Synthesis Of Zr:SAPO 11 Catalyst By Hydrothermal Method And Applied For The Synthesis Of Substituted Chalcones

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Abstract:

SAPO-11 synthesized by the conventional static hydrothermal method at optimized temperature. The calcinations and crystallization gives fine crystallizations. SAPO-11 again calcinated with zirconium nitrate and obtained product was characterized by IR and powder XRD. The catalyst was applied for the synthesis of chalcones via aldol reaction. The reaction proceeds with good yields. The catalyst was recycled and found suitable for reactions. The formed product was characterized by IR, NMR spectroscopy.

Keywords: Aldol reaction, Hydrothermal, Zr:SAPO-11,Chalcones, Catalytic activity, Powder X-RD.

1. Introduction:

Solids are important key to make organic transformations. These solids are categorized as single metal component oxide, zeolites, supported alkali metals ions, clay minerals, non-oxide etc. Alkaline earth metals are widely used in synthesis of chalcones. The characteristic features of solids in interactions with metals resulted from pore nature of solids and surface area. The acid-base properties are controlled by selecting the appropriate metals and deposited on Si/AI ratio of the zeolite. SAPO-11 is found to be in versatile catalytic activity. Synthesis and characterization of SAPO-11 start with synthesis from alumina phosphate,[1] craking and isomerisation over SAPO-11,[2] one pot synthesis of SAPO,[3] crystaline nature with porosity of SAPO-11,[4] x-ray spectroscopic study,[5] and metal mixed CoSAPO 34,[6] Silicon corporated SAPO-11,[7] silicon in the presence of morpholine as template, supercritical water assisted,[8] acid medium incorporated synthesis of SAPO-11,[9] sucrose facilitated synthesis of SAPO,[10] through mordenite zeolite synthesis,[11] The synthesis of crystalline SAPO-11 by hydrothermal method under ultrasonification condition has meet with the crystallinity which was ell explained by using x-ray diffraction study and IR spectroscopy. As many report available for aldol reaction such as conventional condensation reactions catalysed by $Ba(OH)_2$,[12] LiOH and microwave irradiation and ultrasound irradiation,[13] Suzuki reaction,[14] Witting reaction, Friedel-Crafts acylation, acidic conditions such as HCl,[15] BF_3, p-toluenesulfonic acid in toluene and amino grafted zeolites,[16] zinc oxide, water,[17] Na_2CO_3,[18] PEG400,[19] silicasulfuric acid,[20] $ZrCl_4$ metalmediated and ionic liquid,[21] many metal catalysed reactions. [22] Here, we are reporting zirconium nitrate on SAPO 11. Barium nitrate on sapo11 has been investigated to be a novel and highly competent catalyst for the aldol condensation of aldehyde and ketone under solvent-less conditions, at room temperature. The reaction is very speedy, uncontaminated and environment friendly. On reviewing the references we found that many references are available for the synthesis of chalcones and their derivatives. Here we are enlightening the application of Zr nitrate: SAPO11 made catalyst for Aldol Condensatation. The use of heterogeneous catalyst has many merits such as clean reaction, recyclability of catalyst and more yields.

2. Material and Method:

2.1 Synthesis of Zr:SAPO-11:

The required different gels were prepared using following procedure.

Solution A: In 30gm of distilled water, 19.45gm of Aluminium isopropoxide dissolved and stirring continued for 1hr.

Solution B: In 7.5 gm of distilled water, 1.2gm quantity of fumed silica mixed and stirring continued for half an hour.

Solution C:- In the 7.5gm of distilled water 11.44gm of orthophosphoric acid was diluted and the mixture stirring for 10minuites. After the said procedure, solution A, B and C were mixed together and under stirring 4.985gm quantity of Di-n-propylamine added drop wise in to the mixture to get the gel. Ultrasonic treatment was given to the gel for 20 minutes. pH of the gel was noted and found according in literature. The gel was heated at 160 ^{o}C for 48 hr. The crystalinity and powder x-ray spectra observed exactly as reported literature. The products were calcined at 550^{o}C for 6 hrs with heating rate 2^{o} C/min, in order to remove the template. The molar composition of the reagents was taken as $1.0Al_2O_3$:$1.0P_2O_5$:$0.5SiO_2$:1.0DPA:$49H_2O$.

