Application of magnetic superacid catalyst in synthesis of 2-methylantraquinone

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Abstract. A solid acid catalyst was prepared by impregnating trifluoromethanesulfonic acid (TFMSA) onto mesoporous SiO₂ coated attapulgite (ATP). 2-(4'-methyl benzoyl) benzoic acid (T acid) was used as a compound to evaluate the catalytic activity. T acid is an important dye intermediate. The results show that T acid conversion over the catalyst could reach 100% under mild conditions without concentrated sulfuric acid. It proved that the catalyst was stable after 4 cycles. According to multiple analyses, TFMSA was formed on the surface of ATP.

1. Introduction

Attapulgite (ATP) was first found and described about in 1860, whereas, sometimes named meerschaum, which has long been used in Europe. Large deposits of ATP are of considerable interest as an industrial mineral. ATP with the ideal chemical composition MgAlSi₄O₁₀(OH)₄H₂O, is a hydrated magnesium silicate with a rod-like morphology. ATP is widely applied in many fields, particularly oil refining, wastewater treatment, drug, and catalysts. ATP has some particularly desirable sorptive, and catalytic properties, catalyst supports play very important roles in catalyst activity, and thereby selecting a catalyst support is significant for preparing an highly active catalyst. ATP is an important mineral with rod-like morphology. Because of its special construction of the single rod-like crystal, the high specific surface area, and the excellent thermal stability, ATP is an excellent candidate for catalyst support. In general, the raw ATP is a mixture of minerals, which contains impurities, includes minor carbonates including dolomite and other metal impurities [1-5]. So, it is of great interest to undertake a comparative research of ATP from China.

T acid is a key intermediate for the preparation of dye-gold orange G in VAT dyes. The reaction process consumes a large amount of concentrated sulfuric acid and fuming sulfuric acid. If the process can be completed by replacing the acid with a acid catalyst, a large amount of sulfuric acid will be saved, which is conducive to environmental protection [6-8].

2. Experimental

2.1. Materials

ATP was purchased from Jiangsu Huahong Mining Chemical Co., Ltd., Xuyi City, Jiangsu Province,
and China. T acid is an analytical reagent purchased from Xilong Chemical Co., Ltd, aqueous NH3, cetyl trimethyl ammonium bromide (CTAB), tetraethyorthosilicate (TEOS), hydrochloric acid and TFMSA were purchased from Sinopharm Chemical Reagent Co., Ltd. as analytical reagents.

2.2. Catalyst preparation
ATP was acid activated with 1M hydrochloric acid, and thermal activation in a tube furnace at 420 °C for 4 h to obtain an activated ATP, ATP was ground to pass through 100 mesh sieves. Mesoporous ATP (MATP) was prepared through sol–gel method. The acid activated ATP (9 g) was mixed with CTAB (0.01 mol L⁻¹) aqueous solution (100 mL). Then, 6 mL TEOS and 7 mL ammonia were added into the mixture at 40 °C for 5 h. The resulting white product was filtered, and dried under vacuum at 60 °C for 4 h. The TFMSA/MATP (MSSA) was prepared by impregnation method, and TFMSA (10 mL) was added into MATP (4 g) under N₂ atmosphere at 90 °C for 4 h. Then the resulting product was cooled, filtered, washed with ethyl alcohol, and calcined at 350 °C for 4 h. The amount of TFMSA loaded on MATP is ca. 7.8%, which was calculated on the basis of the mass change after active component loading.

2.3. Catalyst characterizations
Transmission electron microscopic (TEM) analysis was performed with a JEOL 2010 microscope. Specific surface area and average pore size of the samples were measured using an Autosorb-1-MP apparatus under -196 °C. NH₃ temperature-programmed desorption was conducted on a TP-5000 type adsorption instrument. The thermo gravimetric analysis was performed. The analysis was performed in the range of 50 °C-800 °C at 10 °C/min.

2.4. Catalytic Ring-closure of T acid
20 g of T acid and 100 mL of o-dichlorobenzene were added into the three-mouth reaction flask, and an appropriate amount of MSSA catalyst was added. The catalytic reaction was performed at a stated temperature. The reaction was stopped when the content of T acid was below 0.5% for chromatographic analysis. The reaction mixtures were analyzed with HPLC, which is equipped with a capillary column coated with HP-5MS (60 m × 0.25 mm × 0.25 μm), and determining the contents of T acid by the external standard method.

