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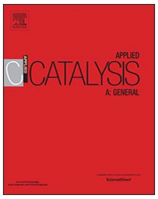

Feature Article

Oxidative esterification of furfural by Au nanoparticles supported CMK-3 mesoporous catalysts

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ABSTRACT

Furfural which is derived from the hemicellulose fraction of abundant lignocellulose has received significant attention to many researchers as its valorization yields useful products such as fine chemicals and transportation fuels. Methyl 2-furoate is one of the important valorized products of furfural as it finds applications in flavor and fragrance industries. Methyl 2-furoate is generally obtained by oxidation followed by esterification of furfural but under acidic and corrosive conditions. Uniform rods of CMK-3 mesoporous materials were successfully synthesized by using nanocasting method. Au nano particles were impregnated into the pores of CMK-3 by wet impregnation method followed by hydrogen reduction at high temperature (673 K). All the catalysts were thoroughly characterized by various analytical techniques. Homogeneous dispersion of Au nano particles ≈3 nm size was found over CMK-3 materials. Qualitative and quantitative analyses of Au were made by XPS and ICP techniques. The effect of impregnating metal ions (Ni, Pt and Pd) and supports (SBA-15, graphite, graphene, MWCNT, activated carbon and $TiO_{2)}$ was studied on the catalytic conversion of furfural. Among them, Au/CMK-3 catalyst was found to be the best. Among the Au/CMK-3 catalysts, 5% Au/CMK-3 catalyst showed remarkable conversion of furfural (99.7%) with very high selectivity towards methyl 2-furoate (99.6%). The stability and reusability of the 5% Au/CMK-3 catalyst was found to be very good even after five catalytic cycles.

1. Introduction

There is a great demand for the ordered porous materials in the area of heterogeneous catalysis, adsorption, drug delivery and electronics [1–4]. Among the ordered materials ordered mesoporous silica (OMS) and ordered mesoporous carbon (OMC) are of great interest and hence the catalyst world has seen several ordered mesoporous materials synthesized by using different soft and hard templates. The first one in the group was M41S series synthesized by Kresge et al. in the year of 1990 [5,6]. These mesoporous silicates have uniform pore size (2–10 nm) with long range ordered nanochannels, high surface area ($> 2000\ m^2/g$) and the adjustable periodicity. To suit different applications, these OMS materials were modified either in the framework with the introduction of hetero elements or surface modification through silanol groups. A detailed information regarding the synthesis, characterization and applications of these various ordered mesoporous silica (OMS) series are found in various literature reviews [7–9]. Among the OMS materials, SBA-15 with hexagonal mesostructure synthesized by using triblock polymer has been studied extensively due to its tunable pore size (4–14 nm) [10].

Similarly ordered mesoporous carbons (OMC) are another group of fascinating carbon materials. They are highly ordered with uniform array of mesopores. Ordered mesoporous carbons (OMC) are generally prepared using ordered mesoporous silica (OMS) as template. Ryoo et al. synthesized one such material using MCM-48 as template in the year of 1999 and it is referred as CMK-1 [11]. OMC materials with tunable pore size, controllable pore structure, surface area, high pore volume, conductivity and stability are generally synthesized by nanocasting method [12,13]. Due to these unique properties of OMC, number of environmental friendly low cost energy storage and conversion devices have been developed. Apart from these applications, these materials also find greater use in the area of catalysis and gas separations. Generally the synthesis of OMC involves stepwise impregnation of carbon precursor (monomer, polymer, etc.) in the pores of mesoporous silica materials to get desired silica to carbon ratio [14]. The precursor within the pores are polymerized and carbonized in the pore structures resulting in the formation of carbon-silica composites. The resulting composite is washed with aq.HF to remove silica template to yield CMK-n. A large variety of OMC with different mesostructures such as CMK-1(MCM-48, cubic *Ia3d*) [15], CMK-2 (SBA-1, cubic *pm3n*)

