

Condensation of acetophenone to α,β -unsaturated ketone (dypnone) over solid acid catalysts

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Abstract

The self-condensation of acetophenone (ACP) to α,β -unsaturated ketone in the liquid phase has been studied using sulfated zirconia (SZ), sulfated titania (ST) and H-beta zeolite as catalysts in the temperature range of 403–433 K. It is found that SZ and H-beta exhibit similar activity (rate of ACP conversion), which is higher than that of ST. From the TPD of NH_3 it is seen that both SZ and H-beta are highly acidic and possess strong acid sites, as seen from NH_3 desorption in the temperature range of 513–873 K, which are responsible for the reaction. The conversion of ACP increases with reaction time, the catalyst concentration and reaction temperature. The SZ is recycled two times to show that there is only a marginal decrease in activity on recycled catalyst with no loss in the selectivity for dypnone. © 2002 Elsevier Science B.V. All rights reserved.

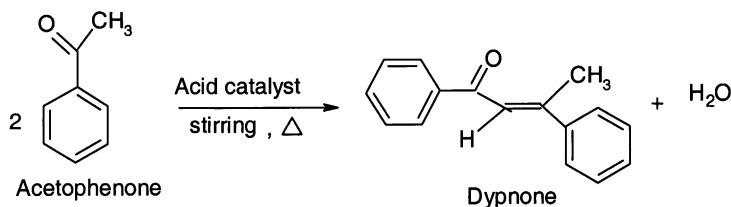
Keywords: Condensation of acetophenone; Preparation of dypnone; Sulfated zirconia; H-beta; Solid acid catalysts

1. Introduction

Dypnone is a useful intermediate for the production of a large range of compounds. It has been used as a softening agent, plastisizer and perfumery base. Dypnone has been prepared conventionally by the action of sodium ethoxide, aluminum bromide, phosphorous pentachloride, aluminum triphenyl, zinc diethyl, calcium hydroxide, anhydrous hydrogen chloride, anhydrous hydrogen bromide, aluminum chloride, aluminum *tert*-butoxide or hydrogen fluoride on acetophenone (ACP) as described in the earlier literature [1–4]. In addition, it has been obtained by the action of aniline hydrochloride on ACP, followed by treatment with hydrochloric acid. Unfortunately, its synthesis is not always an easy task and Lewis

acid catalysts have several disadvantages if applied to industrial processes such as wasting large amounts of catalysts, corrosion of reactor, water pollution by acidic wastewater, and difficulty of catalyst recovery. In addition, AlCl_3 being a strong Lewis acid also catalyzes other undesirable side reactions such as polycondensation of ACP to a mixture of other products. In view of the above, it was of interest to develop a new solid catalyst for the selective synthesis of dypnone. Modified zeolites are known to catalyze selectively aldol condensation of ACP to dypnone [5–8]. The objective of the present work is to replace the conventional Lewis acids catalyst with environmentally friendly solid acid catalysts such as sulfated zirconia (SZ) and sulfated titania (ST), which are open structure and H-beta zeolite is closed three-dimensional porous structure. We have chosen the later among other zeolites because it has been synthesized and characterized in our lab shows a good activity towards a variety of acylation reactions [9–11] and halogenation reactions

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Scheme 1.

[12]. It has also been reported that a comparative study of SZ with H-beta zeolite for alkylation of isobutane [13]. Another objective is to enhance the selectivity for dypnone and to minimize the formation of consecutive products in the condensation of ACP using solid acid catalysts. This paper presents the results of a study comparing the performance of sulfated metal oxides with H-beta catalyst in the condensation of ACP (Scheme 1). The condensation of ACP to dypnone has not been reported yet using such catalysts. The influence of catalyst concentration and reaction temperature is also reported using SZ as catalyst.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of SZ

Zirconium hydroxide was obtained by hydrolyzing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with aqueous ammonia in the pH range of 8–9 at a temperature of 60–70 °C; aqueous ammonia solution (28%) was added drop-wise with stirring into 50 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ dissolved in 1 l of distilled hot water. The precipitated solution was kept at 60–70 °C for 3 h. The precipitate was washed several times with hot water until the filtrate was negative to silver nitrate solution and finally dried at 110 °C. Dried sample was then stirred with 1 N sulfuric acid (2 g/30 ml) for 2 h and filtered. After drying, the sample was calcined at 823 K for 4 h with the flow of air.

