Polymerization on CO-Reduced Phillips Catalyst initiates through the C–H bond Activation of Ethylene on Cr–O Sites

Murielle F. Delley · Matthew P. Conley ·
Christophe Copéret

Abstract Investigation of the polymerization of ethylene on CO-reduced Phillips catalyst (1 wt% chromium) by infrared spectroscopy reveals the presence of new OH bands. In particular, an OH-band appears at 3,605 cm^{-1}, consistent with the interaction of the SiOH group with an adjacent Lewis acidic chromium center, Si–(μ-OH)–Cr. Polymerization with d$_4$-ethylene leads to the formation of the isotopically shifted band at 2,580 cm^{-1}, consistent with heterolytic C–H activation of ethylene over a Cr–O bond to generate the first Cr–C bond in ethylene polymerization with Phillips catalyst, as recently observed on well-defined Cr(III) silicates.

1 Introduction

Polyethylene (PE) is a commodity material produced on very large scales using processes tailored to the particular need of the final polymeric material. Over 80 million tons of PE are produced annually, a figure likely to rise [1]. Robert Banks and J. Paul Hogan at Phillips Petroleum found that chromium trioxide supported on silica (Cr/SiO$_2$) polymerizes ethylene [2], a few years prior to the discovery of Ziegler–Natta catalysts (TiCl$_x$/MgCl$_2$/AlR$_3$). Cr/SiO$_2$, commonly referred to as Phillips catalyst, produces 40–50 % of high density PE globally [3]. The Phillips catalyst polymerizes ethylene without an activator. The

catalyst precursor is prepared by impregnation of CrO$_3$ on silica, followed by high temperature calcination, which leads to the formation of chromate(VI) silicates [4]. Ethylene polymerization occurs only when the surface bound Cr(VI) species are activated in situ with ethylene to form "reduced" chromium species. Because the Cr(VI) species must reduce prior to polymerization initiation there is a pronounced induction period for these materials. Alternatively, the Cr(VI) containing silica material can be pre-reduced in the presence of carbon monoxide at 300 °C to generate a catalyst that polymerizes ethylene with a less pronounced induction period [5].

In general, polymerization catalysts are activated with reagents to form species containing metal-alkyl groups that are capable of coordinating and inserting ethylene to propagate the polymer [6]. This common feature likely applies to heterogeneous Ziegler–Natta catalysts, and extensive studies showed this mechanism operates in well-defined metallocene polymerization catalysts [7]. However, the Phillips catalyst polymerizes ethylene without an activator or a Cr-carbon bond in the pre-catalyst. The active site of the Cr/SiO$_2$ catalyst is unknown [8, 9], and due to the paucity of active polymerization sites [10] it is difficult to obtain unambiguous evidence about the catalytically relevant chromium species in this material, even with advanced spectroscopic tools that, in the end, provide information about mostly inactive surface species [11, 12]. A general consensus from these studies are that isolated Cr(II) sites are catalytically active, though related studies on silica supported Cr(III) salts showed that these are competent polymerization catalysts [13, 14]. We recently showed that well-defined dimeric Cr(III) species are far more active in ethylene polymerization than the analogous Cr(II) materials [15]. In this study we identified key infrared bands at 3,646 and 3,605 cm^{-1}, respectively, assigned to Si–(μ-OH)–Cr(III) originating from the

M. F. Delley · M. P. Conley · C. Copéret (✉)
Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg. 2, 8093 Zürich, Switzerland
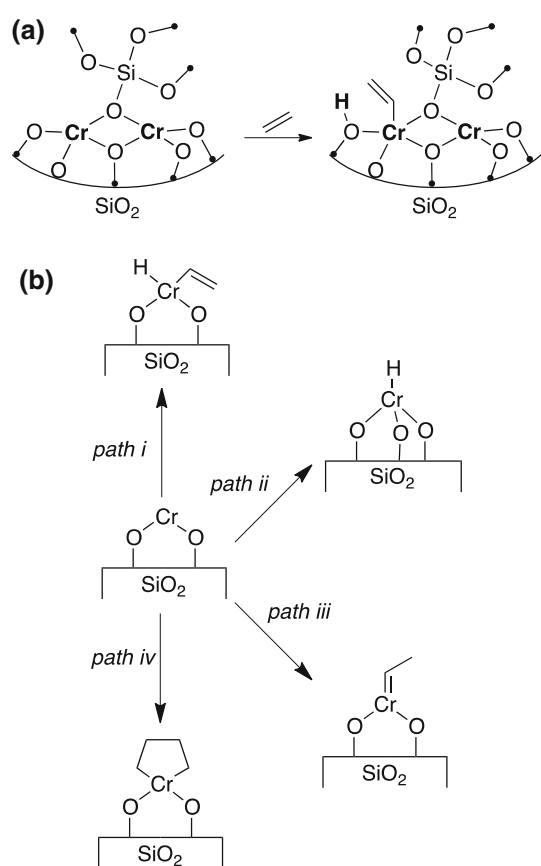e-mail: ccoperet@inorg.chem.ethz.ch

Fig. 1 **a** Heterolytic C–H bond activation of ethylene on a well-defined Cr(III) silicate; **b** Proposed polymerization initiation pathways for Phillips catalyst

heterolytic C–H bond activation of ethylene that we proposed to be the key step in formation of the first Cr–C bond in these silicate materials (Fig. 1a).

