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Insight into regioselective hydrogenation of methyl phenyl glyoxalate to methyl mandelate over Pt/α-MnO_2 nanorods

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MnO_2 as a material possesses several applications in environmental chemistry, electrochemistry, adsorption chemistry, heterogeneous catalysis, etc. In this work different polymorphs of MnO_2 (α, β, γ and δ) were synthesized by hydrothermal synthesis and their compatibility as a support for hydrogenation of methyl phenyl glyoxalate to methyl mandelate was studied. These polymorphs appeared in different shapes like nanorods, nanofibers, spines and urchin like. All catalysts were defined and characterised using different technique such as DSC-TGA, FTIR, SEM, TEM, XRD, TPD, TPR and BET. The activity of all catalysts was tested for regioselective liquid phase hydrogenation of methyl phenyl glyoxalate (MPG). Among all catalysts α-MnO_2 (cryptomalene phase) was the best support for loading platinum metal. Different Pt loadings were studied, i.e. 1 %, 2.5 % and 5 % (w/w). 1 % platinum loading was found to be optimum. The catalyst was active, selective and reusable. A plausible reaction mechanism is presented and kinetic model developed. The activation energy was found 19.7 kcal/mol.

1. Introduction

Since many years, different polymorphs: α, β, γ and δ-MnO_2 (x-MnO_2) have gained special attention. MnO_2 exists in several shapes and crystallographic forms having different applications such as catalysis [1–4], molecule adsorption [5,6], electrochemical industry [7], photo electrochemical [8], magnetic materials [9,10] and membrane synthesis [11,12]. Tailor made crafting of various polymorphs can be done varying the synthetic conditions such as temperature [13,14], types of reactants and their concentrations [15] and time [16]. Literature is obscure on the exact formation of phase, crystal structure and its formation. Little efforts are made to predict the crystal size and shape using different cationic precursors [15]. Several methods for synthesis of x-MnO_2 are reported such as co-precipitation [17], sol-gel method [18], sonochemical [19], reflux [20,21], milling [22], solid state reaction [23], ultrasonic synthesis [24], hydrothermal synthesis [13,25–28] and microwave assisted hydrothermal synthesis [29,30]. Hydrothermal synthesis has emerged as a versatile technique in advanced material synthesis and this technique was used to synthesize the different polymorphs of MnO_2 nanorods.

Orito reaction is widely studied using homogeneous catalysis: ruthenium complexes [31], nonaborane [32], rhodium and palladium based complexes [33] and enzyme catalysis; $Mg(ClO_4)$ and NADH [34,35]. The reaction is widely studied with heterogeneous catalysis in continuous as well as batch process using 5 % Pt/Al_2O_3, combining it with different chiral modifiers [36–39]. A report is also available on $Pt/SiO_2/Fe_2O_3$ [40].

MnO_2 is widely used as an oxidation catalyst for different reactions [20,26,29,41], but very few reports are available on hydrogenation using MnO_2 as catalyst support. Our lab has reported different reduction reactions using octahedral molecular sieves (OMS) as support [4,41–43] . DFT studies have shown that Mn and O atoms present on the surface of MnO_2 help in dissociation of H_2 [44]. Thus low loading of Pt can also facilitate hydrogenation reaction. The enantiomers of methyl mandelate have several advantages [45,46]. The racemisation of methyl mandelate is also reported in our lab [47].

Abbreviations: A, reactant species A, Methyl phenyl glyoxalate; AS_1, chemisorbed species A; C_A, concentration of A (M); C_B, concentration of species B (M); C_{AS_1}, concentration of A at catalyst surface, (mol/g-cat); C_{HS_2}, concentration of hydrogen at catalyst surface, (mol/g-cat); p_{H_2}, partial pressure of hydrogen, (MPa); C_{S_1}, concentration of vacant acidic sites, (mol/g-cat); C_{S_2}, concentration of vacant metallic sites, (mol/g-cat); C_{T_1}, total concentration of acidic sites, (mol/g-cat); C_{T_2}, total concentration of metallic sites, (mol/g-cat); $H.S_2$, chemisorbed hydrogen(mol/g-cat); k_1, reaction rate constant, (mol g-cat^{-1} s^{-1}); K, equilibrium constant for the adsorption of different species (M^{-1}); K_H, equilibrium constant for the adsorptionof hydrogen (MPa^{-1}); M, mol/L; $-r_A$, rate of surface reaction of A (mol L^{-1} s^{-1}); S_1, active acidic site; S_2, active metallic site; w, catalyst loading (g/L).

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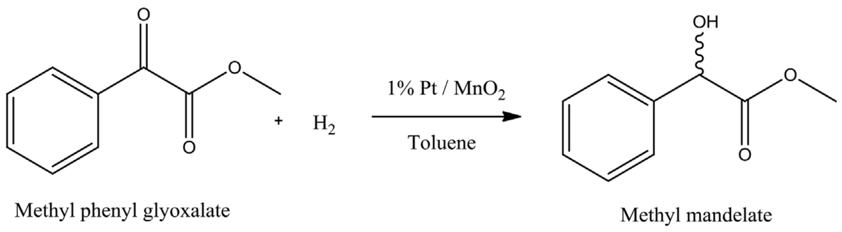

Scheme 1. Hydrogenation of MPG over 1% Pt/MnO_2 to methyl mandelate.