3. Results and Discussion

3.1. characterization and analysis of MATP
TEM was used to analyze the morphologies and structures of MATP and the catalysts prepared. As shown in Fig. 1a, ATP exhibits rod-like structure. The rod-like structures show clear surface, and MATP (Fig. 1b) is similar to that of ATP but the rod-like structures diameters in MATP are significantly increase to between 20 and 30 nm. ATP in MATP seems to be coated by a shell with thicknesses of ca. 10 nm. Conversely, the surface characteristics of MSSA differ from MATP in which an unsmooth surface is observed. Another different feature is appeared irregular grains an average diameter of 10 nm that are uniformly distributed on the MATP surface. Analysis results show the mesoporous catalyst carrier was prepared successfully, and the active components TFMSA was impregnated on the surface of the MATP.
3.2. BET characterization of MATP

Table 1 shows that the specific surface area 411.23 m\(^2\)/g of MATP is significantly larger than that 172.5 m\(^2\)/g of ATP, favoring the subsequent TFMSA loading.

| Sample | Specific Surface Area (m\(^2\)/g) | Pore Volume (cm\(^3\)/g) | Hole Size (nm) |
|--------|-----------------------------------|--------------------------|----------------|
| MATP   | 411.23                            | 0.23                     | 2.58           |
| ATP    | 172.5                             | 0.65                     | 18.27          |

As Fig.2a illustrates, it was found that MATP presented the characteristic IV type isotherms curves \[^9\]. They have a typical type-H4 hysteresis loop, indicating the presence of mesopores in MATP. The results could be attributed to capillary condensation taking place within a narrow range of tubular pores with effective width of 3.3-4.3 nm\[^10\], confirming the high degree of pore uniformity of the pore determined also by TEM (Fig. 1b,c). It could be found that the specific surface area of increase from 172.5 m\(^2\)/g to 411.23 m\(^2\)/g, these results indicated that the mesoporous structure greatly increases the specific surface area of the catalyst support.
3.3. Activity detection of catalyst MSSA

The effects of temperature, MSSA feed, and time on the catalytic closed-loop reaction of T acid were investigated. As Fig. 3 shown, T acid conversion increases with raising temperature, increasing MSSA feed and time, and prolonging time, T acid was almost completely converted at 180 °C over 1 g MSSA for 3 h. When the reaction temperature exceeds 180 °C, the T acid is completely transformed under the same conditions, and when the MSSA feed exceeds 1 g, the T acid is completely transformed at 180 °C for 3 h. So, the optimal reaction conditions ensure T acid complete reaction at 180 °C over 1 g MSSA for 3 h.

3.4. Catalyst stability test

The recycle efficiency of the catalyst MSSA has been studied. Industrial heat reactor requires excellent catalyst stability. Therefore recycle use tests conducted on MSSA were performed. As shown in Fig. 4, T acid conversion only slightly decreases following increasing recycle times, demonstrated good stability of MSSA. The slight decrease of T acid conversion may be concerned with carbon deposition. The NH3-TPD profile of the recycled MSSA shows that there is no significant loss to acidity for the catalyst after used for several times. The above results showed MSSA has high catalytic activity and stability.
As shown in Fig. 5, in order to further investigate the temperature resistance characteristics of the catalyst MSSA, the T acid conversion rates at 200 °C, 230 °C, 260 °C, 290 °C and 320 °C were further studied. The results show that the T acid conversion rate is not affected by temperature change, indicating that the anti-temperature property of the MSSA is good, which is related to the strong bonding between the active component and the catalyst support.

4. Conclusions
T acid was almost completely converted over MSSA at at 180 °C for 3 h, suggesting that MSSA exhibits excellent catalytic activity under mild conditions, which can be used instead of concentrated sulfuric acid. No obvious deactivation was observed even after several cycles. The MSSA catalyst shows a promising new route for construction catalysts applied in closed loop reaction of acidification.

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