Bull. Chem. Soc. Ethiop. **2011**, 25(1), 147-150.
Printed in Ethiopia

ISSN 1011-3924

SHORT COMMUNICATION

SYNTHESIS OF TRIBUTYL CITRATE USING SO_4^{2-}/Zr-MCM-41 AS CATALYST

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(Received March 15, 2010; revised October 4, 2010)

ABSTRACT. Zirconium-containing mesoporous molecular sieve SO_4^{2-}/Zr-MCM-41 was synthesized for catalyst in synthesis of tributyl citrate. The structure was characterized by XRD, N_2 Ad/De isotherms and FT-IR. The results indicated that the solid acids show good catalytic performance and are reusable. Under optimum conditions and using SO_4^{2-}/Zr-MCM-41 as catalyst, the conversion of citric acid was 95%. After easy separation of the products from the solid acid catalyst, it could be reused three times and gave a conversion of citric acid not less than 92%. The structure of tributyl citrate was characterized by FT-IR and ^{1}H-NMR.

KEY WORDS: Mesoporous molecular sieve, Tributyl citrate, Synthesis

INTRODUCTION

Tributyl citrate (TBC) is a high boiling point substance used as a solvent and plasticizer [1] for polymers, especially for PVC and its copolymers subsequently applied to food wrapping film. Among the advantages of tributyl citrate is that it is stable at high temperature and does not discolour when processed into compound resins. It is a plasticizer permitted in the field of food additives, food contact materials and medical products and is widely used in cosmetics [2] and biodegradable polymers [3]. Moreover, TBC is an environmentally, friendly plasticizer because the materials used for synthesis are available from renewable resources by fermentation processes.

The traditional catalysts used in the synthesis of TBC were mainly sulfuric acid and titanate [4]. The sulfuric acid cannot be reused and has other disadvantages, such as corrosion of equipment, additional by-products, tedious workup procedure and environmental problems. The titanate also has the disadvantages like higher cost, difficult separation from products and high energy consumption.

In this paper, Zr-MCM-41 was synthesized by the hydrothermal method using cetyltrimethyl ammonium bromide (CTAB) as a template. SO_4^{2-}/Zr-MCM-41 solid acid catalyst was prepared by impregnation with a solution of H_2SO_4, and the activity of the catalyst was investigated using the esterification reaction of citric acid and butanol. Under optimum conditions and using SO_4^{2-}/Zr-MCM-41 as catalyst, the conversion of citric acid was 95%. After easy separation of the products from the solid acid catalyst, it could be reused three times and gave a conversion of citric acid not less than 92%. The structure of tributyl citrate was characterized by FT-IR and ^{1}H NMR.

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EXPERIMENTAL

Chemicals and instruments. All chemicals (AR) were commercially available and used without further purification unless otherwise stated. Surface area and pore-size distributions were obtained by nitrogen adsorption on a Micromeritics ASAP 2020M instrument (USA) at an adsorption temperature of -196 ^{o}C. Prior to a measurement, the sample was degassed to 10^{-3} Torr at 473 K. The method of Brunauer, Emmett and Teller (BET) was used to determine the surface area. The method of Barrett, Joyner and Halenda (BJH) along with the Halsey equation for nitrogen was used to calculate the mesopore size distributions from the nitrogen-adsorption isotherms [5]. X-ray powder diffraction patterns of the samples were obtained on a X'TRA instrument (ARL, Switzerland) using monochromatic Cu Kα radiation scanning 2θ angles ranging from 1.0 to 15 degree. IR spectra were obtained using a MAGNA-IR 550 spectrophotometer (USA). ^{1}H-NMR spectra were recorded in DMSO on a Bruker AV-500 (Germany) spectrometer operating at 500 MHz.

Catalyst preparation. Zr-MCM-41 was synthesized by hydrothermal method. The mole ratio of reactants was $0.05Zr(SO_4)_2 : SiO_2 : 0.67Na_2O : 0.20CTMABr : 102H_2O$, following the procedure reported in the previous paper [6].

