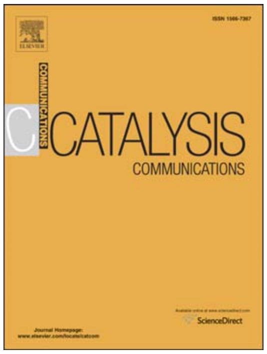

Controllable self-aldol condensation of cyclopentanone over MgO-ZrO$_2$ mixed oxides: Origin of activity & selectivity

Decheng Liang, Guozhu Li, Yanhong Liu, Jinmeng Wu, Xiangwen Zhang

PII: S1566-7367(16)30128-5
DOI: doi: 10.1016/j.catcom.2016.04.008
Reference: CATCOM 4631

To appear in: *Catalysis Communications*

Received date: 5 January 2016
Revised date: 17 March 2016
Accepted date: 11 April 2016

Please cite this article as: Decheng Liang, Guozhu Li, Yanhong Liu, Jinmeng Wu, Xiangwen Zhang, Controllable self-aldol condensation of cyclopentanone over MgO-ZrO$_2$ mixed oxides: Origin of activity & selectivity, *Catalysis Communications* (2016), doi: 10.1016/j.catcom.2016.04.008

Controllable self-aldol condensation of cyclopentanone over $MgO-ZrO_2$ mixed oxides: Origin of activity & selectivity

Decheng Liang, Guozhu Li,* Yanhong Liu, Jinmeng Wu and Xiangwen Zhang

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin 300072, China

E-mail: gzli@tju.edu.cn

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, BET and CO_2-TPD has been carried out to figure out the relationship between catalyst properties and their catalytic activity.

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 $Mg(NO_3)_2·6H_2O$ and $ZrOCl_2·8H_2O$. [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 $20° < 2\theta < 80°$ at a scanning rate of 4 deg/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 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 $2\theta = 42.92^\circ$ 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 4.5h 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.

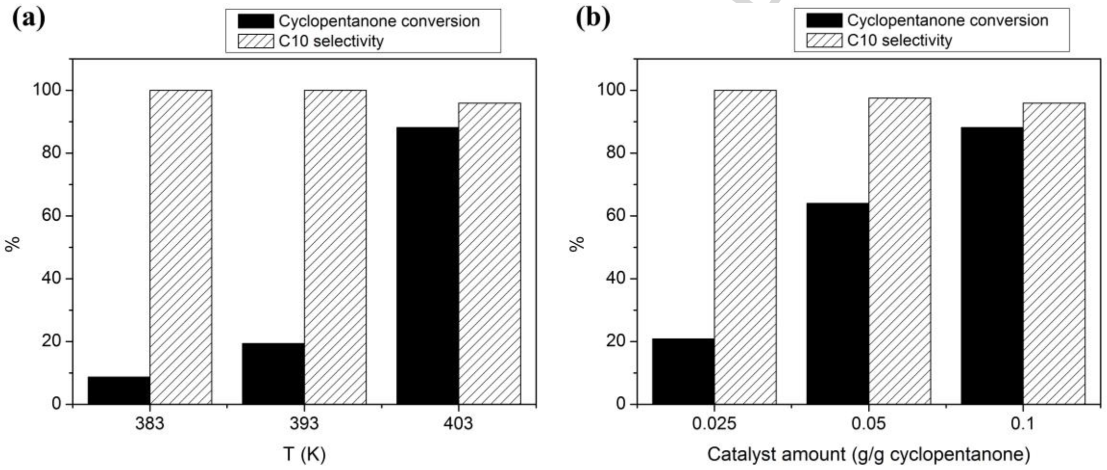

Fig. 1. Effects of temperature (a) and catalyst amount (b) on the conversion of cyclopentanone and selectivity of C10. Reaction conditions: (a) 0.1 g MgZr41/g cyclopentanone, 4.5 h. (b) 403 K, 4.5 h.

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 hours 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 hours 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.

