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Vapour phase acylation of furan and pyrrole over zeolites [*]

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The vapour phase acylation of furan and pyrrole was carried out over HZSM-5(19.7), HZSM-5(30), HZSM-5(280), CeHZSM-5(30), LaHZSM-5(30), HY and CeHY zeolites in a fixed bed reactor at atmospheric pressure using acetic anhydride as an acylating agent. The catalytic activity of the zeolite catalysts was dependent on the reaction temperature and the type of cation promoter used in the modification of the zeolite surface. The activity of the catalysts varied with the acidity of the zeloite systems tested. The yields of 2-acetylfuran and 2-acetylpyrrole with respect to the conversion of furan and pyrrole were 67.5% and 75.5% respectively. The acylation was found to be more active on Brønsted acidic sites available over zeolite systems.

Keywords: zeolite, acylation, furan, pyrrole, acetic anhydride, 2-acetylfuran, 2-acetylpyrrole

1. Introduction

The synthesis of organic intermediates is an important area in fine chemical industry. Many organic compounds are synthesized by Friedel–Crafts acylation [1–9] using Lewis acid catalysts like $AlCl_3$, $FeCl_3$, $TiCl_4$, etc. The major drawbacks of these catalysts are that they are non-regenerable, corrosive and expensive. Therefore most of the research was conducted on the solid acid catalysts so as to enable the replacement of the problematic homogeneous acids. This research plays a key role in the development of environmentally benign chemical processes. In this connection, several solid acids, which include sulfate-ion-doped metal oxides, zeolites, heteropoly acids and their salts, silica–alumina, have been investigated [10–13]. In recent years, zeolites are used as catalysts for acylation reactions due to their high thermal stability, reusability, easy separation and their eco-friendly nature. There is very little literature information available on the synthesis of 2-acetylfuran, and 2-acetylpyrrole. The known processes for the acylation of heteroaromatics such as furan, pyrrole and thiophene involve homogeneous acid catalysts. On a Ce-doped boron zeolite at 200 °C, 2-acetylfuran of 99% selectivity at 23% conversion of furan and 2-acetylpyrrole of 98% selectivity at 41% conversion of pyrrole over boron-containing zeolite doped with Cs of 0.2 wt% have been reported [14]. Ciamician and Silber [15] described the reaction of pyrrole with acetic anhydride as 39.2% of 2-acetylpyrrole and 8.5% of 3-acetylpyrrole formation. Cadamuri, Dughera et al. reported that acylation of pyrrole gives 2-acetylpyrrole as a major product [16]. On the other hand, Albert reported that direct acylation gives mainly 2- and 3-isomers [17]. Reddy states that the reaction with acetic anhydride generates the 2- and 3-isomers at equal concentration [18]. In the case of pyrrole, the acidity of the catalyst and the reaction temperature must be reduced in order to achieve a high selectivity [14]. Otherwise pyrrole tends to polymerize. The reported low yields of 2-acetylfuran and 2-acetylpyrrole in the literature made us re-examine the catalytic screening of several zeolites for obtaining highly active and selective best systems. Furthermore, the nature of the acidic centers in the zeolites for acylation have not been clarified so far inspite of the large volume of literature available. This investigation covers the acylation of furan/pyrrole with acetic anhydride (scheme 1) in the presence of various unmodified and modified zeolites. The acidic strength of zeolites for acylation has been compared. In this study, acylation of furan and pyrrole at the 2-position is of particular interest because of their uses in producing aroma of several fruits, beverages and tobacco smoke.

In the present investigation we have observed high yields of acylated products compared to the reported literature systems for 2-acetylfuran and 2-acetylpyrrole compound synthesis over the tested zeolite catalysts. There was no formation of 3-acetyl and di-acetyl compounds over the catalysts during the acylations of both the reactants.