2.1.2. Preparation of ST

Titanium isopropoxide solution of 150 ml was added into 1 l of distilled water with stirring. Addition of 30% nitric acid solution dissolved the white precipitate, which formed. Ammonium hydroxide

solution (28%) was added into the aqueous solution with stirring until the pH of the solution reached 8. The precipitate was kept for 3 h and filtered. After filtration, the precipitate was washed and dried. The dried sample was then subjected to sulfation as above and calcined as described earlier.

The synthesized zeolite beta was calcined at 823 K in an air stream and changed into its H^+ -form. The crystallinity and phase purity of the catalysts were known by X-ray diffractograms (Rigaku D MAX III VC with $\text{Cu K}\alpha$ radiation source). The catalysts were further characterized by SEM JEOL (JSM-5200) and N_2 adsorption (NOVA) techniques. Acidity of the catalysts was evaluated by the temperature programmed desorption of ammonia from 303 to 873 K (in several steps) using the method described in the literature [14]. The physico-chemical properties of the samples are given in Table 1. Before reaction, the catalysts were dehydrated at 573 K for 3 h.

2.2. Catalytic reaction

Reactions were performed in the liquid phase under batch conditions. In a typical reaction, the activated catalyst (0.5 g) was added to ACP (0.042 mol) and the resulting suspension was magnetically stirred at 433 K. The course of the reaction was followed by analyzing the reaction mixture periodically using a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (HP 5% silicone gum). The products were also identified by GC/MS (Shimadzu, QP 2000 A) analysis. The isolation of pure products was accomplished by silica gel (60–120-mesh) column chromatography with 5% ethyl acetate in petroleum ether as eluting solvent. TLC and GC confirmed the formation of pure compound. The major products obtained in this study are

Table 1
Physico-chemical properties of catalysis

Catalyst	Sulfur content ^a (wt.%)	Surface area ^b (m ² /g)	Particle size ^a (μm)	NH ₃ desorbed (mmol/g)					NH ₃ adsorbed at 303 K (mmol/g)	
				303–353 K	353–433 K	433–513 K	513–653 K	653–773 K	773–873 K	
SO ₄ ²⁻ /ZrO ₂	3.08	100.6	0.2	0.16	0.07	0.17	0.29	0.15	0.61	1.45
SO ₄ ²⁻ /TiO ₂	3.04	145	0.5	0.01	0.14	0.01	0.03	0.01	0.17	0.37
H-beta ^c	–	745	0.5	0.08	0.1	0.15	0.43	0.36	0.07	1.19

^a Measured by SEM JEOL (JSM-5200).

^b Measured by N₂ adsorption (NOVA).

^c SiO₂/Al₂O₃ molar ratio = 26; degree of H⁺-exchange: >98.7%.

in agreement with the spectroscopic data of the pure compound.

Spectroscopic data of dyppone: $^1\text{H NMR}$ (200 MHz) (CDCl_3) δ : 2.48 (s, 3H); 7.05 (m, 1H); 7.05–7.87 (m, 10H). GC-FT-IR (vapor phase): 1610 cm^{-1} ($-\text{C}=\text{C}-$); 1675 cm^{-1} ($-\text{C}=\text{O}$).

The conversion is defined as the percentage of ACP transformed. The rate of ACP conversion is given as the amount of ACP (mmol) converted per gram of the catalyst per hour during the initial period. The selectivity (wt.%) for a product is expressed as the amount of the product divided by the amount of total products and multiplied by 100.