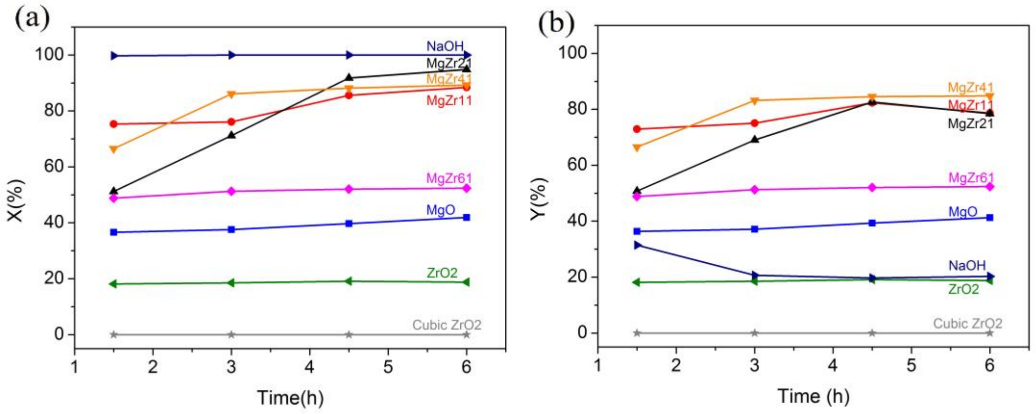

Fig. 2. Dependence of cyclopentanone conversion and C10 yield on time over various catalysts. Reaction conditions: 403 K, 0.1 g catalyst/g cyclopentanone.

The conversion of cyclopentanone and selectivity of C10 over various catalysts have been compared under the same optimized reaction conditions (**Fig. 3**). The most commonly used homogeneous base catalyst, NaOH, was used as background catalyst. 100% conversion of cyclopentanone has been achieved over NaOH. However, its selectivity of C10 is only 19.7%. Therefore, heterogeneous base catalyst with both high activity and selectivity should be developed for controllable condensation of cyclopentanone. Since basicity is one of the key factors affecting cyclopentanone conversion and C10 yield, ZrO_2 and MgO were firstly evaluated in this reaction. Their basicity follows the order of ZrO_2 < MgO, and corresponding cyclopentanone conversions at 4.5 h are 19.1% and 39.7%. However, strong basicity makes it easier to conduct further condensation of C10, yielding low content of C10. This is validated by the experimental results. Herein, C10 selectivity of ZrO_2 (100%) is higher than that of MgO (98.9%). Therefore, to maximize the yield of C10, suitable heterogeneous catalyst with appropriate basicity should be developed.

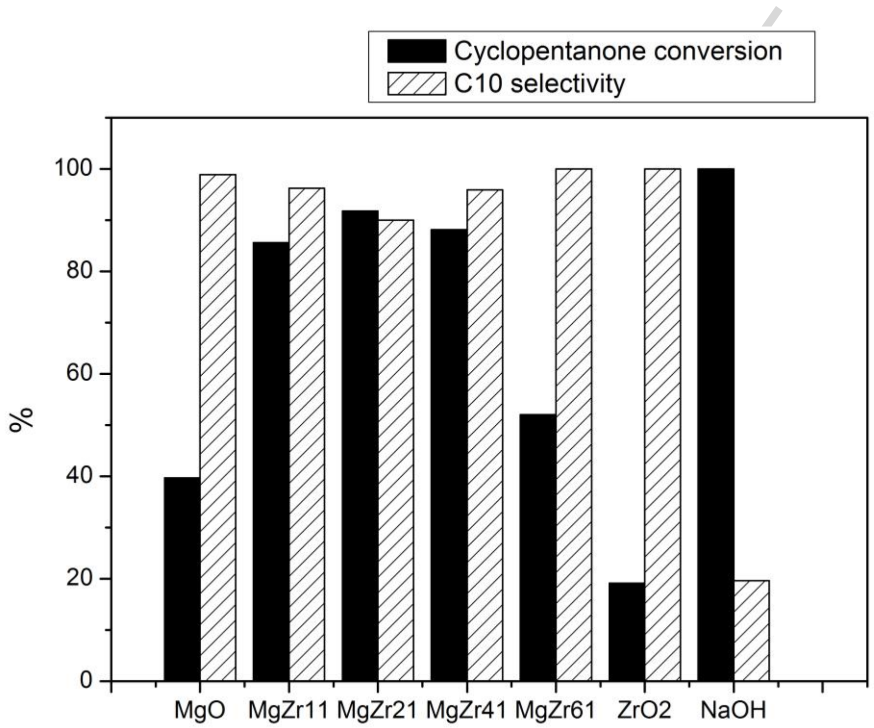

Fig. 3. Cyclopentanone conversion and C10 selectivity over various catalysts. Reaction conditions: 403 K, 4.5 h, atmospheric pressure, and 0.1 g catalyst/g cyclopentanone.