2. Experimental

HY (Si/Al = 2.6) and HZSM-5 (Si/Al = 19.7, 30, 280) used were supplied by PQ corporation of USA, and Conteka of Sweden. Zeolites were modified with 3% Ce and 3% La nitrate salts by the impregnation method. The step-wise temperature-programmed desorption of ammonia (STPD) method was adopted in order to know the acidic strength of the zeolite catalysts. The reaction was carried out using a fixed bed down flow tubular glass reactor. The quantity of catalyst used was 4 g (18–30 mesh size). The conversions were given with respect to the furan/pyrrole. Blank experiment runs were performed in both the cases at temperatures of acylation studies. The reaction mixture

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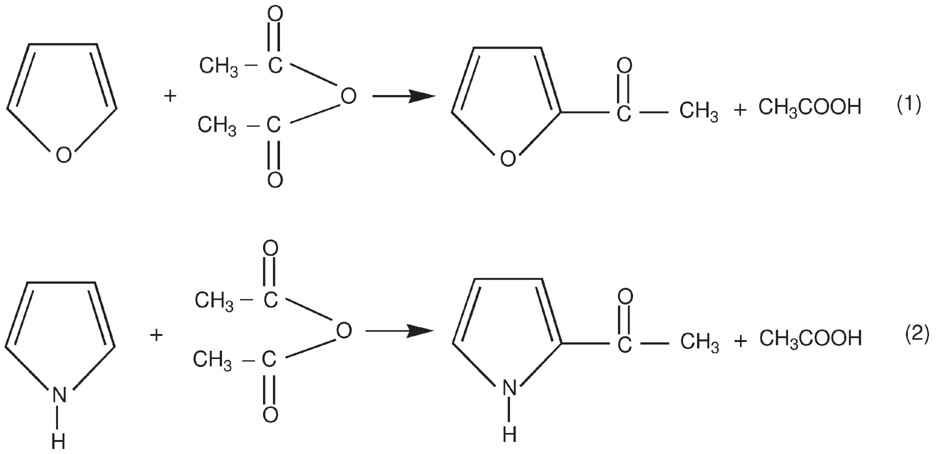


Scheme 1.

of furan/pyrrole with acetic anhydride was fed from the top using a syringe pump (B. Braun). The products were collected at ice-cold water temperature, and analyzed by GC using an SE-30 column. The product analysis was confirmed using mass and NMR techniques.

3. Results and discussion

The vapour phase acylation of furan and pyrrole was carried out over zeolite catalysts such as HZSM-5(19.7), HZSM-5(30), HZSM-5(280), HY, and cation-promoted modified zeolites like CeHZSM-5(30), LaHZSM-5(30), and CeHY. The results are shown in table 1. More insight into the acylation was obtained by carrying out the reaction at various temperatures, WHSV, mole ratios of furan/pyrrole with respect to acetic anhydride, etc. Furthermore, it helps to develop highly active and selective catalysts for 2-acetylfuran/pyrrole compound formation. As per the reported literature [19], the acidity of all the catalysts was measured by the STPD of ammonia method. The three different peak regions are weak, medium and strong. The total acid strength is represented by acid sites due to desorption of NH_3 in the temperature ranges of 150–250, 250–350 and 350–450 °C, as is shown in figure 1. The order of catalytic activity observed for furan acylation is represented as: HZSM-5(30) $>$ HZSM-5(280) $>$ LaHZSM-5(30) $>$ CeHZSM-5(30) $>$ HZSM-5(19.7) $>$ CeHY $>$ HY. And for pyrrole acylation the order is HZSM-5(280) $>$ HZSM-5(30) $>$ HZSM-5(19.7) $>$ HY $>$ CeHY $>$ LaHZSM-5(30) $>$ CeHZSM-5(30). The nature of the active centre of a catalyst on Lewis or Brønsted sites cannot be distinguished by the STPD method, but it has been reported earlier that [2] by increasing the temperature of reaction for zeolite catalysts, the Brønsted acid sites can be converted into Lewis acid sites. Here the acylation of furan and pyrrole may be possible at acid strength of the zeolite which is available in the range of 150–250 °C for the present catalysts. In view of this it may be true that the acylation reaction favours here on Brønsted acidic centres.

As it is known, zeolites contain both Lewis and Brønsted acidic centers. Lewis acidic centers have been referred to as the active centres for acylation in some works [20,21]. Also some groups reported that only Brønsted acidic centers are active [2,22], whereas in some instances Lewis as well as Brønsted acidic centers have been found to be active [23]. The catalytic activity for acylation in this case is seen to be over moderate acidic sites available at HZSM-5(30) and HZSM-5(280) zeolite catalyst systems. The strength of the acidic centers on zeolites changes with respect to reaction temperature and also with the type of cation promoter used during zeolite modification. The acylation over zeolites proceeds largely at the 2-position of the heteroaromatics to yield a somewhat sterically bulkier product. In fact, it is not the shape selectivity, but the electronic and thermodynamic effects which determine the position of the acylation [14]. It is also the acidity of the catalyst which brings about the reaction. In alkylation reactions, product-diffusion shape selectivity of the zeolites leads to the formation of selective isomer compounds. These aspects concur very well with our earlier results on alkylation of toluene with n-propanol over modified zeolites [24].

