The synthesis of acetone from isobutane with the intermediate of di-tert-butyl peroxide

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Abstract. Acetone, a widely used chemical raw material, is synthesized by the cumene peroxide method. At present, the cumene peroxide method has the disadvantage of high raw material cost, low flexibility, and complex process. Isobutane as an important C4 resource is mainly used as liquefied gas, which is a waste of fossil resources. Based on that, a novel acetone synthesis method from isobutane with the intermediate of di-tert-butyl peroxide (DTBP) is proposed. The reaction performance of TiO2-S and the optimal reaction condition for isobutane selective oxidation to DTBP is evaluated, and the selectivity to DTBP is 30 wt%. Then, the ZSM-5 is proved as the optimal catalyst for DTBP decomposition and the acetone selectivity is 38 wt% under the optimal reaction condition. In general, isobutane selective oxidation to DTBP which is further catalytic decomposition to acetone is feasible.

Keywords: Acetone synthesis; Selective oxidation; di-tert-butyl peroxide (DTBP); Catalytic decomposition.

1. Introduction

Acetone, is a kind of important raw material, which is widely used in synthesizing a variety of chemical products such as epoxy resin, polyisoprene rubber, methyl methacrylate, and so on [1]. The reported acetone product method includes the bio-fermentation method, acetylene hydration method, and isopropanol dehydrogenation method [2]. Due to the production efficiency and cost, these methods fail to be scaled up. Currently, the industrial acetone product method uses benzene and propylene as raw materials [3]. Firstly, benzene and propylene are alkylated to cumene, then, cumene is selectively oxidized into cumene peroxide, and finally, cumene peroxide will be converted into acetone and phenol (Fig. 1) [4]. However, this method has the disadvantages of expensive raw materials, low product flexibility, and low acetone selectivity. So, exploring a novel method for the highly efficient generation of acetone is essential.

Isobutane, is an important fossil source, which originated from the cracking reaction. At present, the amount of isobutane consumed as liquefied gas exceeds 60%, which is a waste of oil resources. The main usage of isobutane in industry is the synthesis of isobutene, alkylated oils, and methacrolein/methacrylic acid (MAL/MAA). The isobutane is dehydrogenated to isobutene which is further etherified with methanol to methyl tert-butyl ether (MTBE) [5]. MTBE and alkylated oils are applied as a gasoline additive. With the popularity of electric car vehicles, the consumption of MTBE and alkylated oils has decreased sharply. So, the alkylation and dehydrogenation of isobutane may not be a trusted route of isobutane utilization. The selective oxidation of isobutane is a potential method for isobutane utilization because the product is high-valued and the reaction processes [6]. Some literature reported isobutane can be selectively oxidized into many organic oxygenates. Schindler et al. take Mo-V-P to catalyze isobutane selective oxidation to MAL, and the yield of MAL is 6.4mmol/gcat [6]. Then, they studied the kinetics of isobutane selective oxidation over Mo-V-P. Guan et al. take Mo-V-Te as the catalyst for isobutane selective oxidation to MAL/MAA, the total yield can be 7.1%[7]. Afterward, they introduce the P into Mo-V-Te and the total selectivity of MAL/MAA is up to 68 wt% when the reaction temperature is 400 oC [8]. Pual et al. applied kegging-type polyoxometalates in this process, but the stability was poor [9]. Besides the above process, isobutane can be selectively peroxidized into tert-butyl hydroperoxide

(TBHP), which is applied in the process of the isobutane/propylene co-oxidation process. From the above study, it is inferred that catalysis have an obvious effect on the production of isobutane selective oxidation. So, di-tert-butyl peroxide (DTBP) is widely used as initiator for reaction and crosslinker for olefin polymerization. It may be synthesized directly from isobutane selective oxidation, though it is currently produced by oxidizing tert-butanol with hydrogen peroxide [10].

The catalytic decomposition of organic peroxide is widely used to synthesize ketones such as the catalytic decomposition of cumene peroxide and cyclohexane peroxide [4]. For instance, Zhao et al. found that resin catalysts have excellent activity to catalyze the decomposition of cumene peroxide, but they have been lost through fragmentation [11]. Some researchers reported that zeolites such as ZSM-5, Beta, and Y have better performance for cumene peroxide decomposition [12]. Knifton et al. studied the performance of Lewis acid such as WF6, SiF4, FeCl3, and SnCl4 for cumene peroxide decomposition, they found that cumene peroxide can be totally converted [13]. Selvin et al. revealed that phosphotungstic acid also has excellent performance for cumene peroxide decomposition [14]. Similar reports have been made in the catalytic decomposition of cyclohexyl peroxide. However, the catalytic decomposition of DTBP has not been reported yet.