MgO-ZrO_2 mixed oxides were reported to be active, selective and reusable solid base catalysts for aldol condensation, e. g., reaction between furfural and acetone.[13, 18-20, 22] Concerning the case of heterogeneously catalyzed aldol reactions，[23, 24] it is reasonable to assume that a similar mechanism could take place over MgO-ZrO_2 mixed oxide. Firstly, cyclopentanone adsorbs on the surface of MgO-ZrO_2 mixed oxide. Then, the formation of adsorbed enol or enolate species happens. Finally, this species is added to another cyclopentanone molecule (probably coadsorbed), with the formation of 2-cyclopentylidene-cyclopentanone on the surface following dehydration. Herein, compared with MgO and ZrO_2, catalysts of mixed MgO-ZrO_2 series show remarkable raise in both catalytic activity and selectivity. As seen in **Fig. 3**, their activities follow the sequence of MgZr41 > MgZr21 > MgZr11 > MgZr61 > MgO > ZrO_2. Moreover, all the MgO-ZrO_2 catalysts show high selectivity of C10 (>90%). It is in consistent with previous reports on similar reactions.[18, 20] The acidic-basic properties of the final solid can be modified through tuning Mg/Zr ratio during preparation procedure. For instance, Sádaba et al. [18] found that when Mg/Zr ratio$\geqslant$ 1，the mixed oxides were consisted of $Mg_xZr_{1-x}O_{2-x}$ and MgO. Their results showed that MgO-ZrO_2 with nominal Mg/Zr ratio =1 had the best performance in the aldol condensation of furfural with acetone.

CO_2 adsorption and subsequent desorption can detect the sites with different basic strengths: bicarbonates (weak base sites); bidentate carbonates (bridged and chelating, medium-strength base sites) and monodentates (strong base sites).[25] Based on the desorption temperature of the formed species, it was obtained that base centers associated with bicarbonates correspond with 293-373 K, bridged bidentate carbonate with 373-473 K, chelating bidentate carbonate with 473-573 K and unidentate carbonate with temperatures over 573 K.[26] **Fig. 4** displays the CO_2-TPD results of various MgO-ZrO_2 catalysts synthesized in this study. ZrO_2 has a weak desorption peak at 403 K. While MgO has a strong desorption peak at 463 K and a medium desorption peak at 643 K. New peaks at 431 K and 588 K for mixed oxides appear, which is in consistent with Faba et al.'s results [22]. It indicates the presence of bidentate carbonate (medium-strength base sites) and monodentates (strong base sites). The sequence of the amount of medium-strength base sites at 431 K (bridged bidentate carbonate) is MgZr41> MgZr21> MgZr11> MgZr61, which is identical to that of their catalytic activities. It is reasonable to assume that medium-strength base sites resulting from the presence of $Mg_xZr_{1-x}O_{2-x}$ phase, is the active site to conduct aldol condensation. Base sites on ZrO_2 or MgO are either weaker or stronger than that of mixed oxides, resulting in relative low catalytic activity.

