts, the catalytic properties are more than just a collection of active sites, and the Pd/Mg<sub>3</sub>Al-MMO catalyst possessing 0.1% Pd loading and ~0.4 acid/base molar ratio exhibits the optimal 42.1% acetone conversion and 37.2% MIBK yield, which is among the best reported so far for this tandem reaction under similar conditions. Moreover, the proximity test indicates that the intimate distance between acidic/basic/metallic sites can greatly shorten the diffusion time of the intermediate species from each active site, leading to an enhancement in the catalytic performance.

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## 1. Introduction

Methyl isobutyl ketone (MIBK) is one of the most widely used aliphatic ketones, and is as an excellent solvent in the paint industry and an important reagent for dewaxing mineral oils [1–3]. Traditionally, MIBK is manufactured through a three-step process including the aldol condensation of acetone to diacetone alcohol (DAA), dehydration of DAA to mesityl oxide (MO), and hydrogenation of MO to MIBK. There are common problems in this three-step process, including the intermittent operation and multiple separation and purification of

intermediate species. In addition, a homogeneous acid catalyst (sulfuric acid) and base catalyst (sodium carbonate) are widely used in the process, which causes severe environmental pollution and equipment corrosion [4,5]. Therefore, the conversion of acetone using a practical and efficient process will be highly beneficial. The one-pot synthesis strategy, allowing for different reactions to be carried out in a single vessel without complicated separation and purification between steps, is an alternative to stop-and-go syntheses and has economic and environmental benefits [6–8]. As for the one-pot synthesis of MIBK, the overall process is exothermic ( $\Delta H = -117$  kJ/mol), making

\* Corresponding author. Fax: +86-10-64425385; E-mail: yfhe@mail.buct.edu.cn

# Corresponding author. Fax: +86-10-64437866; E-mail: zhaoyy@mail.buct.edu.cn

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this cascade process a practicable reaction in thermodynamics [9,10]. However, the formation of DAA and MO is thermodynamically limited by unfavorable equilibria; therefore, it is vital to design a catalyst that can simultaneously drive these three steps. The development of heterogeneous multifunctional catalysts enables the one-pot tandem process to be carried out in an environmentally safe and efficient manner.

Pd and Pt, due to their excellent hydrogenation property, are commonly selected as the active metals in the one-pot synthesis of MIBK from acetone [11–15]. Therefore, studies of heterogeneous multifunctional catalysts for the tandem reaction mainly focus on designing and synthesizing suitable supports. For example, Lin et al. [16] reported a Na-modified MgO-supported Pd bifunctional catalyst that showed high acetone conversion due to the enhanced basic strength of the support. Wang et al. [17] deposited Pd nanoparticles on a chromium terephthalate MIL-101, and found that the high density and improved accessibility of acid sites ( $\text{Cr}^{3+}$ ) led to high selectivity towards MIBK; however, this catalyst showed poor stability, with the activity decreasing by 40% after four usages. Furthermore, Robert's study indicated that strong acid sites could promote the dehydration of DAA to MO under mild reaction conditions [18]. In recent years, more and more new materials have been used in the one-pot synthesis of MIBK from acetone, and there is agreement in the literature that the combination of multiple active sites can shift the equilibrium of the condensation step in favor of MO by the simultaneous and irreversible hydrogenation to MIBK [19–21]. However, there have been few in-depth studies on the synergistic effect of these metallic/acidic/basic sites on multifunctional catalysts on the catalytic performance in this tandem reaction, let alone research on the effect of proximity of the multi-active sites.

Layered double hydroxides (LDHs) are a family of two-dimensional (2D) anionic clay materials with the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  represent metallic cations and  $\text{A}^{n-}$  is a charge-balancing anion [22–24]. Based on the construction principle of LDHs, the metal cations within the brucite-like layers are uniformly distributed at the atomic level, and the ratio of  $\text{M}^{2+}/\text{M}^{3+}$  can be tuned in a certain range [25]. In addition, LDHs possess abundant acidic and basic sites associated with the presence of  $\text{O}^{2-}\text{-M}^{n+}$  acid-base pairs within the brucite-like layers [26]. Because of the uniform dispersion of  $\text{M}^{2+}$  and  $\text{M}^{3+}$  cations in the layers and the cation-tunability of LDH materials, the nature, strength and relative number of acidic/basic sites can be finely controlled. The memory effect is another important character of LDH materials; namely, LDHs can be converted to well-dispersed mixed metal oxides (MMO) by calcination at 450–600 °C and retain the nature of the brucite-like layers, such as highly dispersed metal cations and surface acidic/basic sites [27,28]. The large number of adjustable acidic/basic sites on MMOs makes it a class of excellent solid acid/base catalysts. Brucite-like hydroxalite containing  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , or  $\text{Fe}^{2+}$  and Pd/MgAl-hydroxalites have been reported as catalyst precursors or catalysts in the synthesis of MIBK, and the effect of either the acidity or alkalinity of hydroxalites on catalytic performance have been intensively investigated [29–32]. However,

