Acetone condensation over CaO-SnO₂ catalyst

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Aldol condensation of acetone was studied over solid base CaO–SnO₂ catalyst in the 300–450 °C temperature range and at 15–75 atm pressure in a fixed-bed reactor. The main products are mesityl oxide and isophorone. The high stability of CaO–SnO₂ catalyst performance was observed at pressure of 75 atm giving the acetone conversion of 36–41%. Increase in the temperature and pressure led to a simultaneous raise in acetone conversion. The maximum conversion of 41% was achieved at 400 °C, 75 atm and a flow rate of acetone of 8.1 g h⁻¹ (g catalyst)⁻¹.

Key words: acetone, mesityl oxide, isophorone, aldol condensation, CaO–SnO₂.

Acetone is a co-product in the large-scale cumene process for phenol synthesis and is generally used as a solvent as well as a feedstock for the manufacture of a number of important chemicals, such as diacetone alcohol, mesityl oxide, methyl isobutyl ketone, isophorone, and others. These chemicals are produced *via* aldol condensation of acetone in the presence of basic catalysts, such as alkaline and alkaline earth metal hydroxides, followed by acid dehydration of intermediate products.^{1–3} Product purification, catalyst regeneration, and waste treatment processes have the most significant contributions to the final product price.⁴ Thereby, the development of novel effective heterogeneous catalytic processes of aldol condensation of acetone is of special interest.

Earlier, several alkaline earth metal oxides,⁵ MgO and TiO₂ promoted with alkaline metals,^{6,7} as well as Mg-Al⁸ and Mg-Zr^{9,10} mixed oxides have been tested as solid base catalysts in acetone condensation. The reaction was performed in a gas phase in a flow of inert carrier gas at temperatures ranged from 250 to 450 °C.5-10 Much attention of the researchers has been focused on magnesiumcontaining catalysts. At 300 °C, acetone conversion over MgO was 17% (acetone flow rate $V_{\rm W} = 1.2 \text{ g h}^{-1}$ (g catalyst)⁻¹) and selectivity towards mesityl oxide and isophorone was 85 and 15%, respectively. However, after 6 h run, the catalytic activity decreased nearly twice.⁶ Acetone conversion over Mg-Zr mixed oxide reached 32% at 450 °C $(V_{\rm W} = 8 \text{ g h}^{-1} \text{ (g catalyst)}^{-1}).^{9}$ Nevertheless, it could be improved up to 50% by supporting the catalyst on graphite materials with high specific surface area.9 At the same time, the activity of Mg-Zr oxide catalyst¹⁰ was reported to decrease by nearly 50% after 8 h run (350 °C, 1 atm). Jia and co-workers⁸ revealed high catalytic performance of Mg-Al mixture oxides. At 300 °C, the acetone conversion varied from 58 to 78% depending on the Mg_xAlO catalyst composition, and the selectivity towards isophorone varied from 70 to 80% ($V_W = 1.2 \text{ g h}^{-1} \text{ (g catalyst)}^{-1}$). It should be noted that the catalyst deactivation is a significant problem when solid base catalysts are used in aldol condensation. The main reason of deactivation of the catalysts is coke formation and blockage of the active sites of the catalyst.^{11,12} Therefore, considering low stability of the known solid base catalysts for aldol condensation screening of new catalytic systems showing high performance and stability remains a topical issue.

The purpose of the present work is to reveal the features of acetone condensation over $CaO-SnO_2$ oxide catalysts. According to our data, this catalytic system has not been used as a catalyst for aldol condensation.

Experimental

The CaO–SnO₂ catalyst was prepared by coprecipitation of metal hydroxides with 3 *M* aqueous NaOH from the mixed solution containing equimolar amounts of SnCl₄ and Ca(NO₃)₂ (overall concentration was 1.1 mol L⁻¹). The obtained gel was aged for 24 h in a closed flask, filtered, resuspended in water, filtered again (these two steps were repeated two more times), dried at 120 °C, and calcined at 600 °C for 4 h. According to the X-ray diffraction analysis data (DRON-2 diffractometer, CuK_{α} irradiation, 20 range from 10 to 40°), the obtained solid was X-ray amorphous. The catalyst powder was pressed in pellets, granulated and a 0.10–0.45 mm fraction was selected for the experiments.

Acetone condensation was performed in a stainless steel fixed-bed reactor with the inner diameter of 10 mm. The reaction temperature was 300-450 °C and pressure was 15-75 atm. Acetone (reagent grade) was used without additional purification. A mixture of 1.0 cm³ of the catalyst (1.47 g) and 1.0 cm³ of quartz chips of the same size was placed in the middle of the

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reactor. The remained volume of the reactor was loaded with quartz chips. Acetone feed rate was 0.25, 0.5 and 1.0 mL min⁻¹, that corresponds to the weight space velocities (V_W) of 8.1, 16.1 and 32.2 g h⁻¹ (g catalyst)⁻¹. Acetone was fed using a liquid high-pressure Knauer pump. The flow rate was controlled by a valve installed after the reactor. The reaction products were collected in a cold trap (and sampled every 30 min) and then analyzed on a Varian 3700 gas chromatograph using an OV-101 capillary column. The products were identified by GC/MS on a Thermo Focus DSQ-II instrument using a Thermo TR-5ms column.

