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An epoxide ring-opening reaction by using sol–gel-synthesized palladium supported on a strontium hydroxyl fluoride catalyst



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ABSTRACT

Palladium supported on a strontium hydroxyl fluoride catalyst was synthesized by a one-pot fluorolytic sol–gel method. The prepared catalyst was characterized by various physicochemical techniques. The sol–gel method has led to the formation of a high surface area ($57 \text{ m}^2 \text{ g}^{-1}$), mesoporous (pore diameter = 13.0 nm) catalyst with uniform dispersion of Pd nanoparticles of size ~ 7 nm on the surface of strontium hydroxyl fluoride. The catalyst was used for epoxide alcoholysis, and 100% conversion was obtained with 96% selectivity for β -alkoxy alcohols under mild conditions. The catalyst could be recycled for up to three catalytic cycles without any appreciable decrease in conversion and selectivity, indicating the stability of the catalyst under the reaction conditions. Further, the mechanism of alcoholysis was proposed on the basis of the physicochemical characteristics of the catalyst and on the basis of the products formed during the catalytic reaction.

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1. Introduction

Epoxides are resourceful and vital intermediates in the organic synthesis which, undergoes ring-opening reactions to give β -substituted compounds with a variety of nucleophilic species [1]. Epoxides undergo a variety of ring-opening reactions to give β -amino alcohols [2], 1,2-diacetates [3], carbonyl compounds [4], diols [5], β -alkoxy alcohols [6], and β -alkoxy sulfides [7]. This is the convenient, practical and widely employed strategy for the

synthesis of important classes of intermediates in organic chemistry. The opening of epoxides with alcohols is one of the important transformations for the synthesis of β -alkoxy alcohols which are mainly used as valuable organic solvents, versatile synthons, and intermediates [8].

A variety of organic reactions that are catalyzed by Brønsted acids such as H_2SO_4 , HCl , HNO_3 , CH_3COOH , etc. or Lewis acids like AlCl_3 , TiCl_4 , FeCl_3 , ZnCl_2 , etc. has been gradually replaced by heterogeneous catalysts with more efficiency [9]. The conventional mineral acids or bases have been used for alcoholysis of epoxides, which resulted in the formation of polymerized products with low regioselectivity [10]. The use of conventional mineral acids in industrial processes is still widespread, leading to large amounts of inorganic waste, often imposing drastic reaction conditions.

Various catalysts have been used for this transformation including Lewis acids such as FeCl_3 [11], $\text{Cu}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$

This article is dedicated to Prof. Edmond Payen on his 60th birthday.

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[12], InCl_3 [13], $\text{Mg}(\text{HSO}_4)_2$ [14] and heterogeneous catalysts like polymer supported FeCl_3 [15] and $\text{AlPW}_{12}\text{O}_{40}$ [16]. Recently, the use of triflates $\text{Yb}(\text{OTf})_3$ [17] and perchlorates $\text{Fe}(\text{ClO}_4)_3$ [18] has been reported along with other catalysts such as Cp_2ZrCl_2 [19], $\text{K}_5[\text{CoW}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$ [20], CBr_4 [21], tin(IV) porphyrinato trifluoromethanesulfonate [22], and Amberlyst-15 [23] for the alcoholysis of epoxides. Although currently there are a number of methods available for epoxide ring opening, they have one or more disadvantages, such as a long reaction time, high catalyst loading, high reaction temperature, tedious method of catalyst synthesis, and low selectivity. However, in spite of high catalytic activity, perchlorates and triflates are less favored because of their explosive nature and high cost.

The use of harsh reaction conditions is necessary owing to poor nucleophilicity of alcohols, which led to the decrease in regioselectivity of the product [24]. Furthermore, significant and important progress has been made in the development of efficient catalytic methods which are successful under mild conditions [12,25].

