

Side-chain alkylation of acetophenone with formaldehyde over alkali and alkaline earth metal ion modified basic zeolites [☆]

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Abstract

Synthesis of acrylophenone and propiophenone were achieved for the first time by side-chain alkylation of acetophenone using formaldehyde as alkylating agent in heterogeneous conditions over basic zeolites.

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1. Introduction

Synthetic routes to α -methylene carbonyl compounds have received considerable attention due to the importance of this class of compounds as useful intermediates [1]. Conventionally phenylvinyl ketone (acrylophenone) is synthesized by employing following methods. (i) Phenylvinyl ketone was synthesized using condensation of ethylene and benzoyl chloride in the presence of anhydrous aluminum chloride [2]. The process is homogeneous and corrosive the yield of the phenyl ketone is $\sim 25\%$. Phenyl vinyl ketone was synthesized by addition of PhMgBr and sulphones or amides and the yield varied in the range of 10–50% phenyl vinyl ketone. In this method HCl can be liberated as a by-product. (ii) Phenylvinyl ketone was also synthesized by addition of β -propiolactone to phenylmagnesium bromide in ether solution at -6 to 0 °C. In this process β -bromopropionic acid can be formed as a major product [3]. (iii) Synthesis of phenylvinyl ketone is also reported by the treatment of acetophenone with 37% aqueous formaldehyde

solution in the presence of morpholine in refluxing acetic acid [4]. All these methods involve the homogeneous conditions, which poses separation problems and also formation of excessive waste products.

Phenylvinyl ketone is a starting material for the preparation of antibiotic chloramphenicol. α -Methyleneketones (acrylophenone) are structural moieties in a large class of compounds, such as drugs and pheromones [5,6]. Poly(phenylvinyl ketone) is a polymer of phenylvinyl ketone, represents a good model to determine the differences between small-molecule and macro-molecular ketones containing a regularly recurring sequence of chromophores [7].

However, most of these methods suffer from one or more of the following disadvantages: long reaction times, vigorous reaction conditions and the occurrence of side reactions, homogeneous catalysis, separation of catalyst and selectivity of product. Nevertheless, there is still a great demand for solid base catalysts.

Solid-base catalysts have many advantages over liquid bases or organometallics. Such as allowing easier separation and recovery of the products, catalysts, solvent and they are non-corrosive. Thus, solid-base catalysts offer environmentally benign and more economical pathways for the synthesis of fine chemicals. Because of these advantages, research on the synthesis of fine chemicals using solid bases as catalyst has increased over the past decade. The

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studies of solid base catalysts were started by Pines et al. [8]. They showed that sodium metal deposited on alumina acted as an effective catalyst for double bond migration of alkenes. Later in 1970s, studies of solid base catalysts became more popular [9]. The state-of-the-art of base catalysts and various transformations catalyzed by base catalysts were reviewed by Hattori [9,10], Barthomeuf [11] and Dartt and Davis [12].

In recent years, non-oxide type catalysts have been recognized as heterogeneous basic catalysts. The catalysts act as base toward the reactants either by abstraction of a proton from the reactants (Bronsted base) or by donation of an electron pair to the reactants (Lewis base) to form anionic intermediates, which undergo catalytic cycle.

According to Itoh et al. [13,14], both basic and weak acidic sites on the zeolite are required for the side-chain alkylation. By using quantum chemical calculations, it has been suggested that the cooperative action of acid and base sites is very important in the side-chain alkylation; the base site activates the carbon atom of the side-chain of aromatic ring and the acid site adsorbs and stabilizes the aromatic ring [13]. Zeolites modified with cations, such as alkali or alkaline metal ions, exist as cations or hydrated cations or oxide species. In particular, alkali ion-exchanged zeolites behave as base catalysts [15], reflecting the base character of alkali metals.

In this paper, we report base catalyzed syntheses of acrylophenone from acetophenone over alkali and alkaline earth metal ion-modified zeolites like NaZSM-5, KX, NaY, Cs-ZSM-5 (40) etc. We have studied the influence of metal cation, effect of temperature, mole ratio, feed rate and time on stream on conversion and selectivities over various basic modified zeolites.

2. Experimental

2.1. Preparation of catalyst

Each zeolite was pelleted without a binder, crushed, and sized to 18–30 mesh before impregnation. The catalysts were modified by using required amounts of alkali or alkaline cation nitrates by an impregnation method. The required amount of precursor was taken in the form of nitrate or other soluble salts in 30 ml of water. The amount of precursor used in the preparation of modified catalyst was 2.586 g of KNO_3 for 1 g of K. Some of the catalyst (4.0 g) was added to this solution and kept soaking for 12 h. Then the material was dried at 110°C over night

and calcined at 420°C for 4 h before using it for the reaction.

2.2. Alkylation of acetophenone

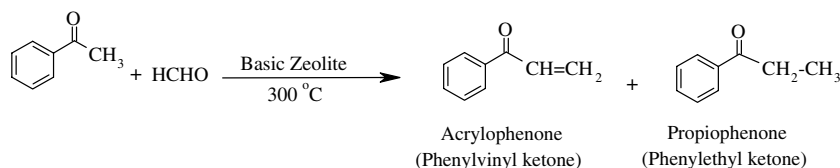
All the experiments were carried out in a fixed-bed Pyrex reactor (with 20 mm internal diameter) with a continuous down flow at atmospheric pressure. The catalyst bed temperature was measured with a thermocouple placed in the middle of the catalyst bed. Mixtures of reactants were fed from a syringe pump (B. Brown or Sage) at a rate of 2 ml h^{-1} . The effluents from the reactor were cooled and periodically collected with an ice trap. A typical procedure for side-chain alkylation of acetophenone as follows: 12 g of acetophenone is mixed with 16.2 g of formaldehyde (37 W/V% in water) in 7.3 g of methanol as solvent (1:2:1 molar ratio of acetophenone:HCHO:MeOH). The resultant solution is taken as feed and the reaction temperature is 300°C .

Quantitative analyses of product mixtures were carried out by gas chromatography (GC). Samples were analyzed by GC (Shimadzu-17A and -14B) fixed with an OV-17 (2mm \times 0.125 in. OD) on a chromosorb W-HP column with a flame ionization detector. The carrier gas was N_2 (200 kPa) and the analysis temperature was 150°C (oven temperature), 250°C (injector) and 300°C (detector). The retention times were compared with those of authentic compounds. The product was confirmed by mass spectra, GC-mass spectroscopy and NMR techniques. The mass-balance was >90–95%.

3. Results and discussion

In the present study, synthesis of acrylophenone and propiophenone were achieved for the first time by side-chain alkylation of acetophenone using formaldehyde as alkylating agent in heterogeneous conditions over basic zeolites. Alkali and alkaline-earth metal modified X catalysts were employed to obtain acrylophenone and propiophenone selectively in vapor phase conditions at atmospheric pressure (Scheme 1).

The characterization of alkali modified ZSM-5 catalysts is given elsewhere [16]. The XRD patterns of alkali metal ion modified ZSM-5 catalysts showed the high crystallinity with little decrease in peak intensity of large size cation like Rb^+ . A decrease in surface area was observed with an increase in the loading of the alkali metal ions. With the increase in size of the cation the surface area was also



Scheme 1.

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