



Short communication

Characterization of carbon deposits on coked lithium phosphate catalysts for the rearrangement of propylene oxide



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ABSTRACT

Basic lithium phosphate catalysts for the rearrangement of propylene oxide can be easily deactivated due to carbon deposits. In-situ DRIFTS, TG–DTG, NMR and XPS were used to study carbon deposits. Results showed that carbon deposits were mainly in the form of C_xH_y and C_xH_yO , which could be decomposed in a mixture of N_2 and O_2 atmosphere at higher than 300 °C or in N_2 atmosphere near 500 °C. A shorter period of time was needed in the atmosphere containing O_2 .

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1. Introduction

The rearrangement of epoxides to allylic alcohols or carbonyl compounds is a fundamentally important transformation with significant synthetic and industrial utility. A wide range of catalysts are associated with this reaction, and this transformation has been attracting great attentions [1–3]. The constitution of the rearrangement products was influenced by the acidity or basicity of the catalysts [4–6]. Lithium compounds have been attractive candidates as catalysts for the rearrangement of epoxides. For liquid phase catalysis or asymmetric catalysis [7–10], lithium compound bases [6,11,12] or Schlosser's Li/K mixed superbases [13] are often applied in the arrangement of functionalized, aryl or chiral epoxides into allylic alcohols. For epoxides with small molecule, especially propylene oxide (in abbreviation, PO), basic lithium phosphate is often used to catalyze the rearrangement to allyl alcohols [14,15].

There are two processes for the rearrangement of PO to allyl alcohol, gas–solid phase and slurry phase. Gas–solid phase process is much simpler and cleaner than the other, but carbon deposition has always been a major problem. Therefore, it is important to analyze the carbon deposits on the deactivated catalysts. In our previous work, Li_3PO_4 catalysts gradually got deactivated as reaction time increased and its BET surface area decreased obviously due to carbon (or coke) deposition [16]. This investigation is mainly focused on carbon deposits concurrent with the decomposition or removal of carbon deposits.

2. Experimental

2.1. Catalyst preparation

Lithium hydroxide monohydrate (20.14 g) was dissolved in 125 mL of de-ionized water at 65 °C in a 500 mL three-necked flask with a stirrer. A solution prepared from sodium phosphate dodecahydrate (45.61 g) and water (125 mL) was dropped into the flask with stirring for 1 h. After the mixture was ripened for 3 h, the resultant white precipitate was collected by filtration, dried at 120 °C for 12 h and then calcined at 320 °C for 8 h.

Catalytic isomerization reactions were conducted in a $\phi 10$ mm fixed-bed reactor at 290 °C using a mixture of N_2 and vaporized propylene oxide stream, with weight hourly space velocity (WHSV) value of about 9 h^{-1} [17]. A series of used or coked lithium phosphate catalysts were obtained.

2.2. Catalyst characterization

Used or coked catalysts were characterized by thermo gravimetric analysis (TG, Mettler-Toledo TGA/SDTA851e) at the rate of 20 °C/min in both nitrogen (99.999%, 30 mL/min) and air atmosphere. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer). All binding energies were referenced to the C1s neutral carbon peak at 284.6 eV. ^{13}C CP-MAS-NMR spectra were performed on a Bruker DSX400 spectrometer. Tetramethylsilane was used as external reference for the chemical shifts (δ).

In situ DRIFTS was used to investigate the decomposition of the carbon deposits at different temperatures. Pure KBr was used as background and the mixture of KBr and the used catalysts (3:1) was used

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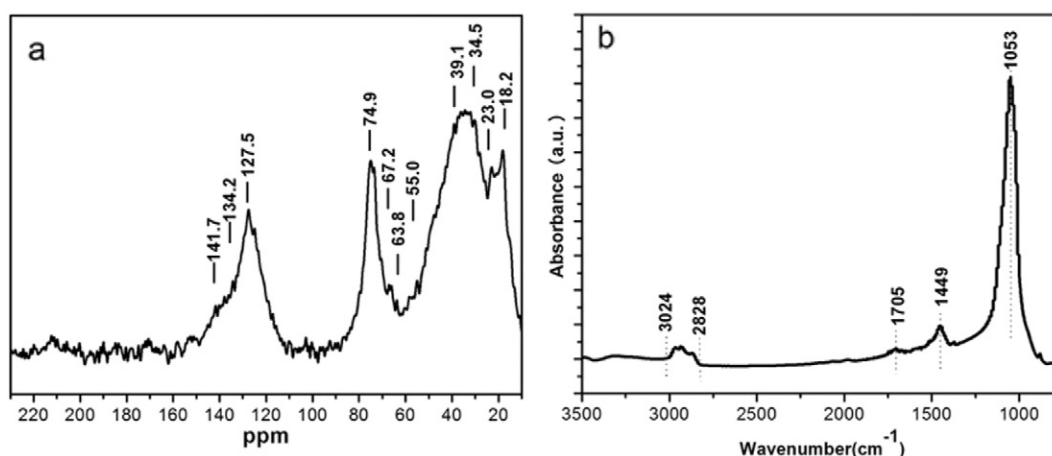


Fig. 1. ¹³C MAS-NMR (a) and DRIFTS spectra (b) of used catalysts (24 h).

as samples. The spectra were recorded on a Nicolet iS10 spectrometer equipped with an iZ10 Auxiliary Module, which consists of a liquid-N₂-cooled high-sensitivity MCT-A detector and a DRIFTS cell (Spectra-Tech) with KBr windows. All spectra were recorded at an accumulation of 20 scans with a resolution of 4 cm⁻¹. The spectra began to be recorded as soon as the sample was heated in pure N₂ gas flow. When the temperature reached the set value, O₂ was introduced into the cell. The IR data are reported as log 1 / R, where R is the sample reflectance. The function log 1 / R (=“absorbance”) gives a better linear representation of the band intensity against sample surface coverage than that given by the Kubelka–Munk function for strongly absorbing media such as those based on oxides [18].