Current study emphasizes development of new catalytic system (Pt/MnO_2) with different platinum loading, wherein platinum loading was studied for 1, 2.5 and 5 % supported on α-, β-, γ- and δ-MnO_2. The best metal support combination: 1% Pt/α-MnO_2 was studied for selective hydrogenation of methyl phenyl glyoxalate (MPG) to give methyl mandelate. The kinetic model is developed to calculate rate constants and activation energy.

2. Experimental

2.1. Chemicals and catalyst

All the chemicals were purchased from reputed vendors and used as received. Methyl phenyl glyoxalate was purchased from Merck (India): toluene, potassium permanganate, manganese sulphate monohydrate and acetonitrile (HPLC grade) were purchased from Thomas Baker, Mumbai, India and potassium persulphate, hexachloro-palatinate and ortho phosphoric acid (HPLC grade) were purchased from S D fine chemicals, Mumbai.

2.2. Catalyst preparation

Polymorphs of MnO_2 were prepared using different combinations of precursors, concentration and temperature (Table 1). Temperature has a pivotal role in formation of different polymorphs. In typical generalised methods of preparation, precursors and distilled water were taken in Teflon-lined hydrothermal stainless steel reactor to get clear solution and the reactor was sealed tightly. This reactor was kept in oven at required temperature for specific period of time and thereafter cooled to room temperature to obtain wool like MnO_2 suspension. This suspension was filtered and washed with distilled water several times. It was dried at 120 °C for 24 h.

2.3. Loading of Pt metal

1 % w/w platinum was supported on different polymorphs of MnO_2 by wet impregnation method [45]. Well dispersed heterogeneous solution of MnO_2 and water were prepared in beaker on magnetic stirrer. Homogeneous solution of $H_2PtCl_6.H_2O$ was prepared separately to add dropwise in above solution of nanorods. This solution was stirred for 6 h and excess water was evaporated at 60 °C. The remained mass was dried at 120 °C. Further the catalyst was reduced in dry ethanol using hydrazine hydrate at 25 °C. The catalyst was filtered, dried under vacuum and stored in sealed bottle.

2.4. Reaction procedure

All the reactions were done in an autoclave (Amar Equipments, Mumbai) equipped with 45° inclined-four bladed-pitched-turbine-impeller, digital pressure sensor, temperature controller, and speed regulator (±5 rpm). MPG (0.0012 mol), toluene (30 ml) and 6 mg/cm^3 (0.2 g) of catalyst were charged in autoclave. Reaction mixture was flushed with N_2 for three cycles to remove traces of air and then H_2 pressure (1.5 MPa) was applied. This reaction mixture was heated to optimized temperature and zero minute sample was taken before turning on the agitation. Samples were withdrawn for analysis in certain time frame. Hydrogenation reaction of methyl phenyl glyoxalate is given in Scheme 1.

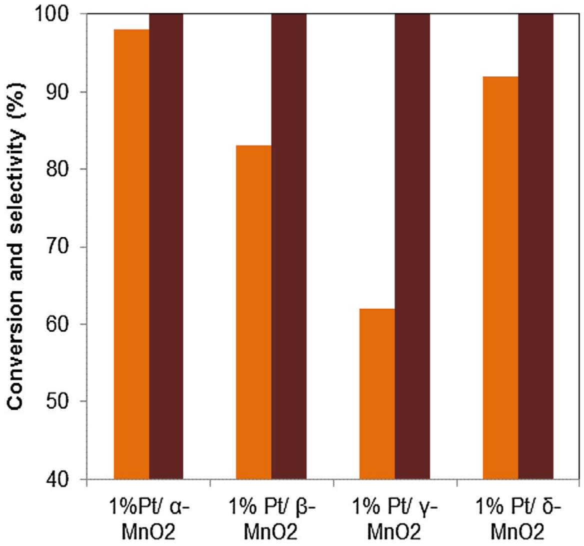

Fig. 1. Conversion and selectivity of MPG for 1% Pt/x-MnO_2 🟩 Conversion 🟫 Selectivity.

2.5. Method of analysis

Progress of reaction was analyzed by HPLC. Sample mixtures were analyzed on Agilent 1260 infinity HPLC system (auto-sampler G1329B, pumps G1311C diode array detector G1315D) using carbowax C18 column. Mobile phase composition was 90 % hexane: 10 % isopropyl alcohol (v/v). Flow rate was 1 ml/ min at 25 °C column temperature.

3. Results and discussion

3.1. Efficacy of different Pt supported polymorphs

All the catalysts supported with 1 % Pt were screened for hydrogenation of MPG. Each catalyst shows varied activity towards hydrogenation with constant selectivity (Fig. 1). The surface properties of each polymorph change with their phase structure and so the reaction was governed by combined effect of surface area, crystallite size, phase stability and acidic sites present on the surface of catalyst. All these properties are well explained in catalyst characterization further. The order of conversion of MPG at the same reaction conditions (MPG: 0.008 g/cm^3, H_2 pressure: 1.5 MPa, catalyst loading: 0.008 g/cm^3, temperature: 120 °C, toluene: 25 cm^3, time: 180 min) is given as 1% Pt/α-MnO_2 > 1% Pt/δ-MnO_2 > 1% Pt/β-