3. Results and discussion

3.1. Effect of various catalysts

The catalytic activity, rate of ACP conversion and selectivity to dyppone formation with different catalysts, under similar reaction conditions, are given in Table 2. The results with AlCl_3 are also included for comparison. As seen from Table 2, *trans* and *cis* dyppone together with ketene are formed in the condensation of ACP. The aldol condensation of ACP produces dyppone as a major and primary product while ketene is a secondary product.

As can be seen from Table 2, SZ and zeolite H-beta exhibit similar and higher activity compared to the ST. However, the selectivity for dyppone over all catalysts remains nearly constant. The conversion of ACP, rate of ACP conversion and selectivity for dyppone over SZ, ST and H-beta are found to be 40.1, 28.5,

40.8 wt.%, 6.7, 4.8, 6.8 $\text{mmol g}^{-1}\text{ h}^{-1}$ and 86, 86 and 85 wt.%, respectively. AlCl_3 catalyst is found to be more active ($180.5\text{ mmol g}^{-1}\text{ h}^{-1}$) with comparable selectivity (84 wt.%) to dyppone. The higher conversion of ACP over SZ and H-beta seems to be due to the fact that these catalysts exhibit stronger acid sites (Table 1). These results indicate that strong acid sites are the most important factor to enhance both the protonation and the dehydration and consequently to force the aldol condensation of ACP to dyppone. Optimization of the reaction condition was done with catalyst SZ and other catalysts were compared under optimized conditions.

3.2. Duration of the run

Fig. 1 shows the time dependence of the conversion of ACP (wt.%) over SZ, ST, H-beta and AlCl_3 under similar conditions. H-beta showed a lower initial activity compared to SZ and AlCl_3 , because of diffusional resistance in H-beta. However, after 2 h of reaction time H-beta performed better than AlCl_3 . The lower activity of AlCl_3 after 2 h may be attributed to the amount of AlCl_3 (in relation to ACP) used in the reaction, which was less than the stoichiometric amount normally required. The ST catalyst was considerably less active than H-beta and SZ due to its lower acidity and weaker acid sites (Table 1). Based on this conversion of ACP after 1 h of reaction time, positive trend in activities for the catalyst SZ was studied varying other reaction parameters. Fig. 2 shows the conversion of ACP and product distribution over SZ with the increase in reaction time up to 10 h. Reaction conditions were detailed in Table 2. It can also be seen from the

Table 2
Condensation of ACP^a

Catalyst	Conversion of ACP (wt.%) ^b	Rate of ACP conversion ($\text{mmol g}^{-1}\text{ h}^{-1}$) ^c	Product distribution (wt.%)	
			Dyppone	Others ^d
$\text{SO}_4^{2-}/\text{ZrO}_2$	40.1	6.7	86	14
$\text{SO}_4^{2-}/\text{TiO}_2$	28.5	4.8	86	14
H-beta	40.8	6.8	85	15
AlCl_3 ^e	36.1	180.5	84	16

^a Reaction conditions: catalyst (g) = 0.5; acetophenone (mol) = 0.042; reaction temperature (K) = 433; reaction time (h) = 5.

^b Conversion of ACP is defined as the percentage of ACP transformed into product; ACP: acetophenone.

^c Rate of ACP conversion ($\text{mmol g}^{-1}\text{ h}^{-1}$) is expressed as the ACP converted per hour per gram of the catalyst.

^d *cis* form of dyppone and ketenes.

^e Reaction time (h) = 0.16.