Results and Discussion

Figure 1 illustrates the time dependences of the acetone conversion at 400 °C on pressures of 15, 50 and 75 atm. At 15 atm, the acetone conversion showed a twofold decrease within 3 h, from 12 to 6%. Higher pressure improved the acetone conversion and the stability of the catalyst. Thus, at 75 atm acetone conversion remained between 36 and 41% during the entire experiment. Mesityl oxide and isophorone were found to be the main products of the reaction. The results of the analysis of the products of the acetone condensation over CaO-SnO₂ catalyst are summarized in Table 1. As it can be seen, pressure positively affects not only acetone conversion but also the composition of the products. As pressure increases, a fraction of the compounds formed from three or more acetone molecules grows. Thus, at 15 atm the selectivity towards isophorone was 1%, whereas at 75 atm it reached 24%.

The effect of temperature on acetone conversion is illustrated in Fig. 2. The experimental data show that at temperatures below 350 °C the acetone conversion is insignificant (only several percents). Raising the reaction temperature significantly increases the acetone conversion up to 18 and 40% at 400 and 450 °C, respectively. In comparison, the conversion at 350 °C was only 3% (P = 75 atm, $V_W = 16.1$ g h⁻¹ (g catalyst)⁻¹). At the same time, the total selectivity towards two isomers of mesityl oxide decreases from 90 to 60%.

In addition, we examined the effect of an acetone feed rate on the acetone conversion and composition of the product mixture (see Table 1). At 400 °C and a weight space velocity of 8.1 g h⁻¹ (g catalyst)⁻¹, the acetone con-



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Fig. 1. Acetone conversion (*K*) as a function of the reaction time (*t*) over CaO–SnO₂ catalyst at pressures of 15 (*1*), 50 (*2*), and 75 atm (*3*) (T = 400 °C, $V_W = 8.1 \text{ g h}^{-1}$ (g catalyst)⁻¹).



Fig. 2. Temperature dependences of acetone conversion (*I*) and selectivity towards mesityl and isomesityl oxides (2), α -isophorone (3), and other reaction products (4) over CaO—SnO₂ catalyst (P = 75 atm, $V_W = 16.1$ g h⁻¹ (g catalyst)⁻¹, t = 60 min).

version reached its maximum value of 41%. When a weight space velocity increases twice, *i.e.*, the contact time between the substrate and the catalyst is reduced, nearly linear decrease in the conversion (up to 18%) is observed.

Entry	<i>P</i> /atm	$V_{\rm w}$ /g h ⁻¹ (g catalyst) ⁻¹	Conversion (%)	Selectivity (%)					
				Mesityl oxide	Isomesityl oxide	Phorone	α-Iso- phorone	Mesitylene	Other products
1	15	8.1	12	70	23	0	1	1	5
2	50	8.1	32	51	18	1	16	4	10
3	75	8.1	41	43	15	1	24	3	14
4	75	16.1	18	62	21	1	10	1	5
5	75	32.2	2	68	23	0	3	0	6

Table 1. Acetone condensation over CaO-SnO₂ catalyst (T = 400 °C)



Scheme 1

Moreover, the selectivity towards isophorone decreases from 24 to 10%. At $V_{\rm W} = 32.2$ g h⁻¹ (g catalyst)⁻¹, the conversion was only 2%.

Based on the literature data^{7,9} and the present results, we suggest the following scheme of acetone transformations over CaO—SnO₂ catalyst (Scheme 1). At the first step, the aldol condensation between two acetone molecules yields diacetone alcohol, which then, transforms to mesityl oxide *via* dehydration. The subsequent addition of an acetone molecule results in either phorone or 4,6-dimethylhepta-3,5-dien-2-one. Isophorone is formed from phorone *via* intramolecular Michael reaction, and mesitylene is produced from 4,6-dimethylhepta-3,5-dien-2one *via* intramolecular aldol condensation. The main product of the process is mesityl oxide. At low pressure (15 atm) and low temperature ($350 \,^{\circ}$ C), the total selectivity towards mesityl and isomesityl oxides exceeds 90%. An increase in the reaction temperature and pressure or decrease in the weight space velocity improve the conversion of acetone. Herewith, the selectivity towards isophorone *via* condensation of three acetone molecules increases.

In summary, the performance of CaO—SnO₂ catalyst has been studied in aldol condensation of acetone. Mesityl oxide and isophorone were found to be the main reaction products. High acetone conversion (36-41%) and stable work of the catalyst were observed at 75 atm. With increasing temperature and pressure, a simbate increase in acetone conversion was demonstrated. The maximum acetone conversion of 41% was achieved at 400 °C, 75 atm, and the acetone weight space velocity of 8.1 g h⁻¹ (g catalyst)⁻¹.

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