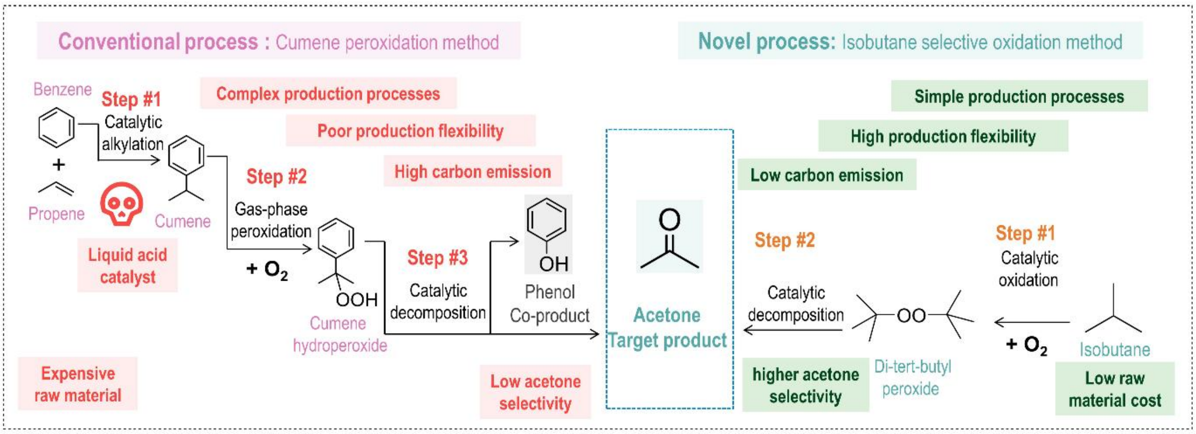

Fig. 1 The novel method for acetone synthesis from isobutane

To overcome the above issues in acetone synthesis, DTBP synthesis, and DTBP catalytic decomposition, a novel method is proposed to synthesize acetone with the raw material of isobutane and take DTBP as an intermediate (Figure 1). Compared with the cumene peroxide method, the DTBP method to synthesize acetone has the advantage of low raw material cost, high production flexibility, and shorter process.

In this work, the feasibility of the acetone synthesis from isobutane selective oxidation with the intermediate of di-tert-butyl peroxide is checked. The performance of TiO2-S for isobutane selective oxidation to DTBP is ensured. Moreover, ZSM-5 is ensured as the optimal catalyst among ZrO2, FeCl3, H3PW12O40, and ZSM-5 for catalyzing DTBP decomposition. And, the acetone can be detected in the DTBP decomposition product. In conclusion, this work provides a new method for isobutane unitization and acetone synthesis.

2. Experimental section

2.1 Catalyst preparation

The sulfated TiO2 was prepared from the calcination of TiOSO4 at 600 oC for 3h and denoted as TiO2-S. The ZSM-5 (SiO2/Al2O3 = 38) zeolites were purchased from Nankai University Catalyst Co. Ltd.

2.2 Characterization method

The temperature-programmed desorption of ammonia (NH3-TPD) was empirically examined utilizing a TP-5078 apparatus, specifically to assess both the catalyst's acid properties. For each experimental trial, it utilized a 0.1 g catalyst sample endowed with a particle size ranging between 40-60 mesh; this was subjected to high-temperature pretreatment in helium at 550 oC for half an hour, followed by swift cooling down to 100 oC. Subsequently, we let an NH_3 gas stream purify the system for 30 minutes until adsorption attained maximum levels. Then, the helium stream was employed to dissolve the physically bound NH_3. Lastly, as per our methodology, we commenced NH_3 desorption by incrementally raising the temperature within the system from 100 to 800 oC at a prescribed heating rate of 10 oC·min-1 under the blanket of helium. This process allowed us to detect the desorbing species via an online thermal conductivity detector (TCD).

The Pyridine desorption infrared (Py-IR) was performed on a Fourier Transform Infrared Spectrometer (Brucker Tensor 27). Two identical samples were subjected to drying for an additional 12 hours at an oven temperature of 120 ℃, followed by a subsequent vaporization phase of 12 hours using a vacuum oven set at room temperature. Upon completion of adsorption, the sample was subject to desorption at 120 °C in the same vacuum oven for another 12 hours. Post-desorption, a Py-IR analysis was conducted with the untreated reference sample forming the baseline for comparison.

