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Vapor phase acylation of pyrrole over ferrites

Chemistry

KEYWORDS: acylation, pyrrole, acetic anhydride, 2-acetylpyrrole, ferrites.

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ABSTRACT

The vapor phase acylation of pyrrole was carried out over different ferrites $NiFe_2O_4$(NSF-1) $CrFe_2O_4$(NSF-2), $CoFe_2O_4$(NSF-3) $Ni_{0.5}Co_{0.5}Fe_2O_4$(NSF-4) $Ni_{0.5}Cr_{0.5}Fe_2O_4$(NSF-5), $Cr_{0.5}Co_{0.5}Fe_2O_4$(NSF-6) and $Ni_{0.33}Co_{0.33}Cr_{0.33}$ Fe_2O_4 (NSF-7) in a fixed bed reactor at atmospheric pressure using acetic anhydride as an acylating agent. The catalytic activity of the ferrite catalysts was dependent on the reaction temperature, WHSV and molar ratio. The activity of the catalysts varied with the acidity of the ferrite systems tested. The yields of 2-acetylpyrrole were 99.096% and selectivity is 99.95 % found under the optimized condition. On NSF-4 under optimized conditions, Ni^{2+}/Co^{2+} ionic distribution in the spinel lattice influences the acidic-basic properties.

Introduction

Many organic compounds are synthesized by Friedel–Crafts acylation using homogeneous catalysts like $AlCl_3$, $FeCl_3$, etc. The synthesis of organic intermediates is an important area in fine chemical industry [1-9]. The major drawbacks of these homogeneous catalysts are that they are corrosive expensive and non-regenerable. So the problematic homogeneous catalysts replaced by heterogeneous solid catalysts such as sulphate-ion doped metal oxides, silica-alumina and zeolites have been investigated. In recent years ferrites are used as catalysts for the synthesis of many organic compounds because of their high thermal stability, reusability, easy separation and eco-friendly nature. Friedel–Crafts acylation of pyrrole is by far the most popular method for the synthesis of acetyl-pyrroles, which are key pharmaceutical intermediates, especially for 2-acetylpyrrole [10-11]. The known processes for the acylation of pyrrole involve homogeneous acid catalysts and heterogeneous zeolites. The study reported that acylation of pyrrole gives 2-actylepyrrole formation as the major product [12-15]. The 2-actylepyrrole is used in producing aroma of several fruits, used in flavors for tobacco and roasted foods. The present study was done on ferrites. The ferrites are tested for pyrrole acylation and we have observed high yields and selectivity of 2-actyle pyrrole with negligible side products.

Results and Discussion

Effect of variation of catalyst on acylation activity

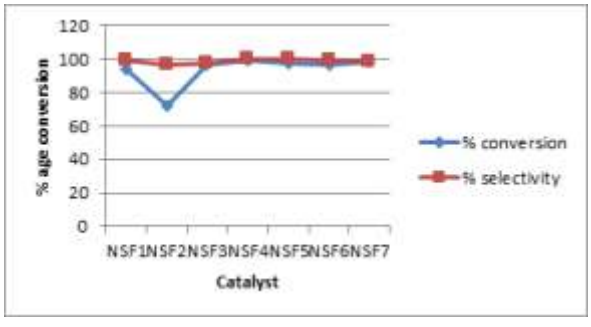

Fig. 1. Effect of variation of catalyst on acylation activity.

From the data in Fig. 1, all the tested ferrites are found to be active catalysts for pyrrole acylation with acetic anhydride under optimized conditions. The maximum yields of acylated products obtained was 99.096% of 2-actyle pyrrole with selectivity 99.95% on NSF-4 catalyst .The other products formed in negligible amounts on optimized condition (molar ratio 1:4, WHSV 0.4h^{-1} and temperature 673 K). The Ni^{2+}/Co^{2+} ionic distribution in the spinel lattice of catalyst NSF-4 plays important role for high yield and selectivity.

Variation of weight hour space velocity (WHSV)

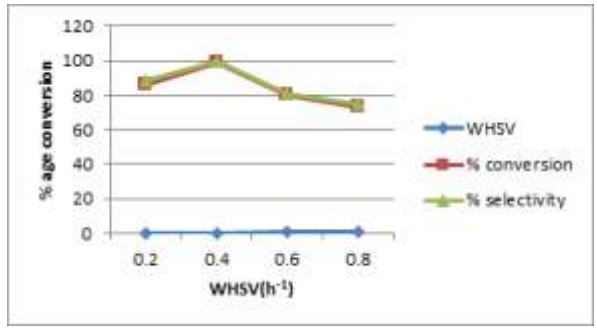

Fig. 2. Variation of weight hour space velocity (WHSV).