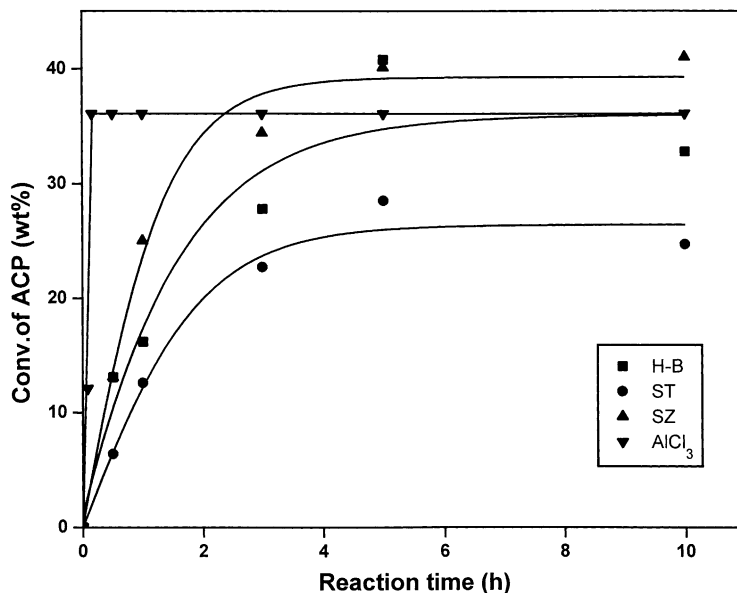


Fig. 1. Conversion of ACP (wt.%) vs reaction time (h) over various catalysts (see footnotes of Table 2 for the reaction conditions).

results that there is a steady increase in the conversion of ACP and the yield of dypnone, which level off after 3 h of reaction time. The result shows that the reaction time influenced the conversion of ACP and product yields in the condensation of ACP.

3.3. Influence of catalyst/ACP ratio on ACP conversion vs reaction time

Fig. 3 compares the conversion of ACP as a function of reaction time using different concentrations of

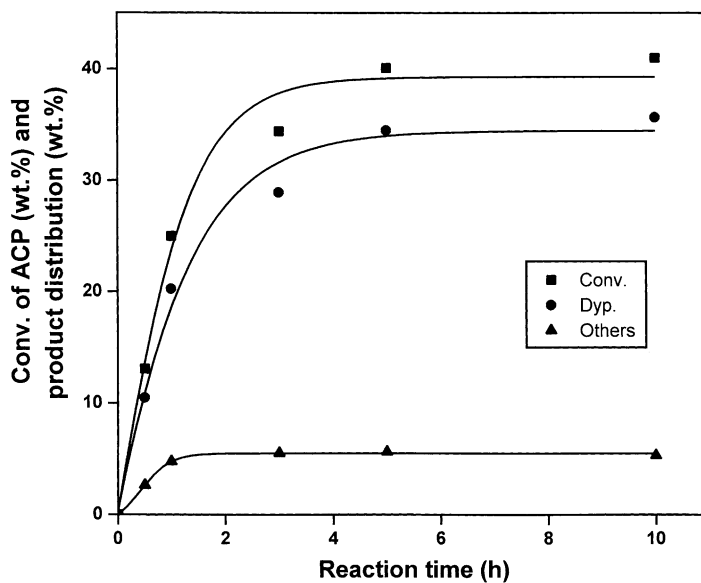


Fig. 2. Conversion of ACP (wt.%) and product distribution vs reaction time (h) over SZ catalyst.

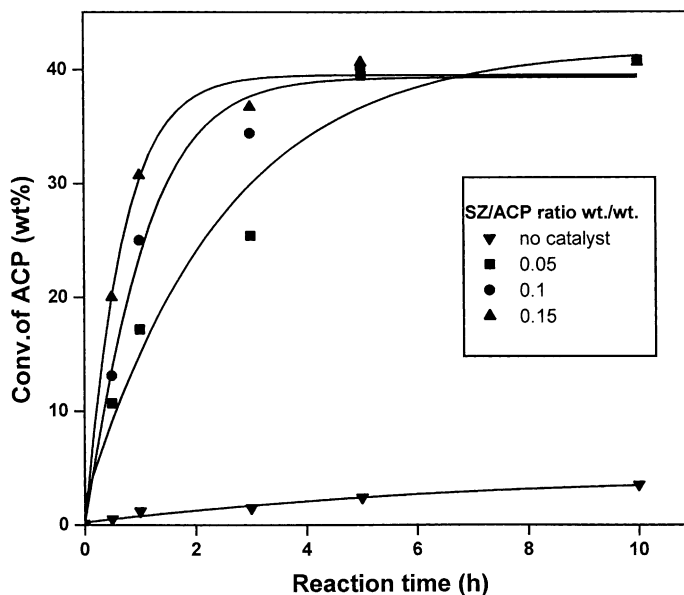


Fig. 3. Influence of catalyst (SZ) concentration (SZ/ACP ratio by wt.) in the conversion of ACP (wt.%) with reaction time (h) (see footnotes of Table 2 for the reaction conditions).