2.3 Catalytic performance test

The catalytic performance test of isobutane peroxidation to DTBP is as follows: before the experiment, an optimal quantity of catalyst was introduced into the reactor. Subsequently, the isobutane gas was infused on five separate occasions to eliminate any residual air present within the reactor. The liquid form of isobutane was subsequently infused into the reactor followed by imparting gas phase oxygen into it. The collective input dosage of isobutane and oxygen amounted to 20 grams and the mole ratio of isobutane and oxygen is 10. The reactor system was subjected to elevated temperatures for an appropriate duration. Upon reaching the designated reaction period, the reactor's temperature was slowly brought down to environmental levels. Most importantly, since the reaction is strongly exothermic, it is necessary to inject the cooling coil with water during the reaction.

The catalytic performance of DTBP was tested in a fixed-bed reactor. The fixed-bed reactor is equipped with a mass flow meter, a liquid high-pressure advection pump, a quartz reactor, and a gas-liquid separation unit. The catalyst was loaded into the quartz reactor before the start of the reaction and gradually heated up to the set temperature under a flow of N_2. An advection pump is activated to pump the DTBP into the reactor and the gas-liquid phase products are collected and metered separately at the gas-liquid separation unit.

The resultant products were scrutinized utilizing a FULI 9720Plus gas chromatograph, incorporating dual flame ionization detectors (FID), and a thermal conductivity detector (TCD). To discern oxygenated chemical entities, the product was directed through an innowax capillary column for detection via an FID. Hydrocarbons, on the other hand, were incorporated into an alumina column, where they were detected through FID. For inorganic gases such as nitrogen (N_2), oxygen (O_2), and carbon oxides (CO_x), a 5A packed column facilitated their separation, subsequently analyzed using a TCD. Notably, small quantities of C1-C6 oxygenated compounds and hydrocarbons inclusive of acetone and CO_x, could be identified. Subsequently, oxygen conversion and product selectivities were computed employing the following equations: $X = (\text{quantity of converted feed}) / (\text{total quantity of feed}) \times 100\%$; $S_{product,\ i} = (\text{mass of i specific product}) / (\text{overall mass of all})$

3. Results and Discussion

3.1 The selective oxidation of isobutane to DTBP over TiO_2-S

To obtain the optimal reaction results of isobutane selective oxidation to DTBP over TiO_2-S, the reaction conditions including reaction temperature, reaction time, the catalyst dosage, and the mole ratio of i-C4o must be studied, the results are depicted in Fig. 2.

It is revealed from Fig. 2 that the main product is TBHP, tert-butanol (TBA), isobutene, and others besides DTBP. And, with the increase in reaction temperature, the oxygen conversion will increase and the selectivity to DTBP will decrease slightly. With the increase in reaction time, the oxygen conversion will increase all the time, the selectivity to DTBP will increase and then decrease and it will get maximum when the reaction is 60 min. When the reaction system is noncatalytic, the main product is TBHP and TBA, which indicates the importance of the TiO2-S catalyst. When the dosage of TiO2-S catalyst is 0.5 g, the selectivity to DTBP and oxygen conversion will both get maximum. Finally, the oxygen conversion and DTBP selectivity will increase together with the mole ratio increase, but it should be chosen as 10 when considering the isobutane conversion. In general, under the optimal reaction conditions (the reaction temperature is 150 oC, the reaction time is 60 min, the catalyst dosage is 0.5 g, and the mole ratio of isobutane to oxygen is 10), the oxygen conversion is 90 %, the DTBP selectivity is 30 wt%.