Solution D: In the synthesized SAPO 11 was added 5 mol % of $Zr(NO_3)_4$ in methanol and again the compound was calcinated at 450^{o}C for 16hr.

2.2 General Procedure for the synthesis of chalcones :

In two neck round bottom flask was charged with a mixture of 5 mol% catalyst. A mixture of acetophenone derivative (6 mmol) and benzaldehyde derivative (6 mmol) was dissolved in ethanol (30 mL) was added. The reaction mixture was stirred for 10 min at room temperature until starting material was totally consumed. Add ethyl acetate and transfer to separatory funnel and washed with H_2O. Separate the organic layer and dried over sodium sulphate. Filter and concentrate on rotary evaporator to dryness and purified by silica gel column chromatography with hexane/EtOAc (90:10 %) to afford desired product (702 mg, 98 %).IR (KBr, υ max cm-1 1662, 1603, 1483, 1444, 1335, 1210, 1092, 1025, 1008, 975, 825, 757, 683. (E)-1,3-diphenyl-2-propen-1-one (1): pale yellow crystals (1.18 g, 96%); m.p = 57–59 °C; ESI-MS [M+H]+ 209.3; NMR ($CDCl_3$) δ 7.92–8.10 (m, 2H); 7.81 (d, 1H, *J* = 18.12 Hz); 7.50 (d, 1H, *J* = 18.12 Hz); 7,62–7.66 (m, 3H); 7.48–7.50 (m, 2H); 7.38–7.42 (m, 3H); ^{13}C-NMR ($CDCl_3$) δ :191.0; 145.0; 133.30; 135.6; 133.0; 129.0; 128.9; 128.8; 128.6; 122.0.

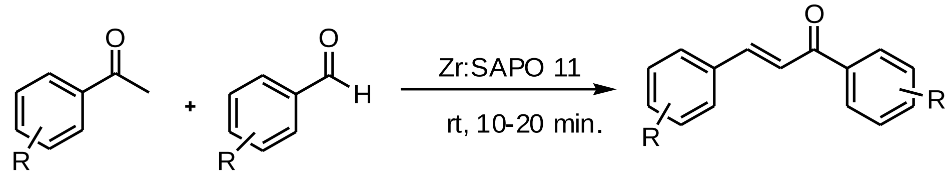
3. Result and Discuss

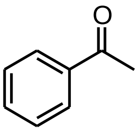
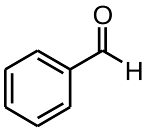
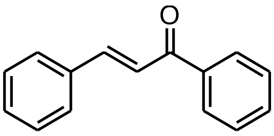
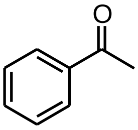
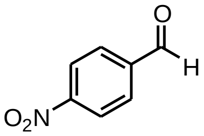
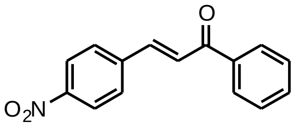
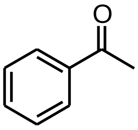
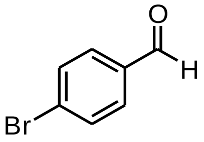
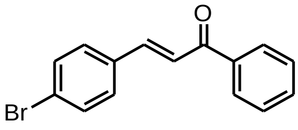
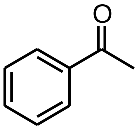
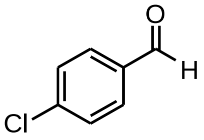
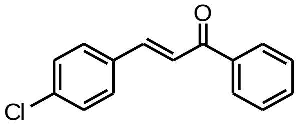
The synthesized compound of Zirconium on SAPO11 was characterized by powder XRD and IR technique. The crystallinity of the product is found to optimum at temperature 450 ^{o}C which intend to shown good catalytic property. Zr catalyst shows better catalytic property in aldol reactions and C-H activation as with increase in temperature, which turns in to increase in catalytic activity. Initially optimization of SAPO-11 was obtained at the condition of 160^oC for 36 hrs and it is matched with reported and standard value of the XRD peaks. It was studied by the synthesis of SAPO-11 at different hours for 160^oC, shown in fig 1. The IR values of sample SAPO 11 shows 1026 cm^{-1}and 1075 cm^{-1}, 1116 cm^{-1} for the formation of Si-O-Si, Al-O-Al bonds as bending vibrations. While XRD pattern of sample indicate only a sharp line at 8.1^o, 9.8, 12.8 ^{o}, 16.1 ^{o}, 21.9 ^{o}, 22.2 ^{o}, 22.4 ^{o}, 25.9 ^{o} and 27.4 ^{o} . Under optimisation the study of different temperature, it leads to formation of amorphous form of the sample and crystallinity was not so observed. As the time for synthesis increased from 9 hrs to 18 hrs in sample **2**, the crystallinity is increased remarkably and it is matched with the reported XRD value.

