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Characterization and reactivity of stannum modified titanium silicalite TS-1 catalysts for transesterification of dimethyl oxalate with phenol

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Abstract

The transesterification of dimethyl oxalate (DMO) with phenol over stannum modified TS-1 was conducted to prepare methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO), which could be used to produce diphenyl carbonate (DPC). The component, structure and phase of TS-1 catalysts with various Sn loadings were investigated. The relationship between the catalytic properties and the Sn loadings was discussed. The results indicated that, although the Sn-modified TS-1 catalysts had fewer Lewis acid sites than the unmodified TS-1, its catalytic activity was increased greatly by the interaction of Sn with Ti–O–SiO_3 weak Lewis acid centers. The catalyst of TS-1 with 2 wt% Sn loadings performed best, giving 50.3% conversion of dimethyl oxalate and 99.2% selectivity to the target products. By means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX), the relationship between the catalytic properties and the structure of Sn dispersed on the surface of TS-1 was studied in detail. At Sn loadings below 2 wt%, Sn was highly dispersed, but at higher loadings it was crystallized into bulk tin dioxide, where the interaction between Ti and Sn was not evidently observed, leading to decreased catalytic activity. XPS results showed that Ti could not be detected even at 1 wt% Sn loadings. EDX results indicated that the content of Ti on the surface decreased with increasing Sn loadings, but the decrease in Ti content was much less than the increase in Sn content. Moreover, NH_3-TPD and FTIR analyses of adsorbed pyridine showed that there were only weak Lewis acid centers on all catalysts and the Sn loadings hardly affected the acid strength of the catalysts.

Keywords: Sn-modified TS-1 catalyst; Transesterification; Diphenyl carbonate; Diphenyl oxalate; Methyl phenyl oxalate; Promotional effect

1. Introduction

Aromatic carbonates have come to occupy an important position as useful organic chemicals for a variety of industrial and synthetic applications. They are used as solvents and as reagents in the transesterification reactions with glycols and bisphenol-A for the production of polycarbonates (PCs) [1].

The industrial methods most commonly employed for the synthesis of aryl carbonates are based on the reaction between a corresponding aromatic alcohol with phosgene in the presence of bases.

Oxidative carbonylation of phenol and transesterification reaction of phenol with dimethyl carbonate (DMC) or dimethyl oxalate (DMO) have been studied to synthesize diphenyl carbonate (DPC) because all these processes [1–10] have avoided using the highly toxic and corrosive phosgene.

Among them, the transesterification of DMO with phenol via a three-step reaction has been deemed as a promising and possible route for DPC synthesis [11,12] from the raw materials such as carbon monoxide, phenol and oxygen. In the first step, dimethyl oxalate is produced by carbonylation of methanol [13]; then, diphenyl oxalate (DPO) is obtained

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from transesterification of DMO with phenol; and finally, the decarbonylation of DPO is carried out to produce DPC and carbon monoxide [14], as shown in Eqs. (1)–(3).

$$2CO + 2CH_3OH + 1/2O_2 \rightarrow (COOCH_3)_2 + H_2O \quad (1)$$

$$(COOCH_3)_2 + 2C_6H_5OH \rightarrow (COOC_6H_5)_2 + 2CH_3OH \quad (2)$$

$$(COOC_6H_5)_2 \rightarrow CO(OC_6H_5)_2 + CO \quad (3)$$

The thermodynamic equilibrium constant of reaction (2) at 453 K is estimated at 1.1×10^{-8} [10], from the thermodynamic calculation made with group contribution of liquid components. This indicates that the transesterification between DMO and phenol is not favorable in the thermodynamics. Moreover, the synthesis of diphenyl oxalate follows a two-step reaction module consisting of transesterification of DMO with phenol into methyl phenyl oxalate (MPO) and further disproportionation of MPO into DPO [11,12].