General procedure for synthesis of TBC. Weighed amounts of citric acid (0.1 mol), butanol and catalyst (5%) were added to a flask with a reflux condenser, a water segregator and magnetic stirrer. The esterification reaction was typically carried out for 2-6 h at the desired temperature with vigorous stirring. After the reaction, the unreacted butanol was recovered by distillation. Then the reaction mixture separated into two phases. The upper phase, which was mainly the desired TBC, could be isolated simply by decantation; the lower phase, solid acid catalyst, could be reused. Conversion data were based on citric acid measurements using the NaOH titration data.

RESULTS AND DISCUSSION

Optimum reaction conditions for synthesis of TBC. The optimum reaction conditions were examined and the results obtained are given in Table 1.

Table 1. Synthesis results of TBC under different reaction conditions.

Reaction time (h)	Catalyst amount (%)	n(citric acid) : n(butanol)	Conversion (%)
2	5	1:6	93
3	5	1:6	95
4	5	1:6	95
5	5	1:6	95
3	3	1:6	94
3	2	1:6	92
3	1	1:6	86
3	3	1:4.5	95
3	3	1:5	94
3	3	1:7	93

From Table 1, the optimum reaction conditions for synthesis of TBC are as follows: n(citric acid) : n(butanol) = 1:6, citric acid 0.1 mol, reaction time 3 h, catalyst 3%.

Reusability of the solid superacid catalyst. The reusability of the catalyst was also investigated (Table 2). From Table 2, the SO_4^{2-}/Zr-MCM-41 solid acid catalyst can be used three times without obvious decrease in catalytic activity.

Table 2. Reusability of solid acid catalyst.

Catalyst	Conversion (%)				
	Cycle	1	2	3	4
SO_4^{2-}/Zr-MCM-41		95	95	94	92

Characterization of solid acid catalysts. Figure 1 shows the powder X-ray diffraction patterns of SO_4^{2-}/Zr-MCM-41. It can be seen that SO_4^{2-}/Zr-MCM-41 exhibited the typical hexagonal lattice corresponding to that reported by Beck [7]. It shows three low-angle peaks in the region 2θ = 1.5–10, corresponding to (100), (110) and (200) reflections. It also suggested that SO_4^{2-}/Zr-MCM-41 is of the long range ordering catalyst [8].

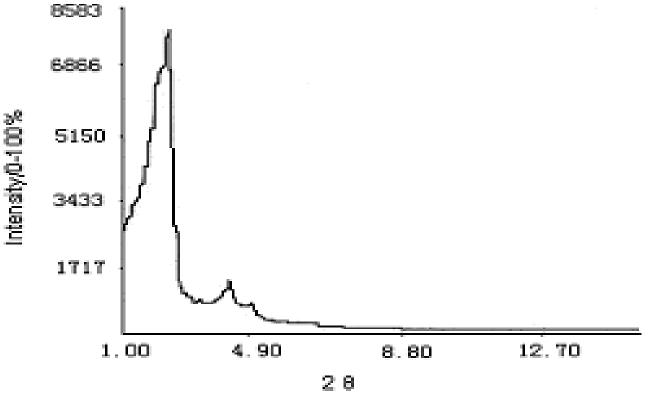

Figure 1. The XRD patterns of SO_4^{2-}/Zr-MCM-41.

We tried to use FTIR spectra to analyse SO_4^{2-} group on surface. It was found that SO_4^{2-}/Zr-MCM-41 exhibits absorption band at 1364 cm^{-1} corresponding to SO_4^{2-}. For solid super acidic catalyst such as SO_4^{2-}/M_xO_y, the band of SO_4^{2-} is at 1380 cm^{-1} that is often regard as the characteristic band of SO_4^{2-} in the solid super acidic catalysts [9]. The band at 1364 cm^{-1} of SO_4^{2-}/Zr-MCM-41 is attributed to the interaction between SO_4^{2-} and metallic element. With the increase of metallic element, this band becomes more intense [10]. All these mean that SO_4^{2-} exists in the skeleton of Zr-MCM-41. In the IR spectra, the asymmetric and symmetric stretching vibration bands of framework Si-O-Si appeared at about 1088 cm^{-1} [11].