4. Variation of catalyst on acylation activities

From the data in table 1, all the tested zeolites are found to be active catalysts for furan and pyrrole acylation. The high yields of acylated products obtained were 67.5% of 2-acetylfuran at 93% conversion of furan and 75.5% of 2-acetylpyrrole at 77.5% conversion of pyrrole over HZSM-5(30) and HZSM-5(280) respectively. The other possible by-products like CH_3NH_2, $C_2H_5NH_2$, HCHO, etc., are due to the low boiling nature of reactants and they undergo cracking easily over the present catalysts. Moreover, acetic acid is also observed in each case as a by-product. The catalytic activity of HY is low due to its high acidity compared to HZSM-5(30) and HZSM-5(280) catalysts, as is summarised in figure 1. This shows that the present acylation reactions prefer moderate acidic centers. It has also been reported in the literature that the Ce- and La-modified

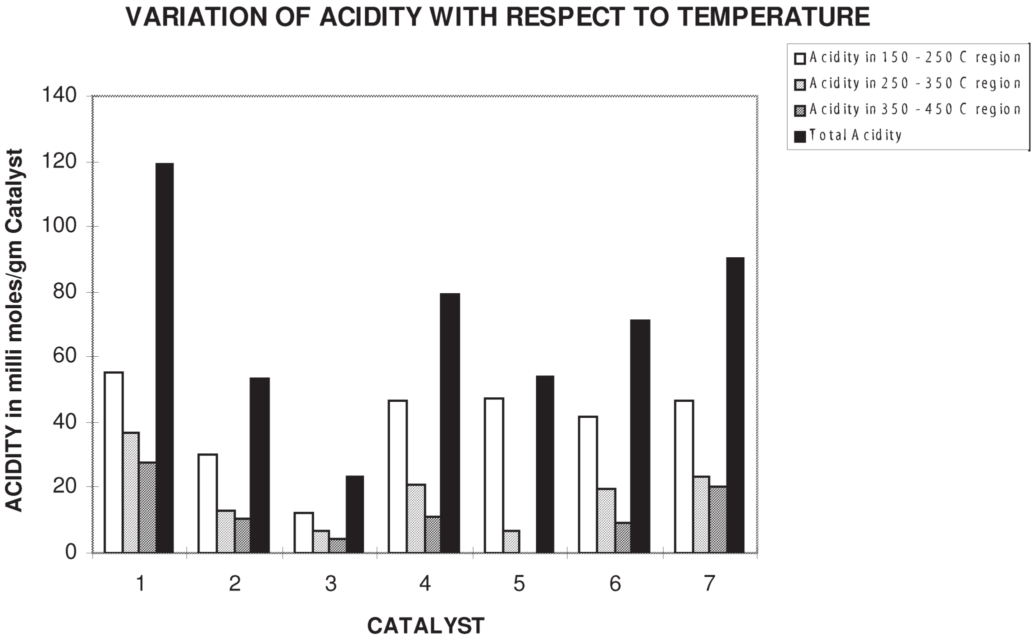


Figure 1. Acidity of: (1) HZSM-5(19.7), (2) HZSM-5(30), (3) HZSM-5(280), (4) CeHZSM-5(30), (5) LaHZSM-5(30), (6) HY, and (7) CeHY catalysts at 150–450 °C temperature.

