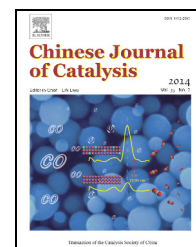


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## Article

# Cyanoethylation of alcohols and amines by cesium-modified zeolite Y

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## ABSTRACT

Zeolite Y modified by cesium and magnesium ions was prepared by ion-exchange and impregnation methods, and its activity in the cyanoethylation of aliphatic and aromatic alcohols and amines was investigated. During the preparation of some samples, the transformation of zeolite Y into a pollucite-type phase occurred. This phase exhibited good activity in the cyanoethylation of aliphatic alcohols. The prepared solids modified by the impregnation method were more active than the ion-exchanged solids. The activities of the catalysts, in contrast to other basic solids, were scarcely affected by the presence of air or moisture. A correlation between catalyst basicity and catalytic activity is discussed. The catalysts were characterized by X-ray diffraction, volumetric nitrogen adsorption surface area measurement, and CO<sub>2</sub> temperature-programmed desorption. Scanning electron microscopy revealed that the particles of the modified nanocatalysts were < 40 nm. The reaction of acrylonitrile with linear alcohols in the presence of the catalysts was accelerated by microwave irradiation.

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## 1. Introduction

The catalytic addition of alcohols or amines to a carbon-carbon double bond provides a useful method for the preparation of ethers and amines [1]. Cyanoethylation, the addition of alcohols or amines with active hydrogen to acrylonitrile, has attracted significant interest for the synthesis of drug intermediates, plasticizers, insecticides, emulsifiers, additives for synthetic rubber, and physiologically active compounds [2]. The resulting nitriles can be converted to different types of amines after hydrogenation or can form the related carboxylic acid. Usually, cyanoethylation can be promoted in the presence of a base [2,3]. The homogeneous basic catalysts [2,4] so far reported for the cyanoethylation of alcohols are alkali hydroxides [3], alkali alkoxides [4], tetraalkylammonium hydroxides [5], alkyl mercaptans, cresols, and partial pyrophosphate esters [6]. Neutralization of these soluble catalysts

prior to purification of the product generates waste and reduces the product yields. In most cases, bleaching steps are necessary for the removal of color arising from impurities. Low selectivity is an additional problem.

Anion exchange resins have been used as heterogeneous catalysts for cyanoethylation reactions [7–9]. The problem associated with use of these resins is their deactivation after a few runs probably due to the formation of polyacrylonitrile layers on the surface. Hattori and Kabashima [10] studied the cyanoethylation of alcohols over alkali metal oxides, hydroxides, carbonates, and alumina-supported KF as basic catalysts. They found that magnesium oxide is a very active catalyst for the cyanoethylation of alcohols. In the last decade, modified layered double hydroxides (LDHs) have been used and show high catalytic activity in several reactions. The hydroxyl groups on surface of Mg–Al–OH layered double hydroxides are capable of acting as Brønsted basic sites in catalytic reactions such as

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cynoethylation [11–16].

Zeolites are aluminosilicates constructed from  $\text{TO}_4$  tetrahedra (T: a tetrahedral unit built around Si and Al) with apical oxygen atoms shared with neighboring tetrahedra, and these materials have great potential as basic catalysts and catalyst supports. While tetrahedra containing  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  are attached to form a three-dimensional zeolite framework, there is a negative charge associated with each  $\text{Al}^{3+}$  atom. The negative framework charge is balanced by an exchangeable cation, achieving electrical neutrality. The basicity of ion-exchanged zeolites arises from the negative charge on the framework [17].

Two approaches have been used to create basicity in zeolites. The first method uses ion-exchange with alkali metal ions. In this method, the nature of the alkali metal affects the basic strength of the modified zeolites. The second method employs impregnation of the zeolite pores with entities that can act as bases [18,19].

In this research, we modified zeolite Y with alkali metal ions by ion-exchange and impregnation methods. Zeolite Y is a three-dimensional zeolite with large cavities present in the structure that are interconnected by 12 member ring channels, which means that there are 12 cations ( $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ ) and 12  $\text{O}^{2-}$  anions present in the ring. These structural properties made it suitable as a selective heterogeneous catalyst [20].

Prepared catalysts were studied in the cyanoethylation of aliphatic and aromatic alcohols and amines. All the reactions were carried out at ambient temperature or under reflux conditions. Correlation of the catalytic performance with the physicochemical structure of the catalysts has been carried out.

