



# Cycloketone condensation catalyzed by zirconia: Origin of reactant selectivity

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## ABSTRACT

Aldol condensation of cycloketone(s) is an efficient reaction path to synthesize polycyclic compounds via C–C bond formation. In this work, aldol condensation of cyclopentanone and/or cyclohexanone over monoclinic ZrO<sub>2</sub> has been investigated by combination of experiments and DFT calculations. Both self-condensation and cross-condensation of cyclopentanone and/or cyclohexanone were carried out at 130 °C in a solvent-free condition under atmospheric pressure. Reactant selectivity and product distribution were analyzed. DFT calculations were performed to investigate the mechanism and reactant selectivity of cycloketone condensation on ZrO<sub>2</sub>, showing the favored cross-condensation between cyclopentanone and cyclohexanone is ascribed to the formation of a metastable state of a seven-membered ring that lowers activation barrier during C–C bond formation.

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## 1. Introduction

Aldol condensation plays an important role in organic synthesis for C–C bond formation, and has numerous applications in the synthesis of fine chemicals [1–4]. For instance, aldol condensation has been extensively employed to tailor molecular structure of lignocellulose compounds from renewable biomass resources for the production of liquid fuels [5–10]. The mechanism of homogeneously catalyzed aldol condensation has been investigated extensively through both experimental and computational studies [1,2,11–13]. Besides homogeneous process catalyzed by strong base, such as sodium and calcium hydroxide, heterogeneous catalysts are preferred because of easy separation and less corrosive, and developed for a better protection of the environment for aldol condensation [14–18]. Metal oxide catalysts, e.g., MgO, ZrO<sub>2</sub>, CaO and their mixtures, have been used to catalyze the formation of new C–C bonds by aldol reactions, and applied to yield high-density diesel and jet fuel by increasing the molecular weight [19–22], forming branched [23–25] and cyclic (especially the polycyclic) [26–29] hydrocarbons. Moreover, it's useful process to convert renewable biomass into valuable chemicals. For instance, polycyclic hydrocarbons with higher density have been prepared

via aldol reactions of the platform compounds derived from lignocellulose [10,26,29,30].

Even though this reaction has been explored for over one hundred years and used extensively for C–C bonds formation, mechanism studies on aldol reaction catalyzed by solid base catalysts are still rare [31]. Recently, a DFT study on the aldol reaction of small molecules (propanal) on zirconia (ZrO<sub>2</sub>) and ceria (CeO<sub>2</sub>) surfaces has been reported by An [32]. The work demonstrated an eight-membered ring transition state for the aldol reaction of propanal on O-terminated ZrO<sub>2</sub>(1 1 1) and CeO<sub>2</sub>(1 1 1) surfaces.

Our goal is to investigate the reaction mechanism for large molecules, e.g., cycloketones, catalyzed by zirconia. We show here that monoclinic ZrO<sub>2</sub> tends to be reactant selective for aldol condensation of various cycloketones to give interesting product distributions. The following work will conduct a study on the reaction mechanism, especially for the selectivity, both experimentally and theoretically.

## 2. Results and discussions

ZrO<sub>2</sub> has become an increasingly popular catalyst for a variety of industrial processes in recent years [33]. As a bifunctional oxide, ZrO<sub>2</sub> possesses weak acidic and basic sites on its surface that are able to catalyze reactions cooperatively. Herein, ZrO<sub>2</sub> catalyst was prepared by a simple precipitation method using ZrOCl<sub>2</sub>·8H<sub>2</sub>O

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as precursor [34]. XRD pattern of the as-synthesized catalyst in Figure S1 shows the  $ZrO_2$  has monoclinic phase. We used this sample as catalyst for aldol condensation reactions of various cycloketones. As two platform compounds from lignocellulose of biomass, cyclopentanone and cyclohexanone have been produced from lignin and hemicellulose, respectively, as illustrated in Scheme S1 [26,35–38]. Moreover, the obtained cycloketones have been used as a potential feedstock for the synthesis of high-density polycyclic molecules [26,27,39].

Despite remarkable progress in the use of heterogeneous catalysts for aldol condensation, the mechanism of this process is not well understood, especially, the origin of reactant selectivity in this reaction is still not clear. Therefore, experiments were performed to investigate the behavior of  $ZrO_2$  during aldol condensation. We selected pure cyclopentanone (C5), pure cyclohexanone (C6) and a mixture of C5 and C6 with a molar ratio of 1:1 as reactants. The reaction was carried out at 130 °C in a solvent-free condition under atmospheric pressure. Condensation reactions of various cycloalkanones were investigated experimentally with monoclinic  $ZrO_2$  catalysts (Fig. 1, Figure S2 and Figure S3). In all the reactions, the selectivity of dimer condensation products was 100%, and no trimer product was detected.