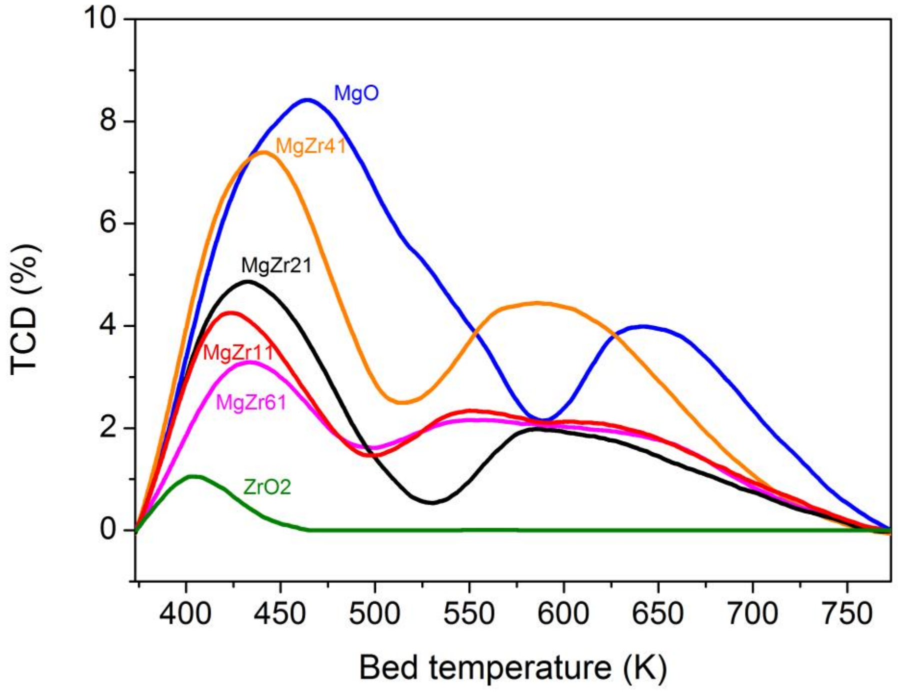

Fig. 4. CO_2-TPD of different MgO-ZrO_2 mixed oxides.

Pore size distribution of MgO-ZrO$_2$ catalysts was measured as displayed in **Fig. S3**. MgO-ZrO$_2$ series with various Mg/Zr ratios have similar distribution of mesoporous size (8.9-22.2 nm). Therefore, no correlation between the selectivity and pore size of MgO-ZrO$_2$ is found.

Similar volcano plots of surface area and yield of C10 oxygenates versus Mg/Zr ratio are displayed in **Fig. 5**. The trend of surface area of the mixed oxide depending on the Mg/Zr ratio is similar to that of C10 yield catalyzed by corresponding oxide. Surface area of MgO-ZrO$_2$ mixed oxides reaches its maximum when Mg/Zr=4/1, where the highest yield of C10 has been achieved. When Mg/Zr ratio is higher than 1:1, both phases of $Mg_xZr_{1-x}O_{2-x}$ and free MgO are formed.[18] During preparation, the presence of MgO with suitable amount controls the crystaline growth of $Mg_xZr_{1-x}O_{2-x}$ phase, which affects surface area of the obtained mixed oxide. Consequently, when Mg/Zr ratio is 4:1, the surface area of the obtained mixed oxide reaches a maximum, leading to the improvement of accessibility of the base sites. Therefore, it can be concluded that medium-strength base sites of MgO-ZrO$_2$ mixed oxides with suitable basicity and good accessibility are responsible for the high yield of C10 oxygenates.[18]

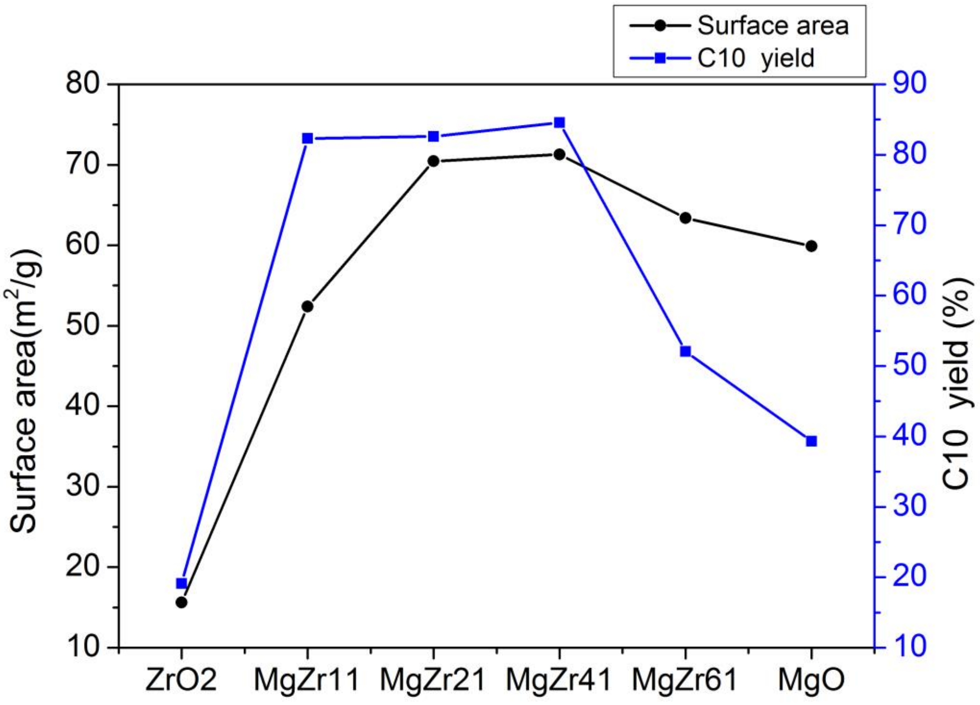

Fig. 5. Surface area and C10 oxygenates yield of different MgO-ZrO_2 catalysts.