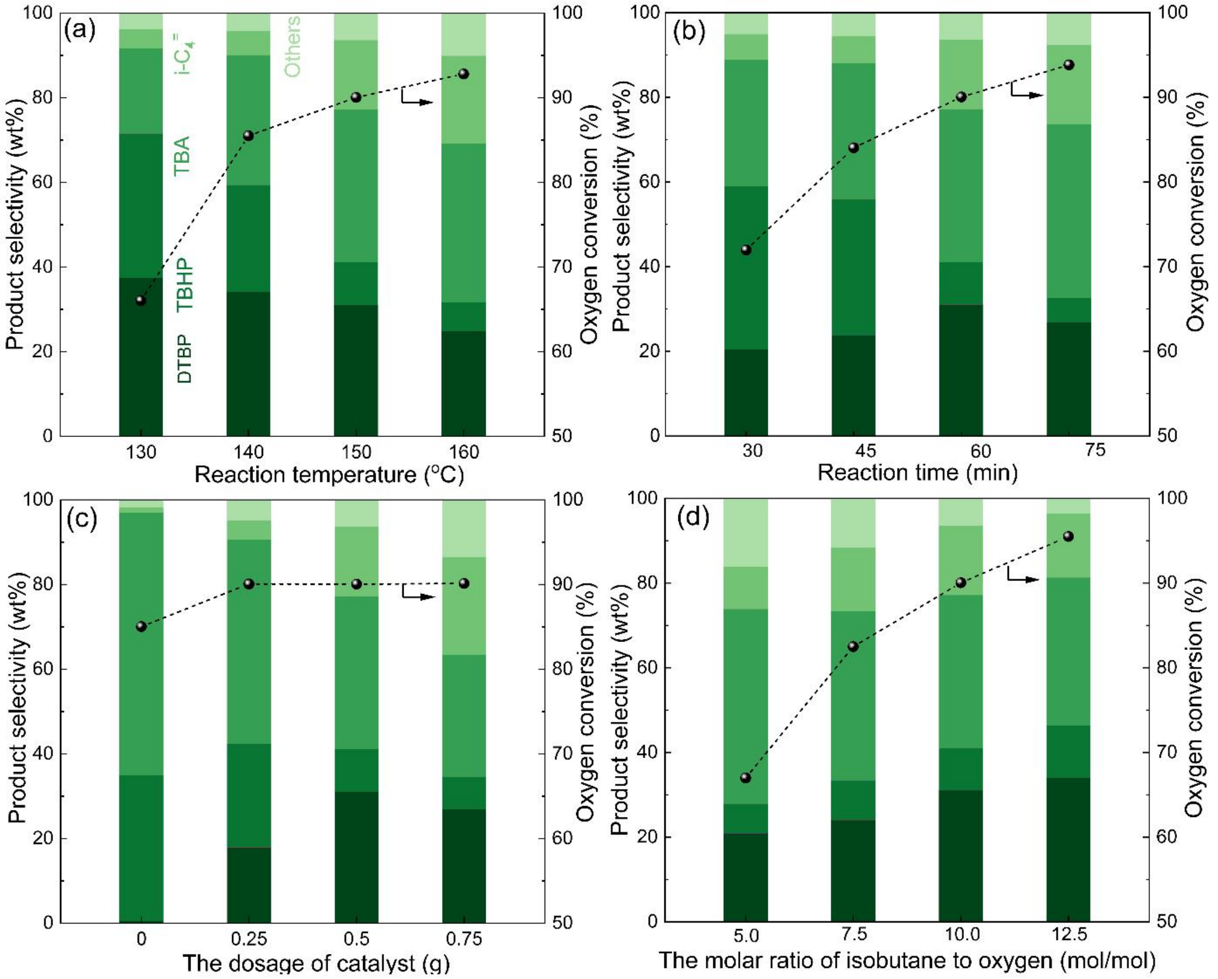

Fig. 2 The optimization of reaction condition of isobutane peroxidation to DTBP: (a) the reaction temperature, (b) the reaction time, (c) the dosage of catalyst, and (d) the mole ratio of isobutane to oxygen.

3.2 The catalytic decomposition of DTBP

3.2.1 The screening of optimal catalysis

To examine the feasibility of DTBP catalytic decomposition to acetone, catalysts such as ZrO2, FeCl3, H3PW12O40, and ZSM-5 which is active for cumene peroxide catalytic decomposition are applied in DTBP catalytic decomposition in this section, and the results are depicted in Figure 3.

It is demonstrated that the main product of DTBP catalytic decomposition includes acetone, TBA, isobutene, and other products. All the catalysts can catalyze the decomposition of DTBP, and there is no significant difference in the type of product. Moreover, the type of catalyst significantly affects the product distribution of DTBP decomposition. ZSM-5 zeolite shows high catalytic activity for DTBP decomposition as well as the highest selectivity to acetone, which may result from the complex pore structure and abundant acid site. The following content takes ZSM-5 as a research key point.