$ZrO_2$  is active catalyst for the self-condensation of cyclopentanone C5 with the conversion of 18.4%, but not for the same reaction with cyclohexanone (conversion is only 0.7%). Surprisingly, the monoclinic  $ZrO_2$  catalyst is even more active for crossed condensation in the presence of both cyclopentanone and cyclohexanone (molar ratio = 1:1). Three dimeric products, 2-cyclo-

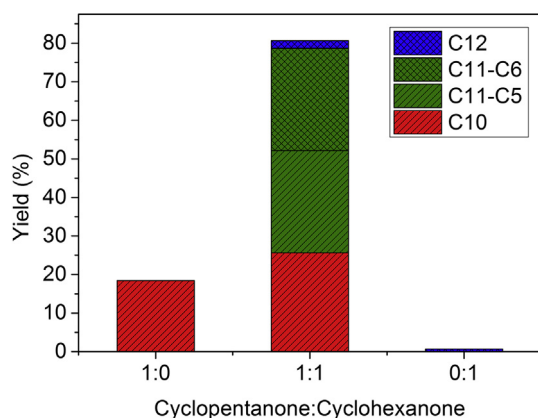
tylidencyclopentanone (C10), 2-cyclohexylidencyclopentanone (C11), and 2-cyclohexylidencyclohexanone (C12), are detected. 2-Cyclohexylidencyclopentanone was the major dimeric product and no 2-cyclopentylidencyclohexanone were observed [40]. The product composition of crossed condensation is summarized in Scheme 1.

Our results show the conversion of cyclopentanone increases from 18.4% in self-condensation to 52.2% in cross-condensation. Similarly, 28.5% of cyclohexanone was converted during crossed condensation, which is much higher than the conversion for its self-condensation (0.7%). In cross-condensation, the fraction of cyclopentanone that went into C10 (49.1%) is approximately equal to that participated in the formation of C11 (50.9%). In contrast, most cyclohexanone joined in the construction of C11 (93.1%), but only small amount of cyclohexanone went into C12.

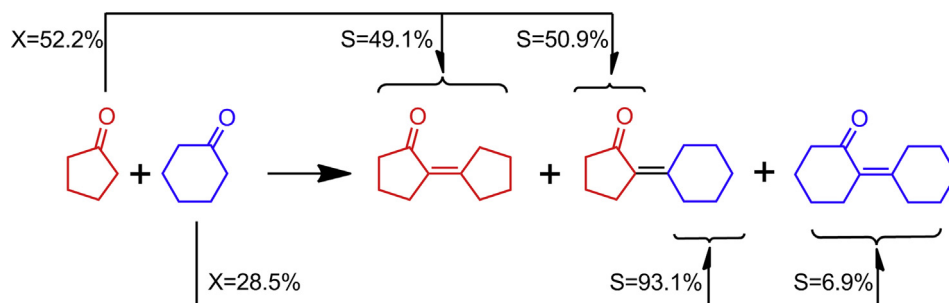
FTIR spectra of the free and adsorbed cyclopentanone/cyclohexanone on monoclinic  $ZrO_2$  were collected *in situ* to initially investigate the interaction between cycloketone and monoclinic  $ZrO_2$  as shown in Figure S4. There are red shifts of the C=O stretching frequency when cyclopentanone and cyclohexanone adsorb on monoclinic  $ZrO_2$  compared with those of free cyclopentanone and cyclohexanone. The red shifts are continuously increased with the increasing of the temperature indicating various interactions between cycloketone and monoclinic  $ZrO_2$ , which is similar to the results of acetone adsorption on  $ZrO_2$  reported by Zaki [41].

Conversion and selectivity of reactants are two most important parameters to investigate the mechanism of catalytic process and evaluate performance of heterogeneous catalysts. In our experiments,  $ZrO_2$  was more active to convert C5 than C6 in corresponding self-condensation. It's also clear that the reactions for both cyclopentanone and cyclohexanone were accelerated when they were co-fed as reactant. The yields of C10 and C12 were also increased somehow in cross-condensation compared with the self-condensation systems with pure reactant. During cross-condensation, it seems that C5 randomly goes into C10 and C11 with roughly equal chance (49.1% vs 50.9%). In comparison, C6 prefers to participate in the formation of C11. In self-condensation, why  $ZrO_2$  is more reactive to convert C5 than C6? In cross-condensation, what really happens during the reaction for the generation of this experimental phenomenon? Is it the fact that C5 randomly goes into C10 and C11 with roughly equal chance (49.1% vs 50.9%)? What is the origin of these interesting experimental results? To explain these observations, we next apply density-functional theory (DFT) calculations to understand the inherent mechanism.

All of the calculations were performed by using DFT as implemented in Vienna ab-initio simulation package (VASP) [42,43]. We examined the mechanism of aldol condensation between various cycloketones on  $ZrO_2$  surface. The role of  $ZrO_2$  will be assessed in the context of these mechanisms on the formation of dimeric products between various cycloketones theoretically. Herein, the



**Fig. 1.** Yields of the products from various cycloketones over monoclinic  $ZrO_2$  (1:1) at 130 °C for 3 h. The carbon yield of the product (C10/C11/C12) is defined as:  $2 \times (\text{the mole of C10/C11/C12 generated during the reaction}) / (\text{the mole of C5 and/or C6 in the feedstock}) \times 100\%$ . Red: carbon yield of C10, green: carbon yield of C11, Blue: carbon yield of C12. Oblique lines: carbon yield from cyclopentanone, grid lines: carbon yield from cyclohexanone.



**Scheme 1.** Percentage conversion of the cycloketones (cyclopentanone:cyclohexanone = 1:1) and selectivity to various bicyclic products over monoclinic  $ZrO_2$  catalyst.

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