The use of microwave ovens in synthetic chemistry has recently shown rapid growth [21–33]. After the first reports of microwave-assisted synthesis in 1986 [34,35], this technique has been widely accepted as a means of reducing reaction times [36–40]. To reduce the reaction time in our case, we carried out the cyanoethylation of aliphatic alcohols with acrylonitrile under microwave irradiation in the presence of the various catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

All the reagents were used without further purification. NaY zeolite with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 5 was prepared according to published methods [41,42].  $\text{Cs}_2\text{CO}_3$  and  $\text{Mg}(\text{CH}_3\text{CO}_2)_2$  were obtained from Merck. Magnesium oxide was prepared by the decomposition of magnesium acetate at elevated temperatures under vacuum. Cs-exchanged zeolite Y was prepared from the synthesized NaY using ion-exchange with cesium carbonate solution. A total of 5 g zeolite Y was suspended in 100 mL of 0.05 mol/L  $\text{Cs}_2\text{CO}_3$  aqueous solution and stirred for 24 h at 70–80 °C. After filtration and washing twice with distilled water, the solid was dried overnight at 100 °C and then calcined at 600 °C for 4 h (catalyst A). Catalyst B was prepared in a different way by mixing NaY zeolite with  $\text{Cs}_2\text{CO}_3$  in a minimum amount of water on a steam bath. The mixture was stirred for 2 h whilst the water content remained constant.

Subsequently the mixture was allowed to dry on the steam bath. This sample was washed with a solution of methanol-water (1:1), then dried overnight at 100 °C and calcined at 600 °C for 4 h. A portion of catalyst B (0.5 g) was impregnated with a mixture of MgO (0.2 g) in ethanol (25 mL) for 15 min in an ultrasonic bath at 25 °C. The solvent was removed by evaporation under vacuum, and then dried overnight at 100 °C and calcined at 600 °C for 4 h (catalyst C). For preparation of catalyst D, the pores of catalyst A (0.5 g) were impregnated with a mixture of MgO (0.2 g) in ethanol (25 mL) for 15 min in an ultrasonic bath at 25 °C. The solvent was removed by evaporation under vacuum, after which the solid was dried overnight at 100 °C and then calcined at 600 °C for 4 h.

The cesium and magnesium contents of the catalysts were determined using an ICP-OES (Varian Vista-MPX) spectrometer. Catalysts A, B, C, and D contained 13%, 40.2%, 35.3%, and 8.5% cesium, respectively. The contents of magnesium in catalysts C and D were 9.1% and 11%, respectively.

### 2.2. Catalyst characterization

The structure and phase purity of all synthesized zeolites were monitored by powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer using  $\text{Cu K}\alpha$  radiation. The scanning range of  $2\theta$  was set between 5° and 50°.  $\text{N}_2$  adsorption/desorption isotherms were obtained at –196 °C using a BELSORP-mini II surface area measurement system after degassing the samples under vacuum at 300 °C overnight. The surface areas of all samples were calculated using the BET methodology. The surface morphology of the catalysts was obtained on a Zeiss DSM-960A scanning electron microscope (SEM) with an acceleration voltage of 10 kV.

Temperature-programmed desorption (TPD) studies of synthesized catalysts were carried out using  $\text{CO}_2$  as a probe for determining the number and strength of active basic sites.  $\text{CO}_2$ -TPD analysis was performed on a ChemBET-3000 (Quantachrome) instrument. The TPD desorption ramp of the chemically adsorbed  $\text{CO}_2$  was run from 50 to 1000 °C with a heating rate of 10 °C/min using helium as the carrier gas. The catalyst sample (0.103 g) with a particle size of 60–80  $\mu\text{m}$  was held in a plug flow quartz reactor that was coupled to a thermal conductivity detector (TCD). The catalyst samples were degassed under a nitrogen flow (10 mL/min) at constant heating rate (10 °C/min) to 500 °C and held at the final temperature for 1 h. Then, a stream of He/ $\text{CO}_2$  with a 19/1 feed ratio was passed over the catalyst bed for 20 min at 50 °C and finally flushed with helium for 1 h at 50 °C. For the determination of the identity and purity of reaction products, a mass spectrometer and a gas chromatograph (GC-MS), Agilent model 7890A with an HP-5 capillary column and an FID detector were used.

Microwave reactions were carried out using a Samsung domestic microwave oven operating at 2.45 GHz with a PTFE closed container of 15 mL capacity as the reaction vessel.

### 2.3. Reaction procedure

Different alcohols or amines (76 mmol, excess amount), ac-

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