Template-free Synthesis of Mesoporous Titanosilicates as Low-cost Solid Acid Catalysts for Biodiesel Fuel Production

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Abstract: A facile template-free synthesis of mesoporous titanosilicate materials as efficient and low-cost solid acid catalysts for the production of biodiesel fuel (BDF) from non-edible Jatropha oil was reported. The thus synthesized materials which were composed of aggregates of loosely packed nanoparticles with high surface area and large mesoporosity could catalyze esterification and transesterification simultaneously and efficiently without significant problem of Si leaching. The optimized material remained highly active after repeated use and the high-quality Jatropha BDFs synthesized under optimal conditions could meet the specifications of EN14214 standard.

Keywords: mesoporous titanosilicate, solid acid catalyst, biodiesel fuel, international fuel standard.

1. Introduction

In the past decades, BDF has been widely regarded as a sustainable diesel fuel for reducing the dependence on fossil fuels because of its renewability, biodegradable, low emissions of greenhouse gases.[1] The industrial process to produce BDF was through acid-catalyzed esterification of free fatty acids (FFAs) and base-catalyzed transesterification of edible oils, which competes with food supply and is costly on separation/purification. Efforts have been made to develop efficient solid catalysts to convert non-edible oils to BDF. Jatropha curcas oil is a potential candidate as non-edible oil source, but crude Jatropha oil (CJO) contains 15-30 wt% of (FFAs that may react with alkali bases to form soap. Recent studies had demonstrated that titanium (Ti)-based materials (e.g. Ti-incorporated SBA-15) exhibited suitable acidity to catalyze esterification and transesterification simultaneously when deal with feedstock oil containing high content of FFAs.[2] In this report, a simple template-free synthesis of mesoporous titanosilciate materials was developed, and the materials were extensively characterized and were applied as solid acid catalysts for the simultaneous esterification and transesterification of CJO to produce high-quality BDF.

2. Experimental

The synthesis involved the homogeneous cocondensation of sodium silicate (SS) and the triethanolamine (TEA)-stabilized titanium tetraisopropoxide (TTIP) that was induced by a pH drop with the aid of ethyl acetate (EA).[3] Typically, 0.19 g of TTIP and 1.37 g of TEA were mixed thoroughly, and the mixture was further mixed with 4.04 g of SS and 570 g of distilled water. After adding 30 mL of EA, the mixture was stirred vigorously for 30 seconds, kept static for 2 h, and then aged at 90 °C for 24 h. The white precipitate with Ti/Si of ~4 mol% was collected, ground and calcined at 540 °C (referred to as 4-mTS). A reference sample of Ti-incorporated SBA-15 with Ti/Si of ~4 mol% (analyzed by EDX, referred to as 4-Ti-SBA-15) was prepared by following the procedures reported by Chen et al..[2] The conversion of Jatropha oil with methanol was carried out at 200 °C in N_2 atmosphere for 1-3 h in a batch-type high-pressure reactor with 2 wt% of catalyst and methanol-to-oil ratio of 27-100.

3. Results and discussion

Mesoporous titanosilicates containing Ti/Si ratio of 1.1-8.6% were prepared by cautiously tuning TTIP/SS or TEA/TTIP ratios. Typically, 4-mTS was composed of aggregates of loosely packed nanoparticles with 5-10 nm in size, leaving quite some space among them (cf. Figure 1A and 1B). It