Reusability tests of MgZr41 were carried out at standard reaction conditions (403 K, 4.5 h, atmospheric pressure, and 0.1 g catalyst/g cyclopentanone), and results are shown in **Fig. S4**. C10 yield dropped to below 30% when the spent catalyst was simply collected, dried and used in the next cycle of reaction (cycle 2 and cycle 3). However, the spent catalyst was reactivated after calcination. C10 yield reached to 80% after calcination of the spent catalyst at 873K for 10h (cycle 4).

4. Conclusions

Various active and selective MgO-ZrO_2 mixed oxides have been synthesized for self-aldol condensation of cyclopentanone using a simple coprecipitation method. The results of CO_2-TPD and BET reveal that mesoporous MgO-ZrO_2 catalysts possess high surface area and new medium-strength base sites. The amount of medium-strength base sites and their accessibility are strongly depended on the ratio of Mg/Zr, which makes MgO-ZrO_2 mixed oxide a tunable catalyst for various potential applications. MgZr41 has been prepared with suitable basicity and good accessibility of active base sites. Cyclopentanone conversion and C10 yield reach 88.2% and 84.6%, respectively, at 403 K under atmospheric pressure in 4.5 h over MgZr41.

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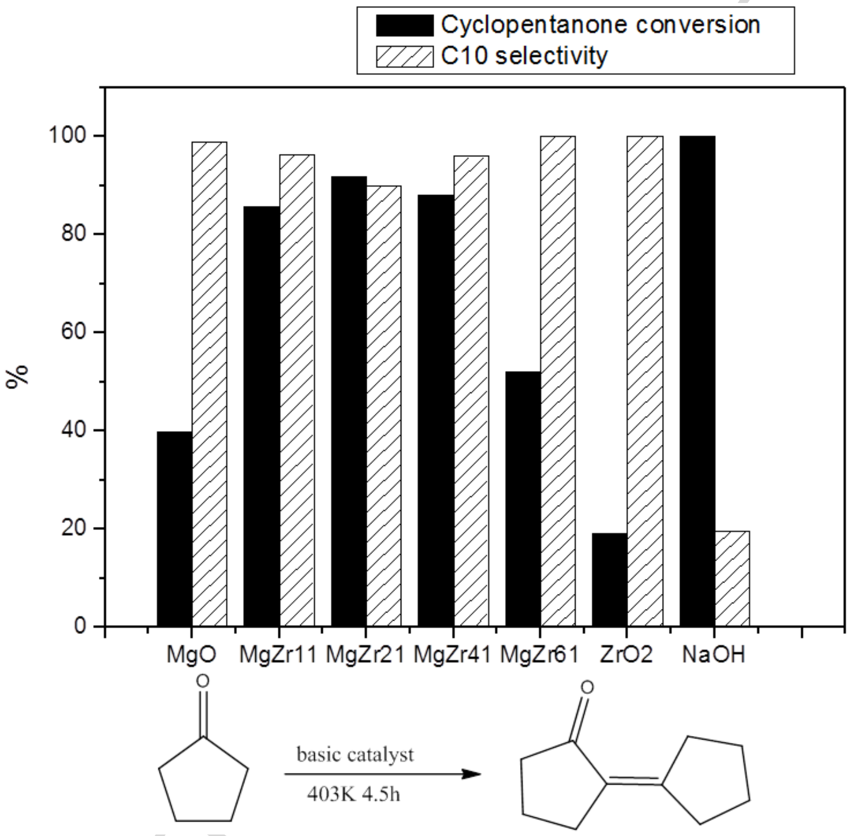
Graphical Abstract



Keywords

MgO-ZrO_2; self-aldol condensation; alkalinity; surface area; cyclopentanone

Highlights

- Synthesis of MgO-ZrO_2 mixed oxides with various Mg/Zr ratio for self-aldol condensation of cyclopentanone;
- Systematical investigation of the effects of temperature, reaction time and catalyst amount on the reaction;
- Exploring the origin of high activity and selectivity of MgO-ZrO_2 mixed oxides;
- Achievement of self-aldol condensation of cyclopentanone with high yield (84.6%) under mild conditions.