catalyst under similar conditions as those depicted in Table 2. The conversion of ACP is found to increase markedly up to 2 h of reaction time with the increase in SZ/ACP ratio from 0.05 to 0.15. However, for longer reaction time (5 h), the conversion of ACP is

similar at all catalyst concentrations. A negligible, lower conversion of ACP (wt.%) is observed in the absence of catalyst. Fig. 4 shows the effect of SZ (catalyst)/ACP ratio (wt./wt.) on the conversion of ACP, rate of ACP conversion and product distribution.

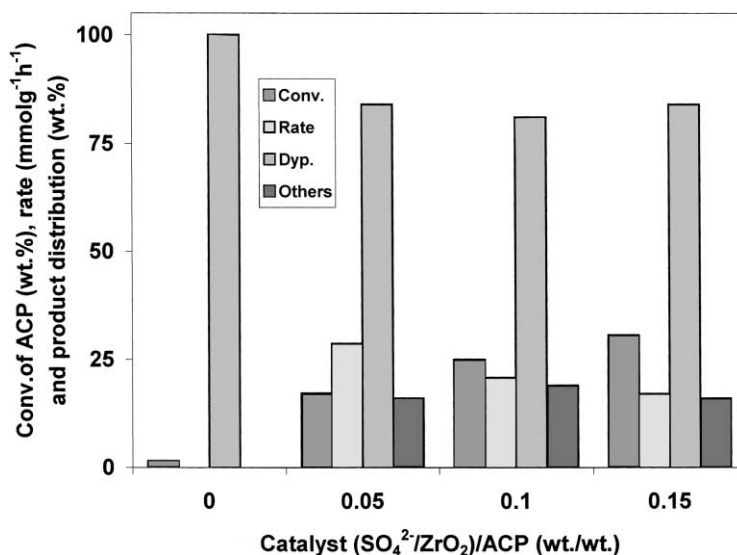


Fig. 4. Effect of SZ/ACP ratio (wt./wt.) on the ACP conversion, rate and product distribution; reaction time (h) = 1 (see footnotes of Table 2 for the other conditions).

The catalyst/ACP ratio was varied from 0.05 to 0.15 by keeping the concentration of ACP constant. The total surface area available for the reaction depends on the catalyst loading. It was found that with an increase in catalyst/ACP ratio the conversion of ACP increases linearly from 17.2 to 30.7 wt.% for the reaction time of 1 h, because of the increase in the total number of acid sites available for the reaction. The corresponding rate decreases from 28.7 to 17.1 $\text{mmol g}^{-1} \text{h}^{-1}$, respectively. No change in the dypnone selectivity is observed with the change in catalyst/ACP ratio. These results indicate the need of a catalyst for decreasing the activation energy barrier in the condensation of ACP to dypnone.

3.4. Influence of reaction temperature on ACP conversion vs reaction time

Fig. 5 shows the effect of the reaction temperature on the conversion of ACP vs reaction time during the condensation of ACP. The reaction temperature was varied between 403 and 433 K. Increasing the reaction temperature increases the catalytic activity sharply up to 3 h of reaction time and the conversion of ACP levels off with reaction time at all reaction temper-

ature studied. The effect of reaction temperature on the conversion of ACP, rate of ACP conversion and product distribution is investigated in the range of 403–443 K using the SZ as catalyst (Fig. 6). The conversion of ACP and rate of ACP conversion increases from 17.1 to 40.1 wt.% and 2.8 to 6.7 $\text{mmol g}^{-1} \text{h}^{-1}$, respectively, when the temperature is raised from 403 to 433 K. However, the selectivity for dypnone remains nearly constant as shown in Fig. 5. A maximum in dypnone selectivity (87 wt.%) over this catalyst is observed at 403 K. The apparent activation energy for the condensation reaction over SZ is estimated to be 40.8 kJ mol^{-1} .