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[16], CMK-3(SBA-15, rod type *p6mm*) [17–20], CMK-4 (MCM-48, *Ia3d*) [21], CMK-5 (SBA-15,tube type *p6mm*) [22], OMC(SBA-16, cubic *Im3m*) [23] and CMK-8 (KIT-6, rod type) [24] were prepared by nanocasting method using various carbon precursors such as sucrose, phenolic resins, furfural alcohol, acenaphthene and acetonitrile [19,22,25–28]. CMK-3 has been used as a support for various transition metals for carrying out a variety of catalytic transformations. Suzuki coupling by Pd/CMK-3, reduction of nitrobenzene and carbonyl compounds over Ru/CMK-3, hydrogenation of carbonyl compounds over Ni/CMK-3, oxidation of alcohols and conversion of amines to imines over FeO_x/CMK-3, aqueous phase reforming of glycerol and ethylene glycol over Pt/CMK-3, etc. have been reported [29–41]. Only scarce attempts such as base free oxidation of glucose to gluconic acid and catalytic reduction of *p*-nitrophenol into *p*-aminophenol were reported by using Au/CMK-3 [42,43].

Herein we report the catalytic activity of Au/CMK-3 in the oxidative esterification of furfural. Furfural is a platform chemical from which number of medicines, pesticides, paints, plastics, commodity chemicals and solvents etc. have been prepared [44]. At present the global production of furfural derivatives is at 947.58 k t (2016) and the demand will grow at a compound annual growth rate (CAGR) of 2.69% to reach 1,172.17 k t by 2024 [45]. Hence furfural is produced in large amounts from the biomass lignocellulose and such biomass is the subject of interest to many researchers [46]. Several fine chemicals such as furfural alcohol, 2-methyl furan, furoic acid, tetrahydrofuran (THF), cyclopentanol, cyclopentanone, 2-methyl tetrahydrofuran, polytetrahydrofuran, tetrahydrofurfuryl alcohol, etc. are also derived from furfural [47]. Recently furfural has been upgraded into gasoline and diesel fuels using efficient catalytic technologies [48]. One of the authors converted several biomasses into green fuels and the present authors have already reported the catalytic activities of Au-Pd/HAP-T and Au-Ag/HAP-T bimetallic catalysts towards the oxidative esterification of furfural [49–53]. The author performed this reaction using TBHP and air or O_2 at atmospheric pressure. However the present paper deals mainly with molecular O_2 or air at different pressures. Increase in pressure of O_2 increases the conversion and selectivity. Further the reaction was performed with O_2 at different pressures without using additional oxidants such as TBHP.

Any valorization process will be economically and environmentally attractive only when it is carried out under mild reaction conditions using non-corrosive reagents. Furfural can also be valorized into methyl 2-furoate which finds application in fine chemicals, flavor and fragrance industries [54]. As the conventional method of obtaining methyl 2-furoate uses strong oxidizing agent such as $KMnO_4$ and followed by esterification using concentrated sulphuric acid in methanol medium it causes harm to the environment. The other method of obtaining methyl 2-furoate also involves the strong bases such as NaOH, $CH_3O^-Na^+$, K_2CO_3, Li_2CO_3, $CsCO_3$ etc. but it is not an environmental benign method [55,56]. Only scarce attempts have been made on the oxidative esterification of furfural to methyl 2-furoate without using bases [57–62]. So herein we report the synthesis and characterization of Au/CMK-3 catalysts and the conversion of furfural to methyl 2-furoate with and without the use of various bases and oxidants (TBHP, air and O_2).

