



Short communication

# An efficient bifunctional catalyst of TiO<sub>2</sub> coating and supported Pd on cordierite for one-pot synthesis of MIBK from acetone

Shoude Zhang, Pengcheng Wu, Lequn Yang, Yonghua Zhou<sup>\*</sup>, Hong Zhong<sup>\*</sup>

Chemistry and Chemical Engineering College, Central South University, Changsha 410083, China

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## ABSTRACT

We report here an efficient bifunctional catalyst of TiO<sub>2</sub> coating and supported Pd on cordierite (T500/Cor&Pd/Cor) for one-pot synthesis of MIBK from acetone. The obtained 75% MIBK selectivity at 60% acetone conversion was the best performance ever reported for metal oxide based catalyst, without obvious deactivation for at least 12 h on stream. The superior performance of T500/Cor&Pd/Cor could be attributed to the dominant base sites and moderate acid sites on TiO<sub>2</sub> coating caused by the nanoscale anatase crystallite, and its combination style of being physically mixed with Pd.

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## 1. Introduction

Methyl isobutyl ketone (MIBK) has been widely used in many areas, such as paint, resins, and coating [1]. Traditionally, MIBK is mainly synthesized via a three-step process, including acid or base-catalyzed acetone condensation to diacetone alcohol (DA), acid-catalyzed dehydration of DA to mesityl oxide (MO), and metal-catalyzed hydrogenation of MO to MIBK [2]. Compared with such three-step process, one-pot synthesis of MIBK catalyzed by Pd/resin has been adopted in industry processes, which can avoid separation of the intermediates DA and MO. However, due to the high reaction pressure and low thermal stability of resin, alternative catalysts are still the research focus [3].

Supported Pd catalyst loaded on metal oxide or zeolite, such as ZSM-5 [4], SAPO [5], Al<sub>2</sub>O<sub>3</sub>-MgO [6], Nb<sub>2</sub>O<sub>5</sub>-SiO<sub>2</sub> [7], ZnO-Cr<sub>2</sub>O<sub>3</sub> [8], hydroxide [9], and SiO<sub>2</sub>-MgO [10] is a new type of catalyst alternative to Pd/resin catalyst over MIBK synthesis from acetone. So far, the highest acetone conversion and MIBK selectivity was reported to be Pd/Zn-Cr (1:1), having a moderate Lewis acid sites (1.2 mmol/g density), and producing MIBK with a selectivity of 78% at 40% acetone conversion [8]. In addition, HZSM-5 covered partially by SiO<sub>2</sub>-ZrO<sub>2</sub> exhibited a decreased acid strength, leading to an improved acetone conversion of 33.4% and MIBK selectivity of 88.1% than that on HZSM-5 [4]. These results suggested that a satisfactory catalytic performance will be probably produced over a Pd catalyst loaded on a support with moderate acidic strength and acidic amount. TiO<sub>2</sub> has been used as solid acid and solid base for Knoevenagel [11] and aldol condensation [12]

reactions. However, TiO<sub>2</sub> is not considered for this reaction yet probably because of its low surface area unsuitable for Pd loading. Besides the effect of acid/base property of catalysts, the mass transfer limitation in pores of catalysts also plays an important role on the MIBK synthesis from acetone. Li [13] synthesized Pd-doped propyl sulfonic acid-functionalized hollow nanospheres for this reaction. These hollow nanospheres exhibited a higher activity than their bulk mesoporous counterparts, due to the short diffusion resistance of hollow nanospheres.

In this study, we deposited TiO<sub>2</sub> coating on cordierite monolith via sol-gel method and then mixed with supported Pd on cordierite, to obtain a novel physically mixed bifunctional catalyst TiO<sub>2</sub>/Cor&Pd/Cor. On the one hand, we adopted physical mixing instead of loading Pd on TiO<sub>2</sub> support, trying to avoid the change of acid/base property of TiO<sub>2</sub> caused by the Pd loading process. On the other hand, TiO<sub>2</sub> coating on cordierite and Pd on cordierite ensured the completely surface distribution of both acid sites and Pd sites. As we expected, TiO<sub>2</sub>/Cor&Pd/Cor presented a high activity and a high selectivity to MIBK.

## 2. Experimental

For the sample preparation, characterizations and catalytic tests have been shown in the experimental section in the Supporting information.

## 3. Results and discussion

## 3.1. Catalyst characterizations

The crystalline type and size of T500 powder were identified by XRD pattern (in Fig. S1) and TEM images (in Fig. 1). It was shown in Fig. S1

<sup>\*</sup> Corresponding authors.

E-mail addresses: [zhouyonghua@mail.csu.edu.cn](mailto:zhouyonghua@mail.csu.edu.cn) (Y. Zhou), [zhongh@csu.edu.cn](mailto:zhongh@csu.edu.cn) (H. Zhong).