Figure 2 showed that the sample exhibits a well-expressed hysteresis of loop type IV [6], which means that all of the samples are of good mesoporous structural ordering and a narrow pore size distribution. A slow increase in nitrogen uptake at low relative pressure corresponding to monolayer-multilayer adsorption on the pore walls, and adsorption curve is identical with desorption curve, which indicates that materials possess broad mesoporous structure. A hysteresis loop exhibits at high relative pressure corresponding to capillary condensation. From BET method and BJH analysis, the mesoporous molecular sieve MCM-41 possesses a uniformly sized mesoporous with diameters 2.8 nm, larger surface area of more than 573 m^2/g.

Characterization of TBC. The structure of TBC was characterized by FTIR and ^{1}H-NMR spectroscopy. Detailed analysis is shown as follows: IR, v/cm^{-1}: 3501 (-OH), 2961 ($-CH_3$), 2874 ($-CH_2-$), 1740 (C=O), 1188 (C-O). ^{1}H-NMR (500 MHz, DMSO): δ 0.86 (m, 9H), δ 1.43 (m, 6H), δ 1.58 (m, 6H), δ 2.72 (d, 2H), δ 2.88 (d, 2H), δ 3.96 (t, 4H), δ4.09 (t, 2H), δ 5.54 (s, 1H).

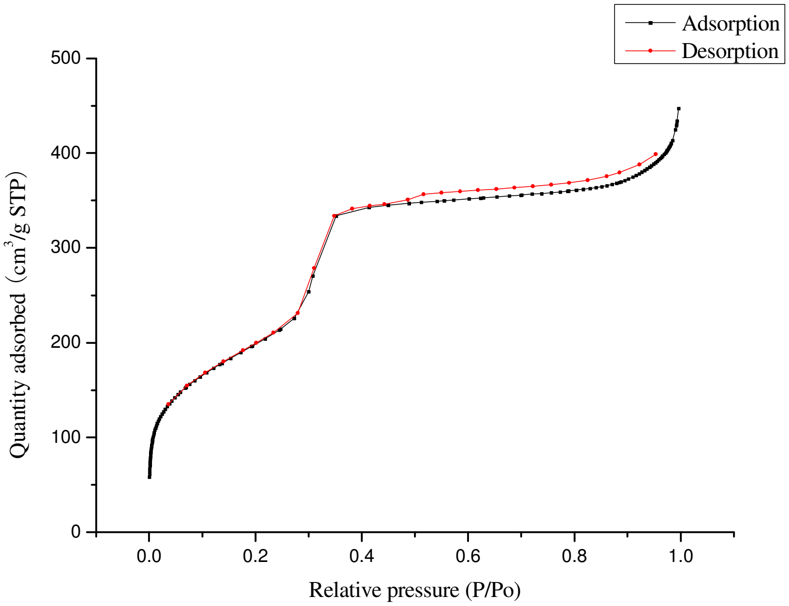

Figure 2. N_2 Ad/De isotherms of SO_4^{2-}/Zr-MCM-41.

CONCLUSIONS

Zirconium-containing mesoporous molecular sieve SO_4^{2-}/Zr-MCM-41 was synthesized. Its structure was characterized by XRD, N_2 Ad/De isotherms and FT-IR. SO_4^{2-}/Zr-MCM-41 was used as catalyst in synthesis of tributyl citrate. The optimum reaction conditions for the synthesis of TBC are as follows: n(citric acid) : n(butanol) = 1:6, citric acid 0.1 mol, reaction time 3 h, catalyst 3%. Under optimum conditions and using SO_4^{2-}/Zr-MCM-41 as catalyst, the conversion of citric acid was 95%. After easy separation of the products from the solid acid catalyst, it could be reused 3 times and gave a conversion of citric acid not less than 92%. The structure of tributyl citrate was characterized by FT-IR and ^{1}H-NMR.

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