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A Highly Selective Aldol Condensation of Cyclopentanone with Valeraldehyde Over Hydrotalcite-type Catalysts

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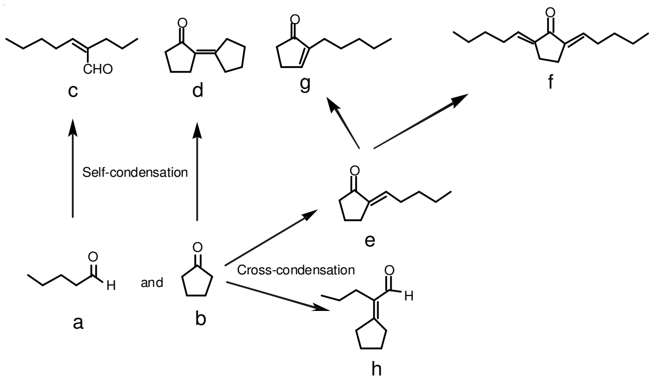
The aldol condensation using cyclopentanone with valeraldehyde was conducted at hydrotalcites catalysis. The catalyst was obtained by calcining the hydrotalcite precursor (Mg/Al = 3:1) at 773 K. Its reaction performance was evaluated on the various molar ratios of cyclopentanone to *n*-valeraldehyde. A good catalytic selectivity of 90 % and a high conversion of 93 % were achieved under mild conditions.

Key Words: 2-Pentylidene-cyclopentanone, Aldol condensation, hydrotalcite, Cyclopentanone, *n*-Valeraldehyde.

INTRODUCTION

Aldol condensation reactions are of fundamental importance in the synthesis of numerous large-volume organic chemicals and fine chemicals which are extensively used in rubber, plastic, coating, pharmaceutical, pesticide and feed additive industries. We successfully obtained 2-pentylidene-cyclopentanone (**e**) through the aldol condensation between the reactants in the title (**Scheme-I**).The target substance is used for some intermediates of biologically active substances or perfumes such as methyl dihydrojasmonate[1,2].



Scheme-I: Aldol condensation reaction between cyclopentanone and valeraldehyde

The aldol condensation reaction of valeraldehyde with cyclopentanone has already been paid much attention. A new catalytic system"AlPON" and "ZrPON" exhibited good performance for the aldol condensation of cyclopentanone with valeraldehyde[3]. Similarly, Wilson *et al*.[4], improved the selectivity of the aldol condensation reaction by controling the title reactants molar ratio to 1.8. The hydrotalcites (HTc) and their mixed oxides as heterogeneous catalyst with finely tunable basicities are developed recently. As their good basicity and stable lamellar structure, these materials have already been used as catalysts for many organic preparations involving aldol condensation reaction[5-9]. The present work deals with the aldol condensation of cyclopentanone (**a**) with valeraldehyde (**b**) to produce 2-pentylidene-cyclopentanone (**e**) with the hydrotalcites (HTc) participated.

EXPERIMENTAL

Preparation of hydrotalcites: Hydrotalcites of 3:1 Mg/Al molar ratios were prepared by coprecipitation at high supersaturation. Solution A was prepared by dissolving 25.6 g (0.10 mol) of $Mg(NO_3)_2{\cdot}6H_2O$ and 12.1 g (0.033 mol) of $Al(NO_3)_3{\cdot}9H_2O$ in 100 mL deionized water. Solution B was prepared by dissolving 10.7 g (0.2675 mol) NaOH and 7.4 g (0.0698 mol) Na_2CO_3 in 100 mL deionized water. Put A into a 250 mL flask, solution B was then added dropwise with vigorous stirring over a 2 h period while keeping the temperature at 60 ºC and the pH value of the solution in the range of 8-10. Then keep the precipitates at 60 ºC for 24 h in a thermostatic bath. The solid was washed several times with deionized water until the filtrate showed no presence of free base and subsequently dried at 90 ºC for 24 h. The hydrotalcites of 3:1 Mg/Al molar ratio was calcined at 773 K for 6 h in a muffle furnace prior for using.

