Short communication

Controllable self-aldol condensation of cyclopentanone over MgO-ZrO$_2$ mixed oxides: Origin of activity & selectivity

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ABSTRACT

Mesoporous MgO-ZrO$_2$ mixed oxides with different Mg/Zr ratios have been synthesized by a coprecipitation method and employed to catalyze self-aldol condensation of cyclopentanone in a solvent-free condition under atmospheric pressure. Effects of temperature, reaction time, catalyst amount and Mg/Zr ratio on the reaction have been investigated. Remarkable raise in catalytic activity and selectivity has been found on MgO-ZrO$_2$ mixed oxides as compared with pure MgO or ZrO$_2$. Characterization including XRD, XPS, BET and CO$_2$- TPD has been carried out to figure out the relationship between catalyst properties and their catalytic activity.

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1. Introduction

Synthesizing jet fuel from biomass platform chemicals has attracted great attention of scientists for a long time since petroleum resource is on the decline [1,2]. Cyclopentanone is an important platform compound from the selective hydrogenation of furfural [3,4], which has been produced on an industrial scale by the hydrolysis-dehydration of the hemicellulose in agriculture wastes and forest residues. As derived from biomass, cyclopentanone is a promising raw material to attain renewable jet fuel [5–9]. Aldol condensation is one of the key steps in the process of synthesizing fuel molecules with high density starting from cyclopentanone.

The steric hindrance of cyclopentanone makes its self-aldol condensation difficult to initiate. Currently, the reaction is catalyzed by homogeneous aqueous-base catalyst such as KOH and NaOH, which are difficult to reuse in industrial procedure. Many efforts have been made for the development of active heterogeneous catalysts for efficient aldol condensation of cycloketones [10–12]. Mono-condensed product is preferred for the production of high-density fuel with suitable viscosity. Because the mono-condensed products can further react with cyclic pentanone to provide di-condensed products. Therefore, the selectivity of self-aldol condensation should also be concerned for catalyst development.

Herein, MgO-ZrO$_2$ mixed oxides [13–21] have been employed to catalyze self-aldol condensation of cyclopentanone in a solvent-free condition under atmospheric pressure. To our knowledge, MgO-ZrO$_2$ has not been used in this specific reaction. We focus on not only catalytic activity and selectivity of various MgO-ZrO$_2$ mixed oxides but also on the correlation between their physical-chemical properties and catalytic performance.

2. Experimental section

2.1. Catalyst preparation

MgO-ZrO$_2$ catalysts were prepared by a simple ultradilution coprecipitation method using Mg(NO$_3$)$_2$·6H$_2$O and ZrOCl$_2$·8H$_2$O [17]. More detailed experimental procedures for the preparation of MgO-ZrO$_2$ catalysts and cubic ZrO$_2$ are described in Section 1.1 of Supporting information.

2.2. Catalyst characterization

XRD patterns of the catalysts were collected by X-ray diffractometer (Rigaku, D/MAX-2500). Measurements were made over a range of 20° < 2θ <80° at a scanning rate of 4°/min. The X-ray photoelectron spectroscopy (XPS) studies were carried out on a PHI5000VersaProbe system, using an aluminum anode (Al Ka, 1486.6 eV). The spot size for these acquisitions was ~100 μm. The takeoff angle was 45°. The pass energy was 188 eV for the survey scan and 47 eV for the region scan. The data of nitrogen physisorption at 77 K were collected by Micromeritics

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ASAP 2020, surface area and pore volume were calculated by BET and BJH approach, respectively. CO_2-TPD measurements were conducted on a Chemisorption Physisorption Analyzer (Altamira, AMI-300) using thermal conductivity detector. The sample was activated at 873 K for 1 h in He flow prior to the adsorption of CO_2 at 353 K. After purging the physically adsorbed CO_2 at 353 K for 45 min, the sample was heated to 773 K with a ramping rate of 10 K/min.

2.3. Catalytic reactions

Self-aldol condensation of cyclopentanone was performed in a three-neck flask using various catalysts. Detailed experimental procedures are described in Section 1.2 of Supporting information. Products at different time were analysed by GC–MS and GC. Cyclopentanone conversion was calculated by its consumption using 2-methyl-2-butanol as internal standard. 2-Cyclopentylidene-cyclopentanone (C10) and 2.5-dicyclopentylidene-cyclopentanone (C15) have been detected in the condensation product. C10 selectivity was determined by peak area normalization method. C10 yield was calculated by the following formula: C10 yield = cyclopentanone conversion × C10 selectivity.