In Phillips catalysts, several proposals for ethylene polymerization initiation from isolated Cr(II) sites are shown in Fig. 1b. The initiation processes (i–iv) involve oxidation of Cr(II) to Cr(IV) to generate a Cr-vinyl-hydride by C–H activation of ethylene (path i) [16], a Cr-hydride by O–H activation of a nearby silanol (path ii) [17, 18], a Cr-alkylidene generated from ethylene (path iii) [19–22], or a Cr-metallacyclopentane from oxidative cyclization of two ethylenes (path iv) [23, 24]. Here we show that the Phillips catalyst exposed to ethylene displays an IR signature consistent with the formation of Si–(μ-OH)–Cr and the heterolytic activation of ethylene on a Cr–O bond (Scheme 1a).

2 Experimental

2.1 General Remarks

Gases were added to activated catalysts using high vacuum (10^{-5} mbar) techniques. Ethylene was passed through activated 4Å molecular sieves and BASF Cu-catalyst to remove oxygen and water prior to use. Infrared spectra were collected in an Ar filled glovebox on a Bruker Alpha FT-IR spectrometer or under ethylene pressure on a Nicolet 6700 FT-IR spectrometer.

2.2 Catalyst Preparation

The CO-activated Phillips catalyst was prepared using a modification of a literature procedure [25, 26]. Sylopol-948 was treated with 3.4 mL of a solution of CrO_3 (103 mg, 1 mmol) in H_2O (10 mL) under ambient atmosphere. The yellow material was heated under high-vacuum (10^{-5} mbar) at 750 °C (2 °C min^{-1}) for 1 h. After cooling to ca. 550 °C, O_2 (50 mbar, 1 mmol) was added to the reactor, which was heated to 550 °C for 30 min. After reevacuation of the reactor, CO (50 mbar, 1 mmol) was added and heated to 350 °C for 30 min, followed by evacuation of the hot reactor. The activated CO treated material is extremely sensitive to air and moisture and must be handled under inert atmosphere.

2.3 Ethylene Polymerization Monitoring

A 500 mL glass reactor equipped with a CaF_2 window for transmission infrared measurements and a side arm attached to a Teflon capped flask containing the CO-reduced Phillips catalyst (40 mg, 8 μmol Cr) was loaded in an Ar filled glovebox. The atmosphere was removed and replaced with ethylene (325 mbar). The flask containing the catalyst was preheated to 70 °C for 5 min and then exposed to the ethylene atmosphere; this was taken as t = 0. Infrared spectra were acquired every 2 min, and the intensity of the band at 2,987 cm^{-1} was used to determine the pressure of ethylene at a given time. The total time of ethylene exposure to the CO reduced Phillips catalyst was 4 h.

3 Results

3.1 Infrared Studies of Ethylene Contacted Phillips Catalyst

We synthesized CO-reduced [25, 26] Phillips catalyst with 1 wt% chromium on Sylopol-948, high surface area silica that fragments under gas phase polymerization conditions. These materials polymerize ethylene under low ethylene pressure to form HDPE without a noticeable induction period, and under low ethylene pressure we obtained an initial rate of 19 kg PE Cr^{-1} h^{-1} at 70 °C.

The IR spectrum of the ethylene exposed CO-reduced Phillips catalyst contains intense υ_{CH} and δ_{CH} bands at