$$(COOCH_3)_2 + C_6H_5OH \rightarrow C_6H_5OOCCOOCH_3 + CH_3OH \quad (4)$$

$$2C_6H_5OOCCOOCH_3 \rightarrow (COOC_6H_5)_2 + (COOCH_3)_2 \quad (5)$$

Nishihira et al. [11,12,14] reported the transesterification of DMO with phenol carried out in the liquid phase using traditional transesterification catalysts such as Lewis acids and soluble organic Pb, Sn, or Ti compounds. In these homogeneous systems, the separation and recovery of the catalysts remains a critical issue when applied to the industrial process. So, the development of active solid catalysts is highly desirable in view of regeneration and separation. Unfortunately, there are few reports on the development of active heterogeneous catalysts for the reaction up to the present time. The goal of our work, therefore, was to develop a heterogeneous catalytic system that combines good catalytic performance with satisfactory recovery of the catalysts used.

Since the discovery of titanium silicate-1 (TS-1) with the MFI structure in 1983 [15], a large number of research projects have been conducted on the synthesis, characterization and catalytic applications of TS-1. TS-1 has unique catalytic properties, being effective in the reaction of a variety of organic compounds at low temperature: epoxidation of alkenes [16–18], epoxidation of olefins [17,19], oxidation of alcohols [20,21], ester exchange [22] hydroxylation, of aromatics [23], and ammoximation of ketones, etc. [18].

More recently, we found that TS-1 can also catalyze the transesterification of phenol with dimethyl oxalate to methyl phenyl oxalate and diphenyl oxalate [24]. The results indicated that the conversion of DMO was not satisfactory although TS-1 showed the excellent selectivity to MPO and DPO. Moreover, there are quite few further studies on the reaction and the characterization of this new catalytic system. Because organic Sn compounds are widely used as ester exchange catalysts [25–28], characterization and activity study stannum modified TS-1 catalyst was performed in this paper for the transesterification of DMO with phenol to find immanent correlation between catalytic performance and catalyst structure.

2. Experimental

2.1. Catalysts preparation

TS-1 (Ti content: 2.5 wt%), obtained from SINOPEC Research Institute of Petroleum Processing, was prepared according to the procedure described in the original patent by Taramasso et al. [15]. It was dried in an oven at 393 K for 2 h to remove the adsorbed water and then calcined in a muffle furnace at 823 K for 4 h in an air atmosphere. This unmodified TS-1 catalyst was stored in a silica gel desiccator prior to use.

To prepare modified TS-1 catalysts with different Sn loadings, the dried TS-1 was impregnated with a toluene solution of dibutyltin dilaurate (as Sn precursor). TS-1 was impregnated with the Sn solutions of different concerntrations to obtain different Sn loadings and the impregnation was performed for 24 h to ensure that the organic Sn compound diffused and dispersed thoroughly on the surface of TS-1. These impregnated samples were dried in an oven for 4 h at 393 K and calcined in a muffle furnace at 873 K for 4 h.

2.2. Characterization techniques

2.2.1. X-ray diffraction (XRD)

X-ray powder diffraction patterns were recorded on a Rigaku C/max-2500 diffractometer using graphite filtered Cu Kα radiation ($\lambda = 1.5405$ Å) at 40 kV and 100 mA with a scanning rate of $8^\circ\,\text{min}^{-1}$ from $2\theta = 5^\circ$ to $2\theta = 80^\circ$. The XRD phases present in the samples were identified with the help of JCPDS Powder Data Files.

2.2.2. X-ray photoelectron spectroscopy (XPS)

The surface composition and structure of catalyst were studied by X-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 1600 ESCA system with Mg Kα 1253.6 eV radiation as the excitation source. The samples were mounted on a specimen holder by means of double-sided adhesive tape. Spectra were recorded in steps of 0.15 eV. The C 1s peak (284.5 eV) was used as the internal standard for binding-energy calibration. An estimated error of ±0.1 eV can be assumed for all the measurements. The scanning of the spectra was done at pressures less than 10^{-8} Torr and the temperature was approximately 293 K.

2.2.3. Transmission electron microscopy (TEM)

The samples examined by transmission electron microscopy (TEM) were prepared as follows: The catalysts were