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## Practical preparation of methyl isobutyl ketone by stepwise isopropylation reaction of acetone

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### ABSTRACT

A stepwise isopropylation reaction of acetone is developed for preparation of methyl isobutyl ketone (MIBK) through acetone condensation and a recoverable Pt/C-catalyzed transfer hydrogenation of mesityl oxide (MO) with isopropanol (IPA). Almost quantitative MO conversion (up to 99.9%) and excellent MIBK selectivity (up to 99.3%) could be achieved by the method. Since IPA can be obtained from propane, a cheap petrochemical product, the by-product acetone (AT) generated in the reduction of MO could be easily recovered and reused in the preparation of MO, and the Pt/C catalyst could be recycled and reused, this H<sub>2</sub>- and waste-free reaction may be a green and practical method for preparation of the useful fine chemical MIBK.

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### 1. Introduction

The bulk chemical acetone (AT) is generated as a by-product during the oxidative cumene process to produce phenol. Currently, each production of 1 t of phenol generates 0.62 t of acetone. Since the demand of phenol is much higher than acetone, the chemical is largely over-supplied in market. Therefore, technologies that convert acetone into useful fine chemicals are of significant meanings to maintain the balance of the materials in chemical industry chain. Our group aims to develop green techniques with application potential [1–6]. Recently, during the cooperation with industrial circles, we became interested in the subject of acetone conversion and have reported a series of related transformations [7–9].

Yet, acetone is employed to produce methyl isobutyl ketone (MIBK), an important industrial intermediate with very broad applications [10–14] and large market requirement. The conversion has been achieved through one-step or multi-steps processes (Scheme 1) [15–25]. However, both of the protocols require H<sub>2</sub> as

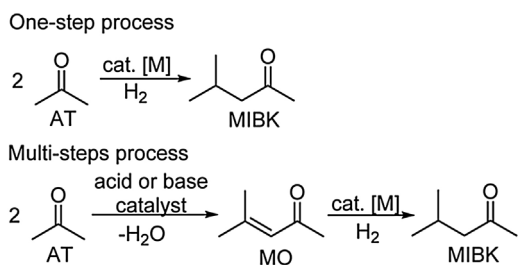
reductant for mesityl oxide (MO) hydrogenation, which is explosive and required specific equipment for long distance transportation. Inspired by our previous studies on alkylation with alcohol [26–29], we wish to develop a similar H<sub>2</sub>-free synthetic route through the isopropylation of acetone with isopropanol (IPA) to produce MIBK.

Recently, we successfully achieved a novel hydrogen-transfer reduction of MO to produce MIBK (Scheme 2). The reaction employed isopropanol (IPA) as the safe hydrogen source instead of H<sub>2</sub> and was performed without additional solvent or additives. The catalyst Pt/C was recyclable, while the by-product acetone could be recycled and reused to produce the starting material MO (Scheme 2, Eq. 1). Thus, the neat result of this technique was the formation of MIBK from one molecule of acetone and an IPA (Scheme 2, Eq. 2). Currently, IPA is industrially produced through the gas phase hydration of propylene, which comes from the dehydrogenation of the cheap petrochemical product propane [30]. Thus, compared with the conventional H<sub>2</sub> reduction protocols, the new technique reduces the cost of production. Herein, we wish to report our findings.

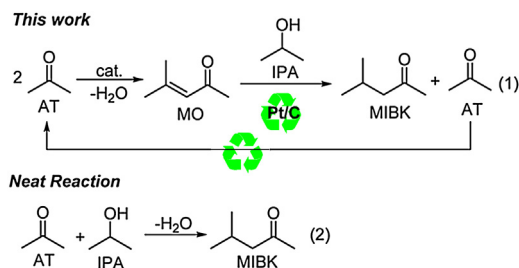
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**Scheme 1.** Conventional methods for preparation of MIBK.



**Scheme 2.** Stepwise isopropylation of MO with IPA: (1) Successive acetone condensation and waste-free recoverable Pt/C-catalyzed transfer hydrogenation of MO with IPA; (2) Neat reaction.

## 2. Experimental

### 2.1. General

Chemicals were purchased and directly used as received without further purification. Zn, ZnCl<sub>2</sub>, ZnO and RuCl<sub>3</sub> were analytical pure. Pt/C contained 1.37% weight ratio of Pt (3% Pt loading on carbon, with 54.5% of water) and was prepared by Evonik Industries AG.; Pd/C contained 2.32% weight ratio of Pd (5% Pd loading on carbon, with 53.7% of water) and was prepared by Evonik Industries AG.; Ru/C contained 2.28% ratio of Ru (5% Ru loading on carbon, with 54.5% of water) and was prepared by Sumitomo Chemical Industry Co. Ltd. GC-mass was determined on the Thermo ISQ type gas chromatography-mass spectrometer. GC analysis of the reactions was performed by using Agilent 7890 B instrument. Acetone conversion and MIBN selectivity were calculated according to the internal standard curve (with methyl benzoate as internal standard). Detailed analytical method was provided in supplementary content.