3.5. Catalyst recycling

SZ sample used in the condensation of ACP was recycled two times (fresh+two cycles). Fig. 7 presents the results of these experiments. The catalyst shows a marginal decrease of the activity after the use of fresh catalyst. However, after first recycle of the catalyst, a minor decrease in the catalytic activity was noticed without losing its selectivity for dypnone. The present study indicates that the catalyst can be recycled a number of times without losing its activity to a greater extent.

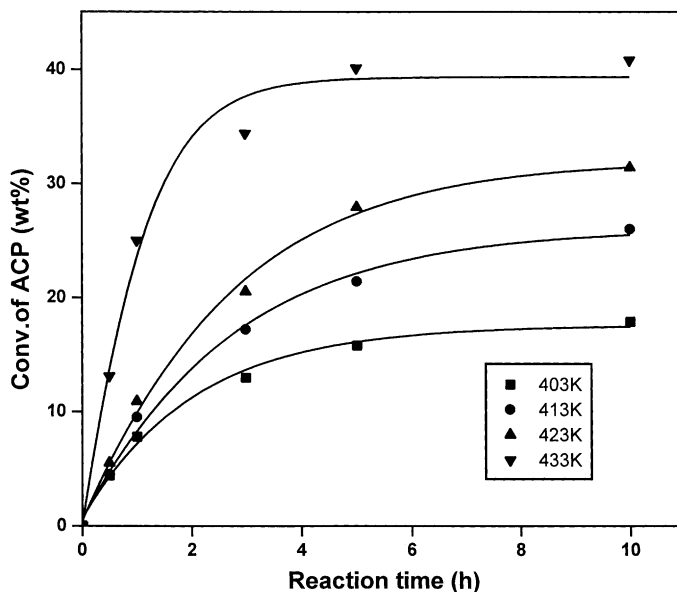


Fig. 5. Influence of reaction temperature (K) on the conversion of ACP (wt.%) over SZ catalyst with reaction time (h) (see footnotes of Table 2 for the reaction conditions).

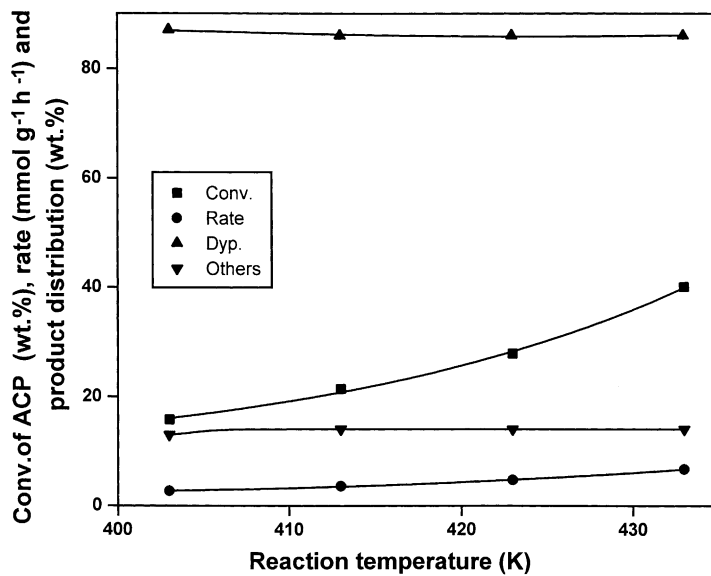


Fig. 6. Effect of reaction temperature (K) on the conversion of ACP (wt.%), rate of ACP conversion (mmol g⁻¹ h⁻¹) and product distribution, over SZ catalyst.