there have been few in-depth studies on the synergistic effect of acidic/basic/metallic sites on catalytic performance in the tandem reaction, especially the effect of the number and proximity of acidic/basic/metallic sites.

In this paper, Pd supported on  $\text{MO}_x$  ( $\text{M} = \text{Ca}, \text{Mg}, \text{Al}, \text{Ti}$ ) and active carbon were prepared for the one-pot synthesis of MIBK to study the effect of acidity and basicity over the bifunctional catalysts on the tandem reaction. A series of multifunctional catalysts with a combination of metallic/acidic/basic active sites were designed using LDH materials. By adjusting the metal ratio within the brucite-like layers of the LDH precursor, the relationship between the catalytic property and density of acidic/basic sites was revealed. We further studied the proximity of the three active sites on the catalytic performance by a physical mixing method, and a possible mechanism was proposed to demonstrate the synergistic effect of basic/acidic/metallic sites in the one-pot synthesis of MIBK from acetone. Moreover, the obtained Pd/ $\text{Mg}_3\text{Al}$ -MMO multifunctional catalyst was optimized by using the deposition-precipitation method, followed by testing of the catalyst stability.

## 2. Experimental

### 2.1. Materials

Analytical-grade chemical reagents including  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{NaCl}$ ,  $\text{MgO}$ ,  $\text{TiCl}_4$ ,  $\text{MgO}$ ,  $\text{AlOOH}$ ,  $\text{Na}_2\text{SO}_3\cdot 9\text{H}_2\text{O}$ ,  $\text{PdCl}_2$ , and urea were purchased from Sigma-Aldrich and used without further purification. The water used in all the experiments was deionized and had an electrical conductivity  $< 10^{-6}$  S/cm.

### 2.2. Preparation of the support precursor

The  $\text{Mg}_x\text{Al}$ -LDHs ( $x = 1, 2, 3, 4, 5$ ) were prepared by a hydrothermal method. For example, to prepare  $\text{Mg}_2\text{Al}$ -LDHs, 7.52 g  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , 5.48 g  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ , and 6.19 g urea ( $n(\text{urea}):n(\text{NO}_3^-) = 1:1$ ) were dissolved in 70 mL of deionized water, then transferred into a 100 mL autoclave and aged at 150 °C for 6 h. The resulting sediment was centrifuged and washed with deionized water several times until the pH reached 7. After drying at 70 °C overnight, the  $\text{Mg}_2\text{Al}$ -LDH precursor was obtained. LDHs with other Mg/Al ratios as well as  $\text{Mg}_3\text{Ti}$ -LDHs,  $\text{MgAl}_{0.5}\text{Ti}_{0.5}$ -LDHs, and  $\text{Ca}_{1.5}\text{Mg}_{1.5}\text{Al}$ -LDHs were prepared via the same method.

The  $\text{Ca}_3\text{Ti}$ -LDH precursor was prepared by a deposition-precipitation method. A NaOH (1.0 mol/L) and  $\text{Ca}(\text{OH})_2$  mixed solution was added to  $\text{TiCl}_4$  (dissolved in diluted HCl with the volume proportion of 1:1) at constant pH = 12. The final product was filtered, washed thoroughly with deionized water, and dried overnight at 70 °C.

### 2.3. Preparation of supported Pd catalysts

Pd was deposited on various supports ( $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , C,  $\text{Mg}_x\text{Al}$ -LDHs,  $\text{Mg}_3\text{Ti}$ -LDHs,  $\text{Ca}_3\text{Ti}$ -LDHs,  $\text{MgAl}_{0.5}\text{Ti}_{0.5}$ -LDHs,

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