3. Results and discussions

3.1. DRIFTS and NMR analysis

In order to analyze the types of carbon deposits, DRIFTS and ¹³C CP-MAS-NMR were used to characterize carbon deposits on the used catalyst for 24 h on-stream [19], as shown in Fig. 1. The assignment of the peaks shown in Fig. 1a is given in Table 1.

Seen from Fig. 1a and Table 1, there are mainly four groups in carbon deposits, —CH₃, —CH₂, C—O—C or C—OH, and —C₆H₅. In the DRIFTS spectrum, the broad peaks at 2828–3024 cm⁻¹ are mainly attributed to symmetrical and asymmetrical C—H stretching vibrations. They are characteristics of alkyl groups of the carbon deposits on catalyst surface. Judged by the peak of δ_{CH} at 1449 cm⁻¹, alkyl species with three or more carbon atoms in the alkyl chains may also exist. Also, olefinic species may exist in the used catalyst because their characteristic stretching vibration frequencies appear at 3000–3024 cm⁻¹.

DRIFTS analysis shows that the composition of carbon deposits is very complicated. Carbon deposits mainly consist of both aliphatic and aromatic hydrocarbons containing oxygen element. Other types of

carbon, such as olefinic species, graphite-like carbon, are also possible. Their chemical shifts or peaks may be merged with those of the main four groups into the broad peaks at 34.5, 74.9, and 127.5 ppm shown in Fig. 1a. The —CHO group, with the characteristic peak at 1705 cm⁻¹ in Fig. 1b, can be seen at 210 ppm in Fig. 1a.

3.2. XPS analysis

Fig. 2 shows the C1s XPS curves of the fresh and used catalysts. For the fresh catalyst, there are three distinct peaks. The peak at 289.4 eV can be attributed to C=O bonds of CO₃²⁻ on the surface of basic lithium phosphates [20]. The peak at 284.7 eV indicates the presence of carbon contamination. In the curve of the deactivated catalyst, there are three main distinct peaks, the peak at 283.8 eV indicates the presence of graphitic carbon species in the form of C_xH_y [21–24]. The peak at 284.6 eV indicates the presence of carbon contamination. And the peak at 285.8 or 285.4 and 285.6 eV can be attributed to the C—O bonds. Moreover, there is a small peak at 288.9 or 288.7 and 288.8 eV, which is due to C=O bonds in species like C_xH_yO [25,26], a kind of carbon deposit containing O element. The binding energy of C=O bonds in C_xH_yO species is lower than that in CO₃²⁻ groups, since CO₃²⁻ disappeared after the catalyst was used for 24 h on-stream at 300 °C.

Table 1
¹³C NMR chemical shifts and their possible assignments [18,19].

δ (ppm)	Possible carbon types
18.2	CH ₃ end group to a long paraffinic chain
23.0	CH ₂ penultimate carbon in a long paraffinic chain
34.4	CH and CH ₂ α to an aromatic ring
39.1	CH α to the paraffinic chain in alicyclic group
75.0	CH ₂ bound to an alkoxy
127.5	Aromatic carbons bound to hydrogen
134.2	Aromatic carbon bound to CH ₃
141.7	Aromatic carbon bound to substituted groups excluding CH ₃
210.0	—CHO

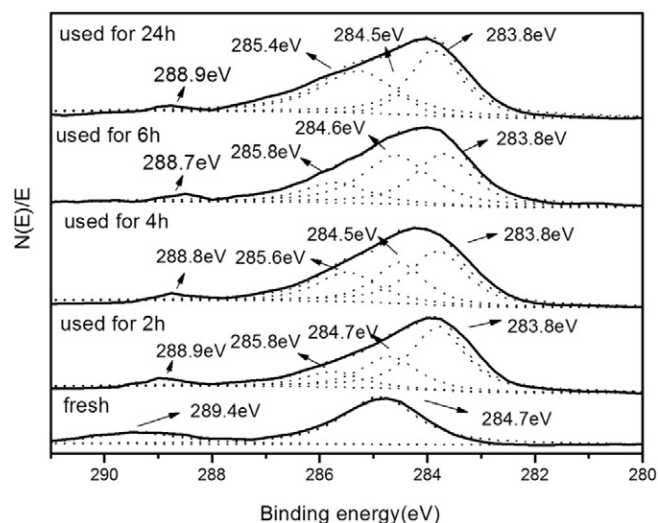


Fig. 2. XPS curves of fresh and used catalysts.

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