3. Results and discussions

XRD patterns and XPS results of the as-synthesized catalysts are depicted in Fig. S1 and Fig. S2, respectively. In XRD patterns, cubic phase of MgO and ZrO_2 has been observed in the MgO-ZrO_2 mixed oxides. However, pure ZrO_2 maintains monoclinic phase at low temperature (Fig. S1). Moreover, the diffraction peak of MgO at $2\theta = 42.92°$ is unobvious in MgZr11. Similarly, binding energies of Zr(3d) are almost the same for both ZrO_2 and MgZr11 in Fig. S2(b). Mg^{2+} and Zr^{4+} have similar ionic radius, which makes it possible for Mg^{2+} to replace Zr^{4+} in the ZrO_2 structure and form $Mg_xZr_{1-x}O_{2-x}$ phase [18]. The dissolution of Mg^{2+} in ZrO_2 unit cell results in phase transformation (from monoclinic phase to cubic phase) of ZrO_2 as well as the "absence" of MgO in both XRD pattern and XPS spectrum of MgZr11. In the MgZr11 and MgZr41 samples, the $Mg_xZr_{1-x}O_{2-x}$ mixed oxide is observed (Fig. S2). In the MgZr61 sample, the shape of Zr(3d) peaks is different to those observed for MgZr11 and MgZr41. Moreover, the peaks are shifted towards lower binding energy, indicating that the enrichment of MgO which covered the $Mg_xZr_{1-x}O_{2-x}$ mixed oxide particles. Because the capacity of ZrO_2 to accommodate Mg^{2+} ions into its structure is limited, when MgO content continues to increase, free MgO phase is able to form and can be detected by XRD and XPS. It can also be validated by the increase of peak intensity of MgO with the increasing Mg/Zr ratio from 1:1 to 6:1. Therefore, it can be concluded that MgO and ZrO_2 are not simply mechanically blended in the obtained mixed-oxide catalysts. The formation of $Mg_xZr_{1-x}O_{2-x}$ mixed oxide may bring changes in many aspects, such as surface area, pore size, and basicity.

Then, the obtained solid base oxides had been used to catalyze aldol condensation of cyclopentanone. To optimize the reaction conditions, we studied the effects of temperature and catalyst amount on the conversion of cyclopentanone and selectivity of mono-condensed product (C10).

According to Arrhenius equation, reaction temperature has great impact on reaction rate. Cyclopentanone conversion increases sharply from 8.7% to 88.2% within 4.5 h when the reaction temperature varies from 383 K to 403 K, as shown in Fig. 1(a). We observed that the reaction system would boil at 403 K under atmospheric pressure. Moreover, the selectivity of C10 decreases slightly from 100% to 95.9% when the temperature is increased from 383 K to 403 K. Therefore, 403 K is the optimized temperature for self-aldol condensation of cyclopentanone.

The positive correlation between catalyst amount and conversion of cyclopentanone is displayed in Fig. 1(b). But the effect of conversion promotion will be weakened with the increasing of catalyst amount. It is noticed that yield of C10 oxygenates has reached 84.6% using 0.1 g catalyst/g cyclopentanone, which is already very high compared with the result reported previously [9]. Therefore, 0.1 g catalyst/g cyclopentanone has been considered as a suitable value for cyclopentanone condensation.

Fig. 2 shows that 100% of cyclopentanone has been converted within the first 1.5 h in the presence of NaOH due to its high activity. But only 31.4% of cyclopentanone has been selectively converted to C10 oxygenates. The yield of C10 drops to 20.2% with the prolongation of reaction time. It seems that homogeneous base catalyst is not suitable for catalyzing cyclopentanone condensation.

Conversion of cyclopentanone reaches to 40% and 20% in 6 h over MgO and monoclinic ZrO_2, respectively, as displayed in Fig. 2(a), indicating their low activity. Though their selectivity of C10 is high (98.9% for MgO, 100% for monoclinic ZrO_2), the yield of C10 is still very low due to low conversion. It's interesting that cyclopentanone did not conduct any condensation in the presence of cubic ZrO_2.

In comparison, the behaviors of various mixed-oxide catalysts are obviously different and strongly depending on the Mg/Zr ratio. Similarly, conversion of cyclopentanone becomes nearly unchangeable after 4.5 h. Yield of C10 is increased with time at first, and then decreased with time growth due to further condensation of C10. Reaction time should be limited to 4.5 h to attain maximum C10. Therefore, the optimized reaction conditions are under 403 K for 4.5 h, and with 0.1 g catalyst/g cyclopentanone.

The conversion of cyclopentanone and selectivity of C10 over various catalysts have been compared under the same optimized reaction
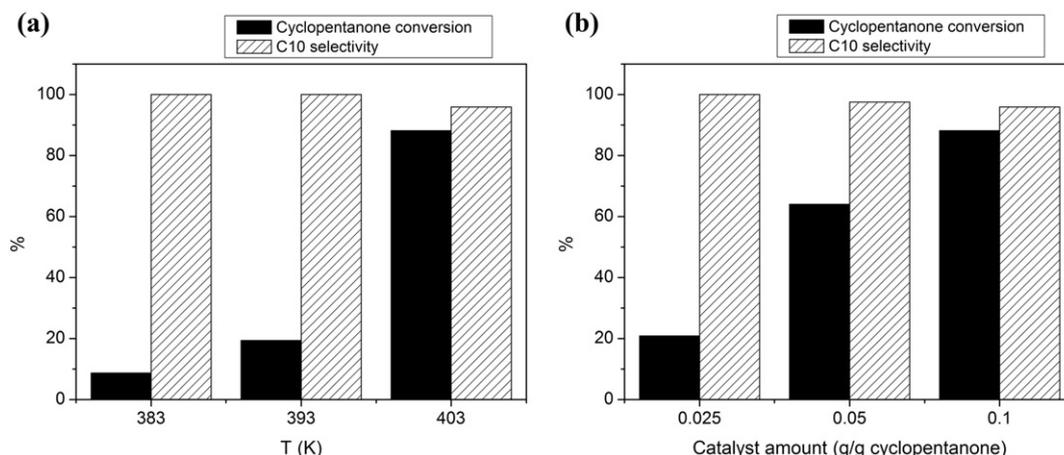
Fig. 1. Effects of temperature (a) and catalyst amount (b) on the conversion of cyclopentanone and selectivity of C10. Reaction conditions: (a) 0.1 g MgZr41/g cyclopentanone, 4.5 h. (b) 403 K, 4.5 h.