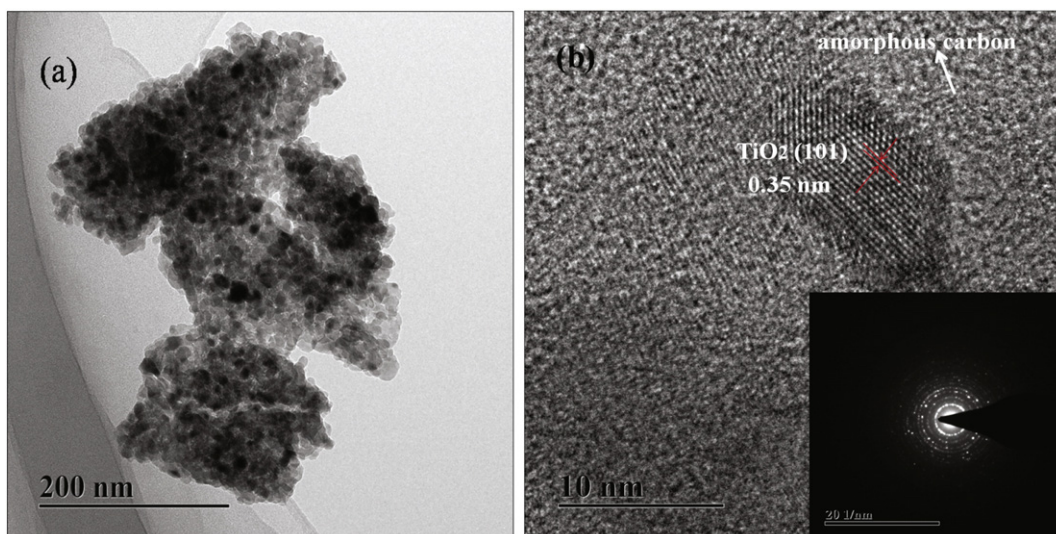


Fig. 1. TEM images of T500 powder.

that T500 was presented in the anatase phase and the crystallite size was estimated by the FWHM of characteristic peak using Scherrer's equation to be 14.1 nm (in Table S1). It was observed in Fig. 1(a) that T500 exhibited a wormhole-like morphology with small particles. The HRTEM image in Fig. 1(b) showed that TiO<sub>2</sub> crystallite size was about 10 nm, which was near to that estimated from XRD pattern using Scherrer's equation. In addition, carbon material was found among the TiO<sub>2</sub> crystallite, which was probably ascribed to the incomplete hydrolysis of tetrabutyl titanate.

The successful coating of TiO<sub>2</sub> on cordierite was revealed by XPS spectra and FT-IR spectra in Fig. 2. The peaks at binding energy 458.4 eV and 464.1 eV for Ti 2p could be attributed to TiO<sub>2</sub> [14]. The O 1s spectra were composed of two contributions. The peak at 529.5 eV for O 1s indicated that Ti ions were in an octahedral environment, which agreed with the values reported for TiO<sub>2</sub> [15]. In addition, a small shoulder peak at 532.1 eV denoted the presence of surface –OH groups. As for the C 1s spectra, three peaks at 284.5, 285.9, and 288.1 eV could be assigned to C–C, C–O, C=O bonds, respectively,

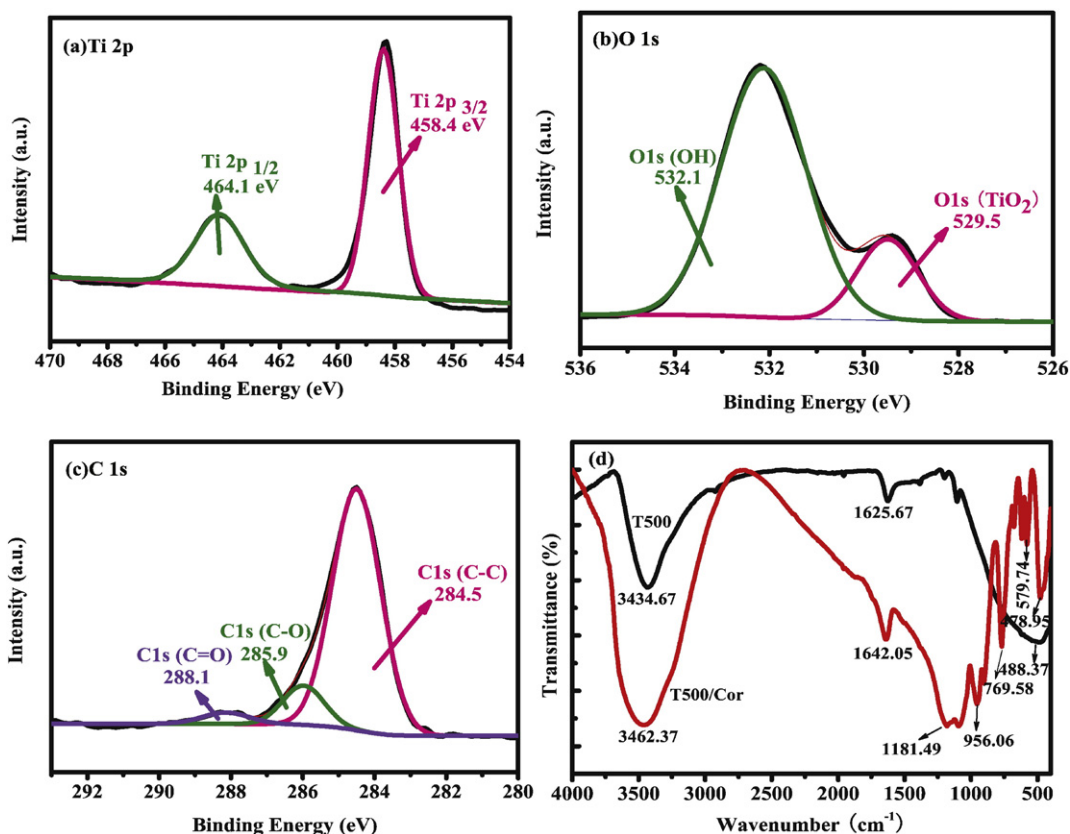


Fig. 2. XPS spectra of T500/Cor (a) Ti 2p core level, (b) O 1s core level, (c) C 1s core level, and (d) FT-IR spectra of T500 powder and T500/Cor.

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