Table 1
Effect of variation of catalyst on furan and pyrrole acylation.[a]

Sample No.	Catalyst	Reactant	TOS[b] (h)	Reactant conversion (wt%)	Product yield (wt%)	Product selectivity (wt%)	CH_3COOH and others[c]
1	HZSM-5	Furan	3	44.1	37.0	83.9	7.1
	(19.7)	Pyrrole	2	76.1	57.9	76.0	18.2
2	HZSM-5	Furan	2	93.0	67.5	72.0	25.5
	(30)	Pyrrole	2	69.8	67.6	96.8	2.2
3	HZSM-5	Furan	2	94.2	62.8	66.6	31.4
	(280)	Pyrrole	2	77.5	75.5	97.4	2.0
4	CeZSM-5	Furan	3	65.0	48.0	73.8	1.7
	(30)	Pyrrole	2	36.8	31.0	84.2	5.8
5	LaZSM-5	Furan	2	85.8	51.8	60.5	34.0
	(30)	Pyrrole	1	60.7	39.2	64.5	21.5
6	HY	Furan	2	58.3	21.6	37.0	36.7
		Pyrrole	1	58.1	55.2	95.0	2.9
7	CeHY	Furan	1	48.8	30.0	60.4	18.8
		Pyrrole	2	60.7	44.0	72.0	16.7
8	No	Furan		0	0	0	Traces of
	catalyst	Pyrrole		0	0	0	acetic acid

[a] Reaction temperature = furan at 150 °C, pyrrole at 250 °C, WHSV = 0.5 h^{-1}. Feed mole ratio (furan/pyrrole : acetic anhydride) = 1 : 1.

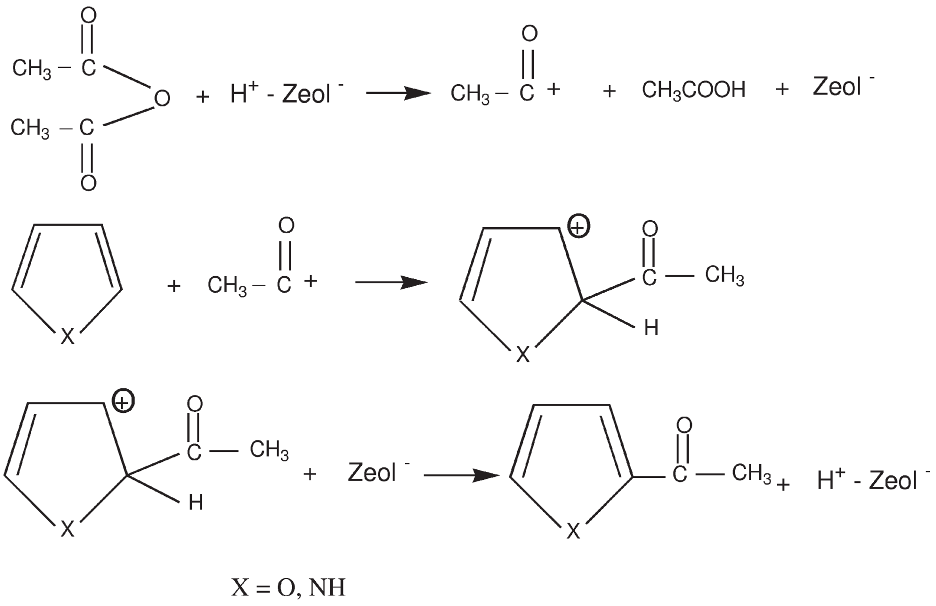
[b] Time on stream = (TOS).

[c] Others = CH_3NH_2, $C_2H_5NH_2$, HCHO, etc.

zeolites are good acylating catalysts [2], but in the present instances, when acidity of the modified zeolites increased, the catalytic activity for acylation was found to be low. This acidic strength of the zeolite and the catalytic activity for acylation are depicted in figure 2. Only the catalysts having moderate acidic strength show high activity. Here the modified zeolites are found unsuitable for both the present acylation reactions. Hence, majority of the studies made for acylation reaction are only on un-modified HZSM-5(30) and HZSM-5(280) for optimizing the conditions in getting the best selective and active zeolite catalyst system. A plausible reaction mechanism for furan and pyrrole acylation is given in scheme 2.

5. Effect of temperature on acylation

Temperature effect on acylation was studied over HZSM-5(30) for furan and HZSM-5(280) for pyrrole and the results are shown in table 2. Selectivity for acylation as well as catalytic activity for furan/pyrrole are less favourable at high



Scheme 2.

