Chemical Engineering Journal 309 (2017) 663–673

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Facile synthesis of dicamba ester over heterogeneous magnesium oxide and kinetic modelling

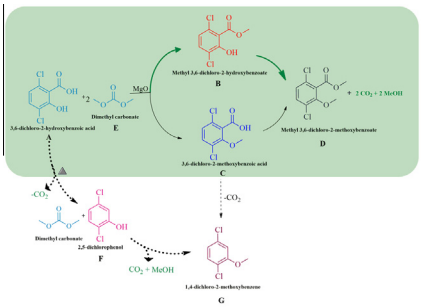
Gunjan P. Deshmukh, Ganapati D. Yadav *

Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400019, India

HIGHLIGHTS

- Solvent free synthesis of dicamba ester.
- MgO as best heterogeneous base catalyst.
- Study O-alkylation for different heterogeneous catalyst.
- Study of reaction mechanism and formation of product.
- Development of kinetic model by LHHW method.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form 5 October 2016
Accepted 8 October 2016
Available online 11 October 2016

Keywords:
Dicamba (3,6-dichloro-2-methoxy benzoic acid)
Herbicide
Solid base catalyst
MgO
Kinetics

ABSTRACT

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is one of the widely used herbicides. Methyl 2-methoxy-3,6-dichloro benzoate (Dicamba ester) is a key intermediate which upon hydrolysis forms dicamba. For the first time esterification as well as etherification of 3,6-dichloro-2-hydroxybenzoic acid (3,6-dichlorosalicylic acid) was studied to achieve dicamba ester as a product using dimethyl carbonate (DMC) as methylating agent as well reaction solvent and MgO as catalyst. Reaction proceeds through the formation of two intermediates, namely, methyl 3,6-dichloro-2-hydroxybenzoate (3,6-Dichlorosalicylate) and dicamba. DMC has emerged as green reagent substituting other alternatives like methyl halide and dimethyl sulphate. Different heterogeneous base catalysts were synthesized and their activity and selectivity studied in the formation of dicamba ester. Calcinated hydrotalcite (CHT), calcinated hydrotalcite supported on hexagonal mesoporous silica (CHT-HMS), ZrO_2, Al_2O_3 and MgO were used for this reaction. Combustion synthesized MgO (CS-MgO) was found to be the best catalyst for this reaction. Activity and selectivity of CS-MgO catalyst were excellent. The catalyst was characterised completely with FTIR, DCS-TGA, SEM, TPD, BET and XRD. Reaction proceeds through formation of two intermediates, finally leading into formation of dicamba ester. Reaction mechanism and kinetics were studied to throw light on the exact path of product formation. The catalyst was found reusable with constant activity and selectivity. The overall process is simple and green using active, selective and reusable catalyst with nontoxic alkylating reagent.

1. Introduction

Dicamba (3,6-dichloro-2-methoxy benzoic acid) is commonly used herbicide all over the world. It selectively kills or controls the weed. Dicamba mimics naturally occurring plant growth

* Corresponding author.
E-mail addresses: gdyadav@yahoo.com, gd.yadav@ictmumbai.edu.in (G.D. Yadav).

http://dx.doi.org/10.1016/j.cej.2016.10.037
1385-8947/

Nomenclature

A	reactant species A, 3,6-dichlorosalicylic acid	E	dimethyl carbonate
B	3,6-dichlorosalicylate	F	2,6-dichloro phenol
C	dicamba (3,6-dichloro-2-methoxy benzoic acid)	G	1,4-dichloro methoxy benzene
C_A	concentration of A, (mol/L)	k_1	rate constant for reaction step 1 [L^2/(mol.s.g-cat)]
C_B	concentration of B (mol/L)	k_2	rate constant for reaction step 2 [L^2/(mol.s.g-cat)]
C_C	concentration of C (mol/L)	k_3	rate constant for reaction step 3 [L^2/(mol.s.g-cat)]
C_D	concentration of D (mol/L)	k_4	rate constant for reaction step 4 [L^2/(mol.s.g-cat)]
C_E	concentration of E (mol/L)	r	rate of reaction (mol/L.s)
D	dicamba methyl ester	*w*	catalyst loading(g/cm^3)

hormone called Auxin. Different salts of dicamba are used in herbicidal formulation [1,2]. Alkylation of phenols and aromatic acids is widely practiced reaction in organic synthesis of petrochemicals, fine chemicals, agrochemicals and pharmaceuticals [3]. Dimethyl carbonate (DMC) has been extensively used in chemical reactions as methylating reagent and solvent. Environmentally benign properties of DMC makes it an easy and popular choice as a methylating agent [3–21]. The co-products, CO_2 and MeOH could be reused to form DMC again in an industrial process. DMC behaves as methylating reagent at more than 120 °C reaction temperature and carboxymethylating agent at 90 °C [5]. In methyl esterification and etherification reaction; methyl halides, dimethyl sulphate and diazomethane are generally used as methylating reagents. These reagents are unsafe to handle. Such reactions have been catalysed by acids (e.g. H_2SO_4, HCl) and bases (NaOH, KOH) which are used in stoichiometric amount and generate hazardous waste and dissolved solids after neutralization of reaction mixture to separate the product.