### 2.2. Preparation of MO

MO can be synthesized through industrially mature base-catalyzed acetone condensation [15–25]. In this work, it was obtained from the semi-works production experiment using the proline catalysis technologies reported by us recently [7–9]. The reaction led to MO, diacetone alcohol (DAA) and isophorone (IP) in up to 96% total selectivity, in which MO was the overwhelming major product. DAA and IP were separable during the rectification processes. The former was reused to produce MO by dehydration, while the later was a nice fine chemical with good profit and market requirement.

### 2.3. Detailed procedures for the conditional optimization experiments

1.02 g of MO (10 mmol), 1.44 g of IPA (24 mmol), 1.5 g of Pt/C (1.05 mol %) and 10 mL solvent were added into a pressure tube charged with N<sub>2</sub>. The pressure tube was then sealed and heated at

90 °C for 7 or 14 h. After cooling to room temperature, the mixture was filtrated with a G4 sand core funnel. The filtrate was analyzed by GC to determine the MO conversion and MIBK selectivity.

### 2.4. Detailed procedures for the solvent recycle & reuse experiments

1.02 g of MO, 10 mL of IPA and 1.5 g of Pt/C (1.05 mol %) were added into a pressure tube charged with N<sub>2</sub>. The pressure tube was then sealed and heated at 90 °C for 7 or 14 h. The mixture was then cooled to room temperature and filtrated with a G4 sand core funnel. The filtrate was analyzed by GC to determine the MO conversion, MIBK selectivity and the acetone and IPA contents in liquid. In the next cycle, the reaction was performed by using fresh Pt/C catalyst and the solvent with IPA/acetone ratio determined by GC in the last turn of reaction.

### 2.5. Detailed procedures for the catalyst recycle & reuse experiments

1.02 g of MO, 10 mL of IPA (rectification residue of Table 3, *vide infra*) and 1.5 g of Pt/C (1.05 mol %) were added into a pressure tube charged with N<sub>2</sub>. The pressure tube was then sealed and heated at 90 °C for 7 or 14 h. The mixture was then cooled to room temperature and filtrated with a G4 sand core funnel. The filtrate was analyzed by GC to determine the MO conversion and MIBK selectivity. The recycled catalyst was dried under vacuum and weighted. After a supplement of the lost catalyst, the recycled Pt/C was reused in the next turn of reaction.

### 2.6. Detailed procedures for the experiments of the recycle & reuse of solvent & catalyst simultaneously

1.02 g of MO, 10 mL of IPA (rectification residue of Table 3, *vide infra*) and 1.5 g of Pt/C (1.05 mol %) were added into a pressure tube charged with N<sub>2</sub>. The pressure tube was then sealed and heated at 90 °C for 14 h. The mixture was then cooled to room temperature and filtrated with a G4 sand core funnel. The filtrate was analyzed by GC to determine the MO conversion, MIBK selectivity and the acetone and IPA contents in liquid. The recycled catalyst was dried under vacuum and weighted. After a supplement of the lost catalyst, the recycled Pt/C was reused in the next turn of reaction, which employed solvent with IPA/acetone ratio determined by GC in the last turn of reaction.

### 2.7. Procedure for the activity test of other catalysts (Zn, Pd and Ru catalysts)

1.02 g of MO (10 mmol), 10 mL of IPA and 0.25 mmol of different types of catalysts (*vide infra*, Scheme 4) were added into a pressure tube charged with N<sub>2</sub>. The pressure tube was then sealed and heated at 90 °C for 14 h. After cooling to room temperature, the mixture was filtrated with a G4 sand core funnel. The filtrate was analyzed by GC.

## 3. Results and discussion

### 3.1. Solvent screenings

Since MO could be easily synthesized through industrially mature base-catalyzed acetone condensation [15–25] or the proline-catalyzed method developed by us recently [7–9] (Scheme 3), the hydrogen transfer reduction of MO with IPA was the only issue that need to be resolved in the process development. We initially performed the reaction in toluene catalyzed by 1.05 mol % of Pt/C with 2.4 equiv. of IPA as the hydrogen source. Heating

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