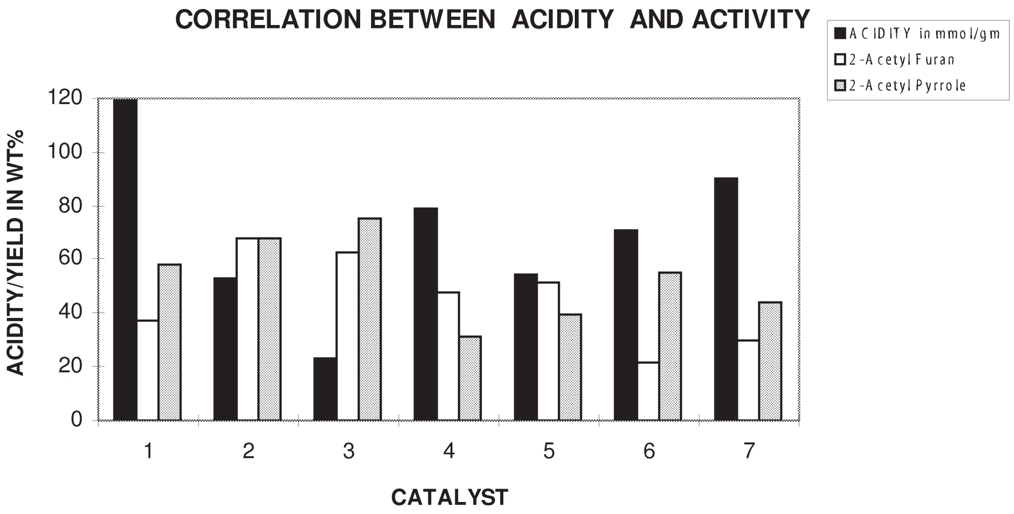


Figure 2. Acidity and catalytic activity for acylation of furan/pyrrole over: (1) HZSM-5(19.7), (2) HZSM-5(30), (3) HZSM-5(280), (4) CeHZSM-5(30), (5) LaHZSM-5(30), (6) HY and (7) CeHY catalysts.

Table 2
Extent of acylation of furan and pyrrole at various temperatures.[a]

Sample No.	Catalyst	Reactant	Reaction temperature (°C)	TOS (h)	Conversion (wt%)	Yield (wt%)	Selectivity (wt%)	CH_3COOH and others
1	HZSM-5(30)	Furan	150	2	93.0	67.5	72.5	25.5
	HZSM5-(280)	Pyrrole		1	64.7	37.6	58.1	27.1
2	HZSM-5(30)	Furan	200	1	73.6	63.7	86.5	9.9
	HZSM-5(280)	Pyrrole		3	65.1	57.0	87.5	8.1
3	HZSM-5(30)	Furan	250	2	87.7	52.0	59.2	35.5
	HZSM5-(280)	Pyrrole		2	77.5	75.5	97.4	2
4	HZSM-5(30)	Furan	300	3	51.0	20.0	39.2	31.0
	HZSM5-(280)	Pyrrole		1	73.1	67.0	91.6	6.0

[a] Feed mole ratio (furan/pyrrol : acetic anhydride) = (1 : 1). WHSV = 0.5 h^{-1}.

Table 3
Feed molar ratio (furan/pyrrole : acetic anhydride) on acylation product yield.[a]

Sample No.	Reactant	Mole ratio	TOS (h)	Conversion (wt%)	Yield (wt%)	Selectivity (wt%)	CH_3COOH and others
1	Furan	0.5 : 1	2	80.8	57.0	70.5	23.8
	Pyrrole		2	74.5	58.5	78.5	16.0
2	Furan	1 : 1	2	93.0	67.5	72.0	25.5
	Pyrrole		2	77.5	75.5	97.4	2.0
3	Furan	2 : 1	3	42.2	36.8	87.2	5.4
	Pyrrole		2	54.4	50.5	92.8	3.9

[a] Reaction temperature of furan at 150 °C, pyrrole at 250 °C. Catalyst for furan = HZSM-5(30) and for pyrrole = HZSM-5(280).