Several reactions have been reported for aromatic alkylation using DMC over heterogeneous solid acid catalysts [9–12], solid base catalysts [13–17] and phase transfer catalysts [18–21].

According to previous reports, 3,6-dichloro salicylic acid undergoes two parallel reactions, namely, esterification and etherification forming 3,6-dichloro salicylate (methyl 3,6-dichlor o-2-hydroxybenzoate)and dicamba intermediate, respectively. These two intermediates further undergo etherification and esterification to form dicamba ester as final product. Dhakshinamoorthy et al. [15]. have reported partial alkylation leading to 47% esterified product and 41% etherified product. Some of the papers with zeolite based catalyst have reported C-alkylation. Decarboxylation of salicylic acid was reported in some papers [22,23].

Combustion synthesis (CS) is a simple and quick method for synthesis of nano crystalline material as has been studied in our laboratory [24–29]. Thus it was decided to study nanocrystalline MgO prepared by CS method for this reaction.

The aim of this current work was to develop a simple and green process using active, selective and reusable catalyst with nontoxic alkylating reagent. Herein for the first time we report the alkylation of 3,6-dichlorosalicylic acid using CS-MgO as heterogeneous base catalyst and DMC as alkylating agent in solvent free condition to synthesize dicamba ester.

2. Experimental section

2.1. Chemicals and catalysts

Solvents and reactants were purchased from reputed suppliers and used without purification. 3,6-dichloro salicylic acid (Coiner Chem. and Pharma, China), DMC (SD fine Chemicals, Mumbai, India), magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, zirconium nitrate, glycine (Thomas baker chemicals Ltd, Mumbai, India).

2.2. Preparation of catalyst

2.2.1. Preparation of MgO by combustion synthesis method (CS-MgO)

Nanocrystalline CS-MgO was prepared by combustion synthesis technique [26]. In a beaker, calculated amounts of magnesium nitrate hexahydrate and glycine were dissolved in water to get a clear solution Oxide (magnesium nitrate hexahydrate) to fuel (glycine); 1:2 mol ratio was used to prepare this solution. Further the solution was transferred into crucible and water was evaporated to get a viscous gel. Meanwhile the furnace was heated at 350 °C and this viscous gel was quickly transferred to a furnace at 350 °C. This resulted in rapid dehydration of the solution with smoldering combustion giving rise to blackish material which was further calcinated at 550 °C for 5 h to remove unwanted carbon. White fleecy powder was obtained after complete calcination. Similarly different metal oxides of Al, Zr were synthesized by fuel rich combustion technique. Calcinated hydrotalcite (CHT) and calcinated hydrotalcite supported on hexagonal mesoporous silica (CHT-HMS) were synthesized by established method in our laboratory [30].

2.3. Reaction procedure

All the reactions were done in an autoclave previously used in our laboratory [17]. 3,6-Dichloro salicylic acid (0.0072 mol), DMC (28 cm^3) and CS-MgO (0.02 g/cm^3) were charged in autoclave. The reaction mixture was heated to a known temperature and zero minute sample was taken before turning on the agitation at a known speed. Samples were carefully withdrawn periodically for analysis. Reaction of 3,6-dichlorosalicylic acid with DMC to give dicamba via two intermediates is shown in Scheme 1.

2.4. Method of analysis

The reaction was monitored using HPLC. Samples were analyzed on Agilent 1260 infinity HPLC system (auto-sampler G1329B, pumps G1311C diode array detector G1315D) using carbowax C18 column. All the intermediates and products were confirmed by GCMS (Perkin Elmer, Clarius Model 500 on elite 1 capillary column of length 30 m and inner diameter 0.25 mm). The progress of the reaction was based on the consumption of the limiting reactant; 3,6-dichlorosalicylic acid. The details of HPLC analytical method are given in Supplementary information.

2.5. Method of catalyst characterization

The surface properties of all catalysts including reused catalyst were evaluated by Micromeritics ASAP 2000 instrument by using nitrogen adsorption–desorption isotherms. Fresh and reused catalyst samples were degassed at 350 °C under vacuum for 4 h. A Fourier transform infrared spectra of all catalysts along with recycled catalyst were recorded on a Perkin Elmer Spectrophotometer in the range of 400–4000 cm^{-1}. All sample pellets were prepared