Catalytic condensation: A 250 mL four-neck round-bottom flask equipped with mechanical stirrer and reflux condenser are charged. 10.5 g (0.125 mol) of cyclopentanone and 0.4 g of the HTc were added in the round-bottom flask and 4.3 g (0.05 mol) of *n*-valeraldehyde was then added dropwise with stirring slowly while keeping the reaction temperature at 80 ºC for 11 h. Then, the Mg-Al mixed oxides was separated by filtration, the filtrate was dried over anhydrous sodium sulfate and analyzed by gas chromatography on an Angilent 6890A chromatograph with FID detector and equipped with a SE-30 column. The desired product of 2-pentylidene-cyclopentanone (**e**) was separated by column chromatography (*n*-hexane:ethyl acetate = 12:1) and its structure was identified by ^{1}H NMR spectrum and MS (Trace DSQ-GC-MS). The ^{1}H NMR spectra were recorded on a Bruker ARX300 instrument with TMS as the interior standard. The ^{1}H NMR ($CDCl_3$) of 2-pentylidene-cyclopentanone (**e**): δ 0.866-0.914 (t, 3H, CH_3), 1.311-1.455 (m, 8H, $4CH_2$), 1.890-1.965 (m, 2H, CH_2), 2.099-2.171 (m, 2H, CH_2), 2.286-2.338 (t, 2H, CH_2), 2.544-2.605 (t, 2H, CH_2), 6.533 (t, 1H, -C=C-H). MS (EI, 70 eV): m/z = 151.94 (M^+).

RESULTS AND DISCUSSION

The catalyst of HTc (773 K) used in the aldol condensation between valeraldehyde and cyclopentanone was achieved by calcinating hydrotalcite precursor HT (Mg/Al = 3) at 773 K. The XRD powder patterns of HT (a) and HTc (773 K) (b) were shown in Fig. 1. The XRD patterns indicated that the lamellar structure of the HT (a) was changed. Moreover, the obvious characteristic peaks of MgO (200) and Al_2O_3 (135) appeared in the XRD patterns.

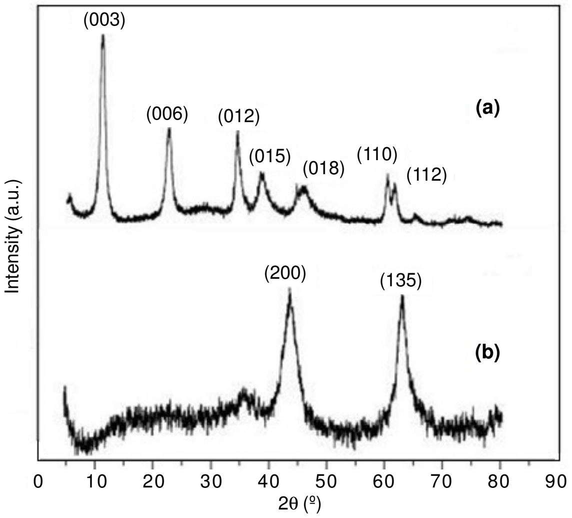
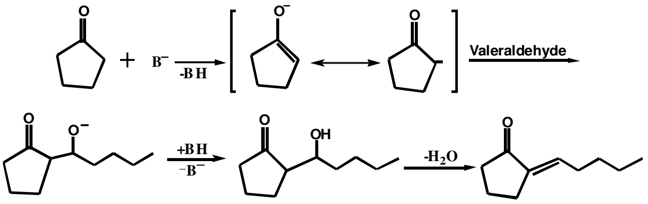


Fig. 1. XRD powder patterns of HT (a), HTc (773 K) (b)

It is well known that the aldol condensation can be catalyzed by both acid and base[10-13]. The base catalyst is favour to the formation of carbanion on the cyclopentanone. However, the acid catalyst can active the carbonyl group on the valeralderhyde easily and strengthen the carbocation of the carbonyl to be attacted by the carbanion species. The catalyst of HTc (773 K) owned both the acid and base catalyst excellences simultaneously for its both strong Lewis basic and Lewis acid sites. The former is due to the presence of oxygen atoms with low cordination, while the latter to Al^{3+} cation[3,7,14].

The reaction procedure of the aldol condensation (**Scheme-II**) is nearly the same as the traditional procedure. The aldol condensation was carried out on basic sites firstly by capturing an α-H atom from cyclopentanone. Then the generated carbanion species will attack the carbonyl group of valeraldehyde. Finally, the ultimate product (**e**) was achieved by dehydrating on the weak acid sites of the HTc (773 K). Although it is easier to form a carbanion on the cyclopentanone in the presence of base properties, the weak acid properties can promote the formation of the protonated carbonyl compound on valeraldehyde to be attacted by the generated carbanion. As a result, the catalyst which has acid-base properties is benefit for the cross-condensation[3,15].