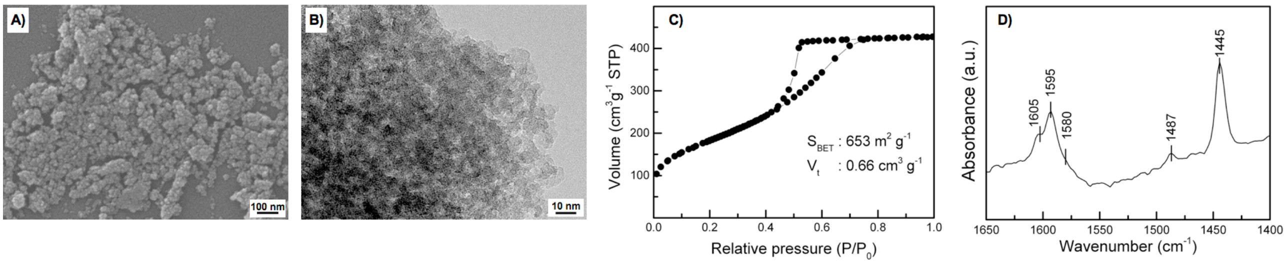

Figure 1. (A) SEM, (B) TEM images and (C) N_2 physisorption isotherm of 4-mTS. (D) FT-IR spectra of 4-mTS after pyridine adsorption and then heated to 200 ℃.

exhibited type-IV isotherm with H_2-type hysteresis loop at relative pressure of 0.45-0.80 (cf. Figure 1C). The average pore size of 4-mTS (analyzed by NLDFT method) was ca. 6 nm, which was commensurate with the observation in SEM and TEM. Figure 1D shows the FT-IR spectra of pyridine-adsorbed 4-mTS at 200 ^{o}C. The presence of the peaks at 1445, 1580 and 1605 cm^{-1} and the absence of absorption at ~1540 and 1634 cm^{-1} suggested that the sample mainly possessed Lewis acid sites.

Catalytic studies showed that 4-mTS gave BDFs with significantly enhanced fatty acid methyl ester (FAME) content to 84.2 wt% and decreased total glycerol (G_T) and FFA (cf. Table 1). The results suggested that 4-mTS could simultaneously catalyze the esterification and transesterification reactions. Besides, the material showed nearly no Si leaching (< 5 ppm). On the other hand, the reference catalyst 4-Ti-SBA-15 showed slightly lower activity and serious problem of Si leaching (86.7 ppm) under the same reaction conditions. This may be correlated to the higher degree of silica condensation for 4-mTS than that for 4-Ti-SBA-15. The used 4-mTS was further washed thoroughly, dried and calcined at 540 ^{o}C for reuse test. The activity of recycled 4-mTS remained almost unchanged after recycling. Finally, high-quality Jatropha BDFs, which met the specifications of EN14214 standard, were obtained under optimal conditions (such as methanol-to-oil ratio > 63 and reaction time = 1 h; methanol-to-oil ratio > 50 and reaction time = 3 h).

Table 1. Profiling of Jatropha BDFs over mesoporous titanosilicates and 4-Ti-SBA-15.[a]

Catalysts	**Ti/Si ratio (mol%)**	**MeOH /Oil**	**Reaction Time (h)**	**FAME (wt%)**	**FFA (wt%)**	**G_T (wt%)**	**Si leaching (ppm)**
No catalyst	-	27	1	17.3	7.3	9.43	-
4-mTS	4.3	27	1	84.2	1.8	3.52	4.8
4-mTS	4.3	63	1	98.3	0.9	0.17	-
4-mTS	4.3	50	3	98.4	0.9	0.19	-
4-mTS-recycled	4.3	27	1	84.5	1.5	3.35	-
4-Ti-SBA-15	3.8	27	1	81.0	1.3	4.32	86.7
EN 14214:2012 Standard	-	-	-	>96.5	<~1.0[g]	<0.25	-

a. Reaction conditions: 200 ℃, 1-3 h, 5 g Jatropha oil, MeOH/Oil = 27-100, 2 wt% catalyst. Abbreviations: MeOH: methanol, FAME: fatty acid methyl ester, FFA: free fatty acid and G_T: total glycerol.

4. Conclusions

The mesoporous titanosilicate materials synthesized by the template-free method were composed of aggregates of nanoparticles and possessed high mesoporosity, high surface area and Lewis acidity. They could efficiently catalyze the simultaneous esterification and transesterification of Jatropha oil, and the catalytic activity remained almost the same after recycling. The high-quality Jatrohpa BDFs synthesized under optimal conditions could meet the specifications of EN14214 standard.

References

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