The effect of WHSV on acylation of pyrrole was studied over (NSF-4) catalyst at a temperature of 673K, at 1:4 molar ratio of pyrrole to acetic anhydride and WHSV (0.2, 0.4, 0.6 and 0.8 h^{-1}). The results are shown in fig.2. Pyrrole conversion increased as the WHSV increased from 0.2 to 0.4 h^{-1} and decreased thereafter. The high contact time causes charring over active sites, hence decreasing the pyrrole conversion. Below 0.4 h^{-1} WHSV pyrrole conversion was decreased due to the low contact time of feed and the catalyst.

Variation of feed with respect to molar ratio

As seen from the results in fig.3., the molar ratio of pyrrole : acetic anhydride varied from 1:2 to 1:8 and the vapor phase acylation of pyrrole was carried out over NSF-4 at temperature 673 K and WHSV 0.4 h^{-1}. Pyrrole conversion and selectivity of 2-actyle-pyrrole increased with increase in the pyrrole-to-acetic anhydride molar ratio, reaching a maximum at 1:4. At higher molar ratio, the selectivity and conversion of 2-actylepyrrole was reduced. This was probably due to the unavailability of active sites for pyrrole over the catalyst surface, because of competition between pyrrole and acetic anhydride adsorption.

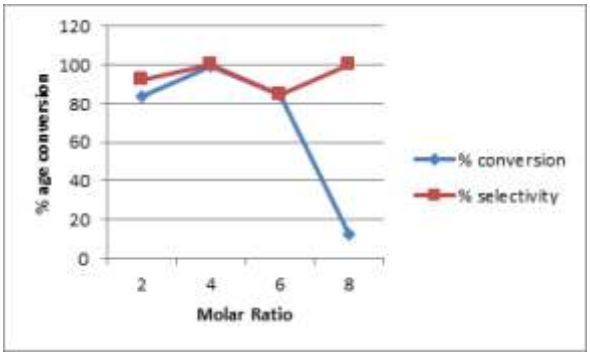

Fig.3. Variation of feed with respect to mole ratio.

Effect of temperature on acylation

An effect of temperature on acylation of pyrrole acetic anhydride was studied over (NSF-4) in the temperature range 573-723 K, WHSV 0.4h-1 and molar ratio 1:4; the results are shown in fig.4. Therefore the investigation of acylation of pyrrole was restricted to only 673 K, where the yield of 2-actyle-pyrrole is high in comparison to the values reported in literature in each acylation reaction. It was also found that the decrease in the yield of the acylated product at higher temperatures is due to the charring of some reactants. These observations draw our attention to conclude that the strong and medium acidic sites favor vapor phase acylation of pyrrole.

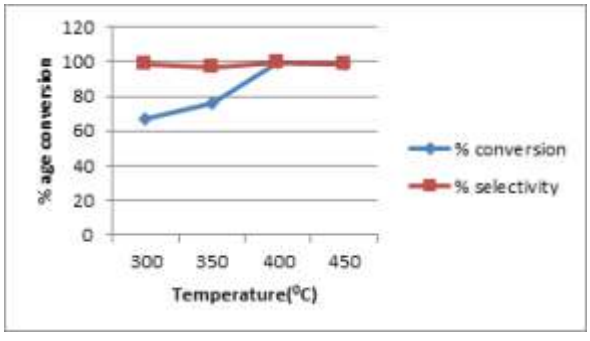

Fig.4. Effect of temperature on acylation.

Effect of time on stream (TOS)

The reaction was carried out for 10 h on all the catalysts. The best results are given by catalyst NSF-4 on optimized conditions i.e. molar ratio 4, WHSV 0.4 h^{-1} and temperature 673K. The results are depicted in fig. 5. The continue decrease of catalytic activity has been observed. The conversion with time on stream decreased gradually but selectivity is not affected very much. This may be due to coke induced selectivity or may be absence of by-products.

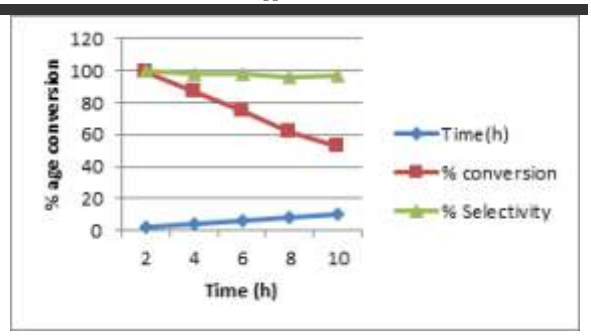

Fig.5. Effect of time on stream

Conclusions

A catalytic activity experiment reveals that strong and medium acidic sites are suitable for the acylation of pyrrole. The catalytic activity of the system was dependent on the reaction parameters. The vapor phase acylation of pyrrole occurred more on NSF-4. The high yield and selectivity depends on Ni^{2+}/ Co^{2+} ionic distribution on spinel lattice of ferrite. The maximum yield of acylated product obtained was 99.096 % of 2-actylepyrrole with 99.95% selectivity, over NSF-4 ferrite and acylating agent is acetic anhydride, at molar ratio 1:4, WHSV 0.4 h^{-1} and temperature 673K. Time on stream conversions was gradually decreasing, observed for the period of 10h.

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