Table 4
Effect of weight hour space velocity (WHSV) of reactants on acylation.[a]

Sample No.	Reactant	WHSV	TOS (h)	Conversion (wt%)	Yield (wt%)	Selectivity (wt%)	CH_3COOH and others
1	Furan	0.25	4	91.9	60.7	74.1	31.2
	Pyrrole		2	72.0	69.2	96.0	2.8
2	Furan	0.5	2	93.0	67.5	72.0	25.5
	Pyrrole		2	77.5	75.5	97.4	2.0
3	Furan	0.75	1	89.2	63.2	70.6	26.0
	Pyrrole		1	52.7	47.0	89.1	5.7
4	Furan	1	2	67.7	50.3	74.2	17.4

[a] Catalyst for furan = HZSM-5(30) at 150 °C and for pyrrole = HZSM-5(280) at 250 °C. Feed mole ratio (furan/pyrrol : acetic anhydride) = (1 : 1).

temperatures. Therefore, the investigation into the acylation for furan/pyrrole was restricted to only 150 and 250 °C, where the yields of 2-acetylfuran and 2-acetylpyrrole are high in comparison with the reported literature values in each acylation reaction. Also it was found that the decrease in the yield of the acylated product at higher temperatures is due to the conversion of Brønsted acidic centers into Lewis acidic centers [2]. These observations draw our attention to state that the majority of vapour phase acylation of furan and pyrrole favours Brønsted acidic centers. It may be inferred that the activation energy for the active-site formation of the catalysts is between 150 and 300 °C temperature. Hence we can well say here that the Brønsted acidic centers are found more responsible for the acylation activity of furan/pyrrole in the present case.

6. Variation of feed with respect to mole ratio and weight hour space velocity

As is seen from the results in tables 3 and 4 the molar ratio of furan/pyrrole : acetic anhydride varied from 0.5 : 1 to 2 : 1 and there was no improvement in the yield of acylated products. Acetic acid was found to be one of the by-products at higher concentrations of acetic anhydride. Similarly, by changing the weight hour space velocity (WHSV) from 0.25 to 1 h^{-1}, the conversion of furan/pyrrol decreased due to the low contact time of feed and the catalyst. The optimum WHSV value obtained was 0.5 h^{-1} to get the best yield of acylated products in both the reaction cases.

A study was conducted on the activity of the catalysts at of 0.5 h^{-1} WHSV and 1 : 1 mole ratios of furan/pyrrole : acetic anhydride feed composition on HZSM-5(30) at 150 °C temperature for furan and on HZSM-5(280) at 250 °C for pyrrole for more than 6 h in order to record time on stream activity of the system. It has been found that the initial yields gradually decrease over a period of time, as is shown in figure 3. This could be due to the formation of coke at the acidic centers of zeolites with time on stream.

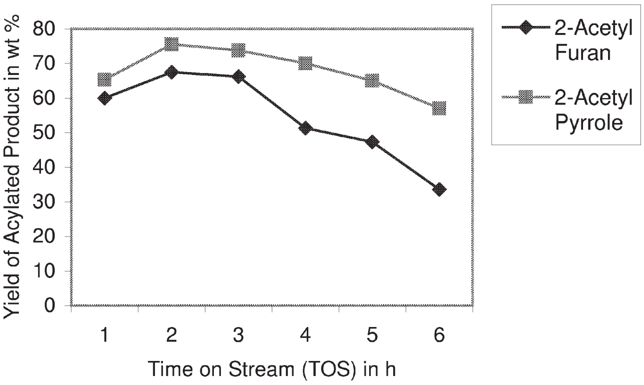


Figure 3. Acylated product yields with respect to time on stream for furan and pyrrole.

7. Conclusions

The following conclusions may be drawn from the data generated. Brønsted acidic centres are suitable for the Friedel–Crafts acylation of furan/pyrrole. The catalytic activity of the systems was dependent on the reaction temperature and cation promoter used for modification. The vapour phase acylation of furan and pyrrole occurred more on unmodified zeolites while more Brønsted acidic centers are easily available. Acidity values of modified catalyst were found to be higher than those of unmodified catalysts. The activity of the catalysts was found to decrease with increasing acidity. The maximum yield of 2-acetylfuran was 67.5% at 93% conversion of furan on HZSM-5(30) at 150 °C temperature, whereas the maximum yield of 2-acetylpyrrole was 75.5% at 77.5% conversion of pyrrole on HZSM-(280) at 250 °C. In both cases the feed mole ratio with respect to acylating agent was 1 : 1 at optimum WHSV of 0.5 h^{-1}. The catalytic activity for the acylation of both the reactions was found to be decrease after 6 h of the run.

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