

Study of the coordinative nature of alkylaluminum modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst by multinuclear solid-state NMR

Zhang Qin-Hui, Yan Fang, Xia Wei* and Liu Chenguang

State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Qingdao, Shandong 266580, China

© China University of Petroleum (Beijing) and Springer-Verlag Berlin Heidelberg 2013

Abstract: Solid-state nuclear magnetic resonance spectroscopy was used to investigate the coordinative states of surface Al species on various alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts. The alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts were examined via ethylene homopolymerization. ^1H and ^{27}Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra clearly demonstrated that the existing states of surface Al species in alkylaluminum-modified catalysts strongly depended on the type of alkylaluminum cocatalyst, concentration of alkylaluminum and the calcination temperature. ^1H MAS NMR spectra of alkylaluminum-modified Phillips $\text{CrO}_x/\text{SiO}_2$ catalysts, calcined at two different temperatures, exhibited similar trends in peak shift. ^1H spectra showed that with an increase of Al/Cr ratio and calcination temperature, the main peak shifted to high field, indicating that the dominant surface proton species changed from hydroxyl to ethoxyl and ethyl groups. ^{27}Al MAS NMR spectra showed the presence of three different coordination states (6-, 5-, and 4-coordinated Al species) in the alkylaluminum-modified Phillips catalysts. In comparison of different alkylaluminum cocatalysts, it was found that the reactivity of alkylaluminum modified Phillips catalyst decreased in the order of TEA>DEAH>DEAE. The amount of 4-coordinated Al species of Phillips catalysts modified by TEA, DEAE and DEAH also decreased in the order of TEA>DEAH>DEAE, indicating that the presence of 4-coordinated Al species is related to the polymerization activity.

Key words: Phillips catalyst, alkylaluminum, ethylene polymerization, solid-state NMR

1 Introduction

Among all the olefin polymerization catalysts, including Ziegler–Natta catalysts, Phillips catalysts, and metallocene catalysts, Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst is well known as one of the most important industrial ethylene polymerization catalysts. About one-third of the world high-density polyethylene (HDPE) is currently produced using this catalyst. Compared with Ziegler–Natta and metallocene catalysts, Phillips catalyst exhibits unique polymerization behavior, and the products (polyethylene) have many unique chain microstructures such as long chain branching, unsaturated chain ends and ultra-broad molecular weight distribution, which contribute to excellent properties for both processing and final applications (Pullukat and Hoff, 1999). Unfortunately, notwithstanding remarkable success in the industrial field and almost 50 years research work, there still exist many problems need to be resolved (Bade, 1998; Clark, 1970; Yermakov and Zakhrov, 1975; McDaniel,

1985; Weckhuysen and Schoonheydt, 1999; Thune et al, 2001; Gaspar and Dieguez, 2004; Liu and Terano, 2001; Liu et al, 2002; 2003; 2004a; 2004b; 2004c; 2005; Xia et al, 2006a; 2006b; 2009). In general, the states of active sites and polymerization mechanisms still remain unclear and controversial.

Phillips $\text{Cr(VI)O}_x/\text{SiO}_2$ catalyst can be prepared by impregnating an aqueous solution of Cr compounds (mostly chromium(III) acetate or chromium(VI) trioxide) onto amorphous silica gel support, followed by calcination in dry air at a temperature around 600–800 °C for several hours. The obtained Phillips $\text{CrO}_x/\text{SiO}_2$ catalyst can be used directly to catalyze the polymerization of ethylene at 100–150 °C without a preliminary activation step using organometallic cocatalysts or other reducing agents. With the development of olefin polymerization technology, nowadays, new Phillips catalyst systems using metal-alkyl cocatalyst have attracted much interest in the industrial field. However, activation of Phillips catalysts by using metal-alkyl cocatalysts has not been fully investigated up to now. To our knowledge, typically there are three stages for the introduction of metal-alkyl cocatalyst: 1) the catalyst preparation stage, 2) the catalyst aging or

*Corresponding author. email: xiawei@upc.edu.cn
Received June 22, 2013