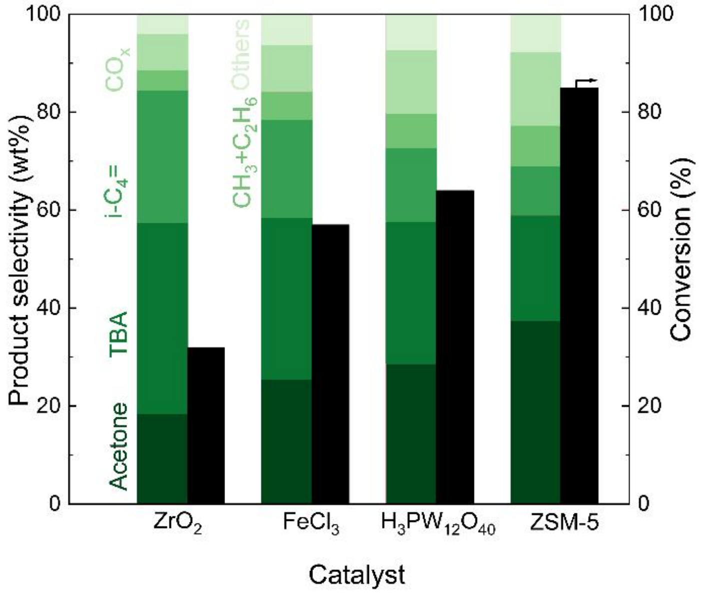

Fig. 3 The screening of optimal catalysis for DTBP catalytic decomposition

3.2.2 The optimization of reaction conditions

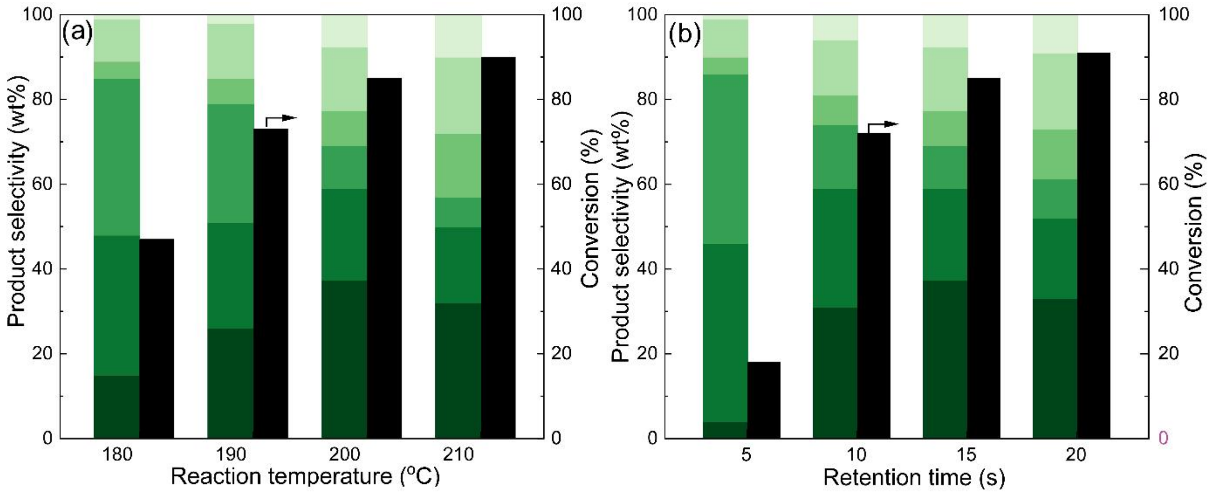

Fig.4. The reaction condition optimization includes (a) reaction temperature and (b) retention time for DTBP catalytic decomposition.

The reaction condition for DTBP catalytic decomposition with the catalyst of ZSM-5 is optimized in Fig. 4. It is revealed from Figure 4a that the DTBP conversion will increase all the time, the DTBP selectivity will increase then decrease and reach the maximum at 200 oC. Fig. 4b revealed the influence of retention time on DTBP catalytic decomposition. The conversion and DTBP selectivity trends with retention time are consistent with changes in reaction temperature. So, the optimal reaction condition for DTBP catalytic decomposition over ZSM-5 is 200 oC and 15s. Under this condition, the DTBP conversion is 85 %, the acetone selectivity is 38 wt%.

4. Summary

This work verified the feasibility of the acetone synthesis from isobutane selective oxidation with the intermediate of di-tert-butyl peroxide. Firstly, the performance of TiO2-S catalysed isobutane to DTBP is evaluated, and the optimal result is 90 % oxygen conversion and 30 wt% DTBP selectivity. Finally, the ZSM-5 is ensured as the optimal catalyst for DTBP catalytic decomposition to acetone. And, under the optimal reaction conditions, 85% DTBP conversion and 38 wt% acetone selectivity can be obtained. In general, this work provides a novel method for acetone synthesis from isobutane.

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