2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS, Merck), non-ionic triblock copolymers (P123, Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (MW-5800); $EO_nPO_mEO_n$, Sigma Aldrich) and HCl (37%, Sigma Aldrich) were used for the synthesis of SBA-15. Autoclavable PP bottles (Nalgene) were used for the hydrothermal preparation of SBA-15. Glucose as a carbon source (SRL) and sulphuric acid (98%, Sigma Aldrich) as a catalyst were used for the preparation for CMK-3. Gold chloride ($AuCl_3{\cdot}3H_2O$, 99.9%) purchased from Sigma Aldrich was used as a gold precursor. MWCNT (10 nm × 4.5 nm × 36 μm, Sigma Aldrich) and activated carbon (Alfa Aesar) were used as such. Graphite flakes were purchased (Natural–325 mesh, Alfa Aesar) and used for graphene synthesis. TiO_2 was synthesized by sol-gel method from titanium-isopropoxide (Sigma Aldrich).

2.2. Synthesis of mesoporous SBA-15 via hydrothermal method

Mesoporous silica SBA-15 with gel composition 1 TEOS: 5.87 HCl: $194H_2O$: 0.017 P123 was synthesized using the silicon source tetraethylorthoslicate (TEOS) and structure directing agent Pluronic P123 in a highly acidic medium [7]. In a PP bottle, 4 g of triblock-copolymer, 130 ml of water and 20 ml of concentrated HCl were added and stirred for 2 h for complete dissolution and the temperature was maintained at 318 K. The silica source tetra ethylorthosilicate (TEOS) was then added directly to the above solution with constant stirring maintaining the above temperature for 24 h. The white suspension resulting was autoclaved at 318 K in an air oven for 24 h and cooled. The resultant white suspension was centrifuged, washed with water and dried at 393 K for 12 h. The white material formed was ground and calcined at 823 K for 6 h for the complete removal of the templates and to obtain mesoporous SBA-15 material.

2.3. Synthesis of mesoporous CMK-3 carbon via nanocasting method

In the typical synthesis of mesoporous CMK-3, SBA-15 was used as a hard template. In order to ensure complete polymerization and carbonization, sucrose coatings were done twice as reported by us [63,64]. To 1 g of the SBA-15 material, 1.25 g of sucrose, 0.1 g of concentrated H_2SO_4 and 5 ml of deionised H_2O were added and stirred until thick slurry was formed. Then it was dried in an air oven at 383 K for 6 h and carbonized at 433 K for another 6 h. The obtained brown material was finely ground and used for the second coating of the sucrose precursor. To the above brown mixture, 0.8 g of sucrose, 0.08 g of conc.H_2SO_4 and 5 ml of deionised H_2O were added, and the same procedure was repeated. The black mass obtained was ground and finally carbonized at 1173 K for 6 h under the flow of N_2. The carbonized material was then stirred with 5% HF solution for 12 h and washed with ethanol to obtain the nanoporous carbon CMK-3.

2.4. Synthesis of mesoporous Au/CMK-3 catalysts via high temperature H_2 reduction

In the typical synthesis, 1 g of CMK-3 was dispersed in 20 ml of acetone and stirred for 5 min. Then yellow colored $HAuCl_3$ solution (0.05 mM) was added and stirred for 2 h. A transparent solution obtained indicates that the Au^{3+} ions were adsorbed onto the nanoporous carbon. The resulting solution was dried at 383 K and reduced under the flow of hydrogen (30 ml/min) at 673 K for 3 h to get 1% Au/CMK-3 (w/w) nanocatalyst. Similarly by varying the amount of gold stock solution, 3%, 5% and 7% of Au/CMK-3 (w/w) nanocatalysts were obtained.

2.5. Synthesis of other catalysts

Graphite oxide (GO) was synthesized from graphite powder via modified Hummer's method and the method reported by us earlier [65]. Then it was ground, dispersed in ethanol and sonicated for 30 min. To this, gold precursor was added and sonicated for another 15 min. For drying, calcination and reduction the procedure described for CMK-3 was adopted. Nano titanium dioxide (TiO_2) was synthesized using sol-gel method as reported by us earlier [66]. MWCNT and activated carbon were used as such without any modification. All these materials were impregnated with 5% Au by following the same procedure given in Section 2.4.