The novel nanoscopic partially hydroxylated inorganic fluoride materials with bi-acidic (Lewis/Brønsted) properties were developed for catalytic applications [26]. The materials were synthesized using classical sol–gel route from metal alkoxide via fluorination with aqueous/non-aqueous HF which led to high surface area metal fluorides [27]. These types of catalysts have been already applied successfully for various catalytic applications viz. synthesis of (all-*rac*)-[α]-tocopherol [28], Friedel–Crafts reaction [29], Suzuki coupling reaction [30], synthesis of menthol [31], synthesis of vitamin K-1 and K-2 chromanol [32], oxidation of ethylbenzene [33], dehydrohalogenation of 3-chloro-1,1,1,3-tetrafluorobutane [34], catalytic C–H bond activation [35] and glycerol acetylation [36].

Recently the palladium supported catalyst was used for phenolysis of epoxides at a high temperature in the presence of bases [37]. The Pd supported on alkaline earth metal fluoride is known for its dual (acidic/basic) properties. These properties play an important role in determining not only the activity but also the selectivity of the catalytic reactions. Therefore the study of synthesis and characterization of palladium supported strontium fluoride and its catalytic activity for alcoholysis of epoxides has been carried out and the results are presented in this article.

2. Experimental

2.1. General

All chemicals were procured from Aldrich Chemical Co., USA and used as received. Hydrofluoric acid (71% aq. solution) and solvents were procured from Merck Chemicals, Germany and used as obtained.

2.2. Catalyst synthesis

Cautions:

1. HF is a highly toxic and irritant compound causing severe burns if it comes in contact with the skin.

2. Strontium is highly reactive with methanol to generate hydrogen hence the rate of reaction needs to be controlled by keeping the reaction flask in an ice bath.

Catalyst preparation was carried out under an inert atmosphere of argon using a standard Schlenk technique. In a 250 mL round bottom flask, metallic strontium (2.103 g, 24 mmol) was treated with dry methanol (300 mL) at room temperature for 16 h in a Schlenk flask to form strontium methoxide solution. A stoichiometric amount (Sr/F: 1/2) of 71% aqueous solution of hydrofluoric acid (5.3 mL, 48 mmol) was added to the solution of strontium methoxide followed by the addition of alcoholic solution of palladium acetate (0.630 g, 1 wt % loading of Pd metal, dissolved in 15 mL of methanol). This solution turned into a gray colored gel which was kept for 16 h for aging. Then the gray gel was dried under vacuum at room temperature and 70 °C to remove solvents (methanol and water). The solid product was further calcined at 250 °C for 5 h. The prepared catalyst is referred hereafter as Pd-SrF₂-71 indicating 71% aqueous concentration of HF used for synthesis.

Similarly, other fluoride based catalysts Pd-MF₂-71 (where, M = Mg, Sr, Ba) were also prepared for comparison of catalytic activity.

2.3. Catalyst characterizations

The Pd-SrF₂-71 was characterized using various physicochemical techniques as mentioned below.

2.3.1. Powder X-ray diffraction (PXRD) analysis

Crystallinity and phase purity of the samples were determined using powder X-ray diffraction (PXRD) analysis. Powder patterns were recorded on an X'pert Pro PANalytical X-ray diffractometer with Ni-filtered Cu-K α radiation (40 kV, 30 mA) in the 2 θ range of 10–80° at a scan rate of 4 min⁻¹ on the glass substrate.

2.3.2. FTIR spectroscopy

A Nicolet Nexus 670 FTIR instrument with a DTGS detector was used to record the IR spectrum of the catalyst in the range 4000–400 cm⁻¹ with a KBr pallet technique in transmission mode. The data were collected at 4 cm⁻¹ resolution averaged over 100 scans.

2.3.3. BET surface area measurements

The specific surface area (BET) of the sample was determined by acquiring adsorption–desorption isotherm (BET method) at 77 K for nitrogen gas using a Autosorb Quanta Chrome corporation instrument. The micropore volume was estimated from the t-plot and the pore diameter was estimated using the Barrett–Joyner–Halenda (BJH) model.

2.3.4. Ammonia-temperature programmed desorption (NH₃-TPD) analysis

NH₃-TPD measurements were performed on a Micromeritics AutoChem 2910 instrument. In a typical experiment, 0.1 g of the catalyst was taken in a U-shaped, flow-thru, quartz sample tube. Prior to measurements, the

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