Lanthanum-doped mesoporous strontium titanate for transesterification of palm oil with methanol to fatty acid methyl esters

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Abstract: Lanthanum-doped mesoporous strontium titanates (LMSTs) were synthesized via self-assembly sol-gel combustion method using Pluronic P123 as a structure-directing agent and citric acid as a metal-complexing agent. The La doping decreased the crystallinity of LMSTs, and at a high La: Sr atomic ratio, enhanced mesoporosity and total basicity. An *in situ* Fourier-transform infrared spectroscopy (FTIR) indicated the formation of coordinatively unsaturated O^{2-} species and new moderate basic sites. The catalytic activity of LMSTs in transesterification of palm oil with methanol was correlated with their basic properties.

Keywords: Strontium titanate, Basicity, Transesterification

1. Introduction

Transesterification is an important process for converting triglycerides, presenting in vegetable oil and animal fat, and methanol to fatty acid methyl esters (FAME), which are basic oleochemicals used in various industries. The conventional process for FAME production is transesterification in the presence of homogeneous base catalysts, which has several drawbacks. Heterogeneous catalysis is an environmentally friendly technology for the production of high-purity FAME and glycerol under moderate operating conditions [1]. Mixed metal oxides are a class of transesterification catalysts [2]. The formation of mixed oxides improved not only the catalytic activity but also enhanced the catalyst stability [3]. Herein, a series of LMST materials were synthesized for the transesterification of palm oil with methanol. Moreover, the effects of La doping on the evolution of new basic species and the characteristics of active sites responsible for the transesterification were studied by *in situ* FTIR using pyrrole as probe molecule.

2. Experimental

The LMST materials were synthesized via a neutral-templated self-assembly sol-gel combustion method using triblock copolymer Pluronic P123 as a structure-directing agent and citric acid as a fuel and metal-complexing agent, as described earlier [4]. $Ti(OC_4H_9)_4$, $Sr(NO_3)_2$ and $La(NO_3)_3{\cdot}6H_2O$ were used as metal precursors. The La: Sr atomic ratio was varied at 0.1: 1, 0.43: 1 and 1: 1, while the atomic ratio of (Sr + La): Ti was maintained at 1: 1. The catalysts obtained were denoted as “LMST-*x*”, where *x* represents the La: Sr atomic ratio. MST was a La-free mesoporous $SrTiO_3$ synthesized without La addition. The transesterification of palm oil with methanol was carried out in an 80-mL autoclave reactor equipped with a magnetic stirrer at a 20: 1 methanol: palm oil molar ratio, 10 wt.% catalyst loading (based on the oil mass) and 170 °C. The FAME composition was analyzed by gas chromatography.

3. Results and discussion

The XRD analysis indicated that MST and LMSTs had cubic perovskite $SrTiO_3$ (PDF: 00-035-0734) and $La_xSr_{1-x}TiO_3$ (PDF: 00-055-0926), respectively, as the major crystalline phases. By increasing the La: Sr ratio, the BET surface area was increased from 24.9 to 37.3 $m^2\ g^{-1}$, while the content of strong basic sites was increased from 15 μmol g^{-1} to 52 μmol g^{-1}. The LMST-1 catalyst with the highest surface area possessed the highest amount of strong basic sites and the highest total basicity (247 μmol g^{-1}) as determined by CO_2-TPD. As shown in Figure 1, the amount of strong basic sites was mainly correlated with an enhanced Sr: Ti atomic ratio on the surface. The contribution of La-rich phase to the strong basicity could not be discarded at the 0.25 La fraction. The results suggested that the existence of Sr-rich, as well as mixed Sr and La, oxides dispersed on the LMST surface was a key to enhance the strong basic character. According to the catalytic activity test, the FAME yield at 3 h was increased from 79.4 to 97.6 wt.% with increasing the La doping amount, which was in the same trend of increased total basicity.

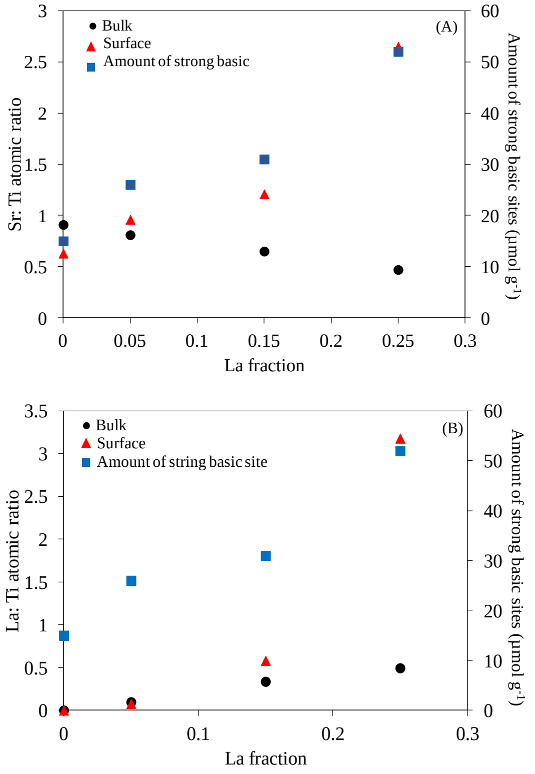

Figure 1. Effects of La^{3+} doping amount on (A) Sr: Ti and (B) La: Ti atomic ratios of the LMST surface, and strong basicity of LMSTs.

The FTIR spectra of MST and LMST-1 after pyrrole adsorption at 30 °C, followed by desorption at the same temperature indicated 4 types of adsorbed pyrrole species, which were corresponded to different basic sites [5]. The monodentate surface hydroxides were newly generated upon the La doping, and the coordinatively unsaturated O^{2-} ions became pronounced for the La-doped mixed oxides. Combined with the elemental and CO_2-TPD analysis, the monodentate hydroxides were present as hydroxyl groups at the defect sites containing in the mixed Sr and La compounds, and the strong basic character should be attributed to the oxygen ions at lattice defects of SrO nanocrystallites and/or mixed Sr and La oxides highly dispersed on the LMST-1 surface.

4. Conclusions

LMST-1 was a potential solid base catalyst in the transesterification of palm oil with methanol, giving the highest FAME yield (98 wt.%) under the optimized reaction condition, and its superior catalytic activity was well correlated with the amount and strength of basic sites. The La doping generated the defect sites, which resulted in the generation of monodentate hydroxides as new basic sites, and enhanced amount of coordinatively unsaturated O^{2-} species. The present study emphasized a role of strong basic sites as catalytically active centers in the transesterification.

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