Scheme-II: Procedure of the cross-condensation between cyclopentanone and valeraldehyde

In order to get a better catalytic performance, reaction temperature was taken into account firstly in our experiments. Varying temperature of 60, 80 and 100 ºC, respectively were carried out with a valeraldehyde/cyclopentanone molar ratio of 1/5 and without solvent. Entries 4, 7, 8 (Table-1) indicated that with the temperature up to 100 ºC, the valeraldehyde conversion was increased. However, the selectivity of **e** was the best when the temperature at 80 ºC. Due to low temperature couldn't activate the carbonyl of cyclopentanone and the catalysts efficiently, the lower temperature could result in low valeraldehyde conversion and selectivity to **e**. On the contray, a product **g** appeared that isomerizing from **e** when the reaction temperature reached 100 ºC. 2-Cyclopenten-1-one (**g**) was more thermodynamically stabler than 2-pentylidene-cyclopentanone (**e**) because the conjugate between the carbonyl and cyclic olefinic bond was more easier and stabler. Higher temperature could favour to activate the catalyst and the procedure of isomerization.

The reaction was also carried out over the different amount of catalyst. From the entries 4, 9, 10, we could see that the valeraldehyde conversion wouldn't increase with the HTc (773 K) used from 0.4-0.6 g. However, the side product **g** also appeared when 0.6 g catalyst was used. 0.4 g HTc (773 K) was enough for the procedure of the reaction under this reaction condition. While increasing HTc (773 K) would decrease the selectivity for producing g as a side product. Less catalyst couldn't activate the substance efficiently and result in low valeraldehyde conversion and poor selectivity to the major product **e**.

The molar ratio between valeraldehyde and cyclopentanone also played an important role in the selectivity between cross- and self-condensation[3,7,9,16]. Entries 1-6 (Table-1) showed that valeraldehyde/cyclopentanone molar ratio of 1/5 was the

TABLE-1
ALDOL CONDENSATION BETWEEN VALERALDEHYDE AND CYCLOPENTANONE WITH HTc (773 K) CATALYZED

Entry	n_1:n_2[a]	Catalyst (m)	T (ºC)	Valeraldehyde conversion (%)[b]	Product distribution (%)[i]					
					(c)	(d)	(e)	(f)	(g)	(h)
1	1:1	0.4 g	80	83	39	0	49	12	0	0
2	1:3	0.4 g	80	89	34	0	58	8	0	0
3	1:4	0.4 g	80	90	12	0	80	8	0	0
4	1:5	0.4 g	80	93	6	0	90	4	0	0
5	1:6	0.4 g	80	83	5	0	88	7	0	0
6	1:7	0.4 g	80	78	0	0	88	12	0	0
7	1:5	0.4 g	60	34	40	0	41	19	0	0
8	1:5	0.4 g	100	97	3	0	76	11	10	0
9	1:5	0.2 g	80	52	15	0	79	6	0	0
10	1:5	0.6 g	80	93	5	0	86	3	6	0

[a] n_1:n_2 = The molar ratio of valeraldehyde:cyclopentanone, the amount of valeraldehyde was 0.025 mol. [b] Detected by GC,GC yield. [i] Detected by GC,GC conversion. (d), (e), (f) were identified by GC-MS, the structure of (c) and (g) were identified by ^{1}H NMR. (c): 2-Propyl-2-heptenal, (d): 2-cyclopentylidene-cyclopentanone; (e): 2-pentylidene-cyclopentanone; (f): 2,5-dipentlidene-cyclopentanone; (g): 2-cyclopenten-1-one; (h): 2-cyclopentylidenepentanal.

optimal reaction condition. The selectivity to **e** was 90 % and valeraldehyde conversion was 93 % at the optimal reaction condition. Decreasing the valeraldehyde/cyclopentanone molar ratio could reduce the selectivity to **c** that was yielded by the valeraldehyde self-condensation and product **c** disappeared when the molar ratio down to 1:7. The low percentages of valeraldehyde decreased the reaction rate and the opportunity of self-condensation. However, according to Table-1 we could also find that valeraldehyde conversion decreased when the molar ratio was in the range of 1/5-1/7. For the reason of steric hindrance, valeraldehyde is a bit activer than cyclopentanone. It is difficult for carbanion gained on the cyclopentanone to attack the carbonyl of the cyclopentanone. Product **d** and **h** didn't appear *via* GC detected, whatever the valeraldehyde/cyclopentanone molar ratio was with 0.4 g HTc (773 K) used at 80 ºC.

Conclusion

2-Pentylidene-cyclopentanone (**e**) was well produced over catalyst HTc (773 K) that was gained by calcinating the hydrotalcite precursor (Mg/Al = 3:1) at 773 K. Though the aldol condensation between valeraldehyde and cyclopentanone could achieve a variety of products, while the selectivity could reach as high as 90 % for the main product at optimal reaction condition.

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