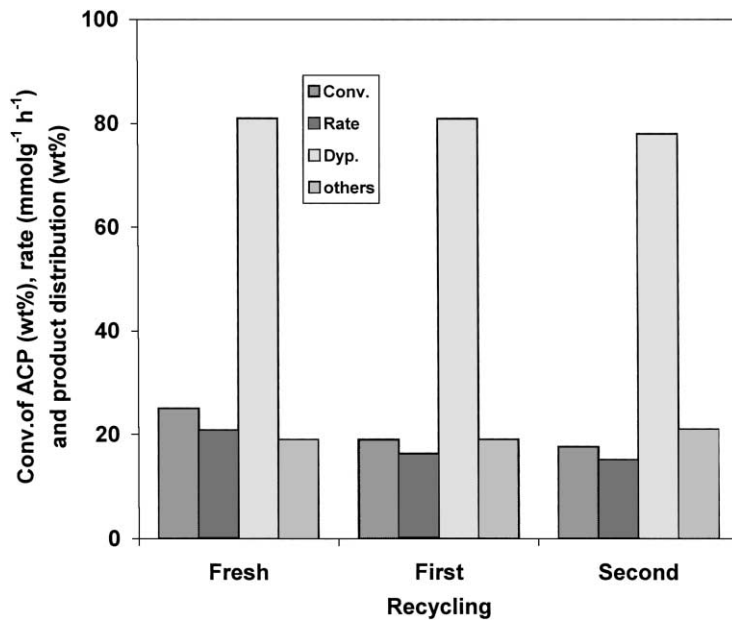
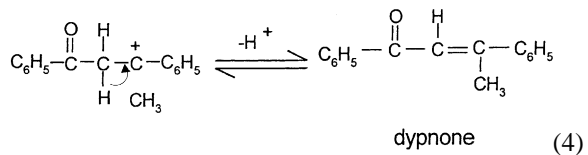
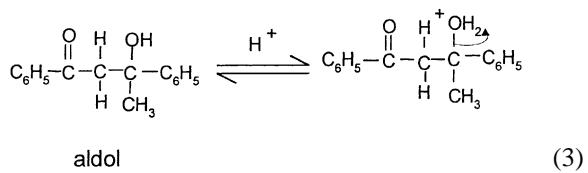
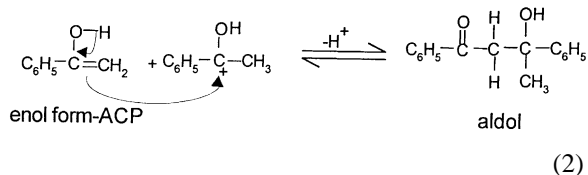
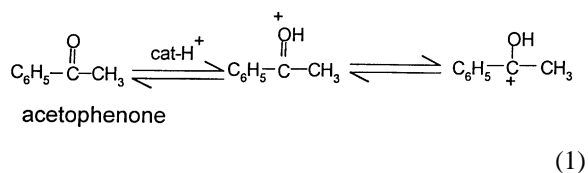


Fig. 7. Effect of recycling of catalyst (SZ); reaction conditions: reaction time (h) = 1 (see footnotes of Table 2 for the other conditions).

3.6. Mechanism

The formation of dyprnone takes place when one of ACP molecule gets protonated and forms its conjugate acid (Eq. (1)). The electrophilic addition of the carbonium ion (conjugate acid) to the enol form of another molecule produces aldol (Eq. (2)). Further protonation of the alcoholic OH of the aldol and elimination of water molecule forms a carbonium ion intermediate (Eq. (3)). Loss of H⁺ from the α-C atom results in the formation of α,β-unsaturated ketone (dyprnone) (Eq. (4)).



4. Conclusions

In summary, SZ and zeolite H-beta can catalyze the condensation of ACP to dyprnone efficiently and selectively. ST is found to be less active. A higher yield of dyprnone is obtained by increasing the catalyst (SZ) concentration and reaction temperature from 403 to 433 K.

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