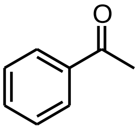
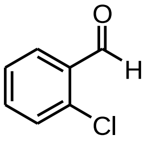
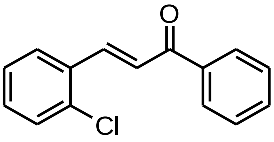
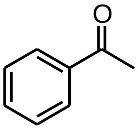
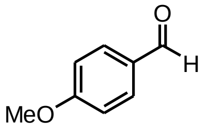
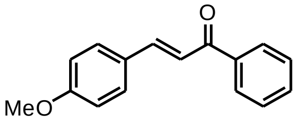
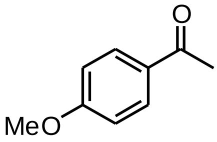
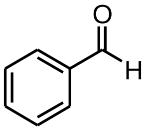
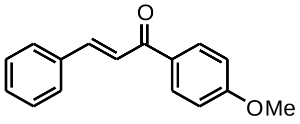
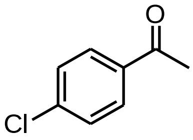
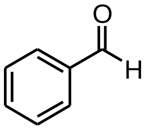
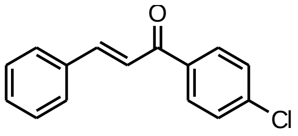
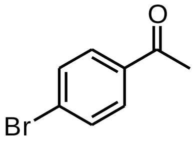
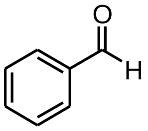
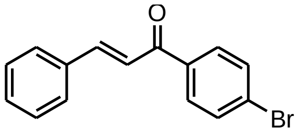
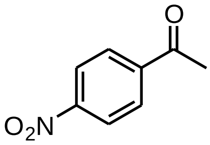
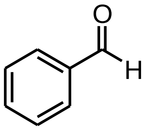
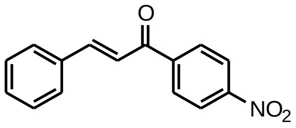
Fig.1:Sample**1** Fig.2:Sample**2**

The synthesized catalyst has been applied for the synthesis of various chalcones. As per the procedure of synthesis, all chalcones were formed with high yield. Here we used substituted aldehyde and acetophenone we found that aldehyde with electron withdrawing favours chalcone formation with fast rate of reaction. While the substitutions at acetophenone side take long time. In this reaction after catalyst optimization starting from 1 mol to 20 mol % it is found that 5 mol % of the catalyst was suitable to furnish the reaction. With this information after completion of reaction the catalyst was washed and dried in oven and reused for the next reaction, it is found that the catalyst activity was not degraded. The reaction was carried out in different solvent such CH_3OH,$CHCl_3$,DMSO, H_2O etc and the role of solvent was not affected the yield of the product.

Scheme 1: General Reaction of Chalcones Synthesis



Sr No	Substituted Acetophenone	Substituted Aldehyde	Product	Reaction Time in Min.	Yield in %
1)				25	96
2)				20	98
3)				20	95
4)				20	95

5)				25	92
6)				20	90
7)				20	85
8)				30	86
9)				30	90
10)				30	88

*All Product yields are after crystallization.

4. Conclusion:

In conclusion, we used catalytic amount of SAPO11:Zr and synthesized in good to excellent yield of substituted chalcones. The catalyst is environment friendly, reaction proceeds without side product formation. Catalyst is recyclable and gives good yield with less time. Catalyst is prepared by hydrothermal method.

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