Fig. 2 OH-region of the transmission IR spectra of the CO-reduced Phillips catalyst before **a** and after treatment with C_2H_4 **b** or C_2D_4 **c** respectively. The insert **d** shows the OD-region of the IR of CO-reduced Phillips catalyst treated with C_2D_4
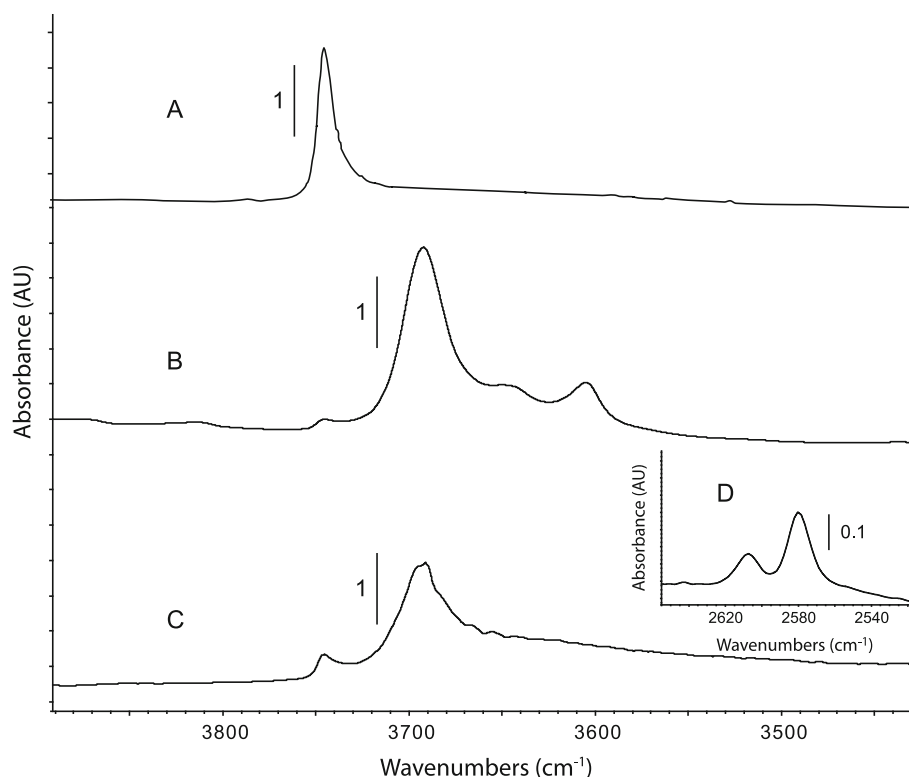
3,000–2,800 and 1,470 cm^{-1}, respectively, after contacting the material with ethylene that are indicative of PE on the silica surface. The OH region of the IR spectrum contains a series of vibrations at 3,745, 3,692, 3,646, and 3,605 cm^{-1} (Fig. 2). The band at 3,745 cm^{-1} is consistent with isolated silanols, which are also present before ethylene treatment in the pristine CO-reduced Phillips material. After polymerization, the band is shifted to 3,692 cm^{-1} and corresponds to silanols interacting with alkyl chains [27]. Noteworthy are the two red-shifted OH vibrations in Fig. 2b at 3,646 and 3,605 cm^{-1}, at positions nearly identical to what is observed on well-defined Cr(III) silicate [15], and assigned to silanols interacting with a nearby Lewis-acidic chromium center [18].

The pristine CO-reduced Phillips material does not contain red-shifted silanol vibrations at 3,646 and 3,605 cm^{-1}, which suggests these signals originate from ethylene. In fact, contacting the CO-reduced Phillips catalyst with ethylene-d$_4$ gives an IR spectrum that lacks signals at 3,646 and 3,605 cm^{-1}, but does contain new OD vibrations at 2,607 and 2,580 cm^{-1} as expected from the harmonic oscillator approximation (2,604 and 2,575 cm^{-1}). This result indicates that these red-shifted silanol vibrations originate from ethylene. A mechanism consistent with these spectral features would be the heterolytic C–H activation of ethylene over a Cr–O bond in these materials that would form a chromium-vinyl species (Fig. 1a) that is capable of inserting ethylene to grow the

polymer chain by a Cossee-Arlman mechanism while conserving the Cr oxidation state. Though heterolytic C–H activation is common on M–O bonds of oxides [28, 29], to the best of our knowledge this type of activation was not invoked in Phillips catalyst polymerization initiation.

4 Discussion

Phillips catalyst is a very important industrial ethylene polymerization catalyst that has a rich history in academic research due to the mystery surrounding the active site and initiation mechanism. Over the past 60 years several polymerization initiation mechanisms were reported, most involving Cr(II/IV) intermediates. However, Cr(III) is in fact detected as a minor species on all "reduced" Phillips catalysts by EPR spectroscopy [30], including the samples studied here. This study shows that heterolytic C–H activation of ethylene is likely a key step in ethylene polymerization, a mechanism that conserves the Cr-oxidation state during catalysis. Heterolytic C–H activation is common on supported metal species, and is probably a key step in alkane dehydrogenation using Cr(III)/Al$_2$O$_3$ catalysts [31], C–H activation on alumina surfaces [32–34], hydrogenation reactions involving supported chromium species [35], and in ethylene polymerization on well-defined Cr(III)-silicates [15]. In addition, the presence of Cr(III) sites according to EPR and the striking similarity of the IR

signatures in Phillips catalyst that implicate heterolytic C–H activation, as previously observed on the well-defined Cr(III) silicate, suggest that initiation takes place via the C–H bond activation of ethylene on a Cr–O bond and that the active site in Phillips catalyst may in fact be Cr(III) and not Cr(II). This mechanistic insight may provide new opportunities to manipulate the active site in Cr-silicates to access polymers with novel architectures with a wider range of properties.

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