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Ethene oligomerization on nickel microporous and mesoporous-supported catalysts: Investigation of the active sites

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ABSTRACT

Nickel-containing mesoporous (using Al₂O₃ or SiO₂-Al₂O₃ support) and microporous (using nano- or micro-crystalline Beta zeolite support) catalysts were prepared by ion exchange and characterized by XRD, SEM, N₂-adsorption, MP-AES and FTIR. The samples were subjected to testing as ethene oligomerization catalysts at T = 120 °C, P_{total} = 29 bar, P_{ethene} = 11.6–25.1 bar. All catalysts were active for ethene oligomerization, and linear butenes were the main gaseous products. However, catalyst deactivation due to retained long-chain alkenes was observed. Ethene partial pressure variation experiments showed that the reaction order in ethene for butene formation was 1.5–1.7 for the mesoporous, and 2.0 for the microporous catalysts. Contact time variation experiments carried out with the microporous catalysts at P_{ethene} = 18 bar showed that product selectivity was independent of ethene conversion, and suggested that 1-butene and 2-butenes are primary products. This result is consistent with the Cossee-Arlman mechanism. The nature of the active sites was investigated with FTIR spectroscopy with CO as probe molecule. The results point to Ni²⁺-counterions as the preeminent active sites, while we suggest that Ni-sites grafted on silanol groups and NiO particles are spectators.

1. Introduction

The world is currently seeing a gradual shift from oil as the dominating source for transportation fuels and chemicals production to other alternative sources, such as natural gas, biomass and coal [1]. Traditionally, naphtha reforming has been the major source of low carbon olefins (C₂–C₆ alkenes), but the recent shift towards ethane cracking favors ethene production over the C₃–C₆ fraction. In addition, the demand for propene and butenes has increased more rapidly than the demand for ethene [2]. This led to a growing interest in selective oligomerization of ethene to C₄–C₈ products [3,4]. Ethene is among the most important base chemicals and has a worldwide production capacity over 130 million tons [2]. It is raw material for a wide range of products; reactions of ethene include oxidation, oligomerization and polymerization [4]. The commercial processes for ethene oligomerization utilize homogeneous catalysts (transition metal catalysts in organic solvents [5]). In these processes, a co-catalyst such as Al(C₂H₅)₃ is required to start the catalytic cycle. The mechanism of alkene oligomerization with homogeneous catalysts has been reviewed by McGuinness [5] and the two widely recognized mechanisms, metallacycle and

Cossee-Arlman, are shown in Scheme 1.

In recent years, significant effort has been made to develop heterogeneous catalysts for the ethene oligomerization reaction, as they potentially offer a more environmentally friendly alternative to the homogeneously catalyzed process [4].

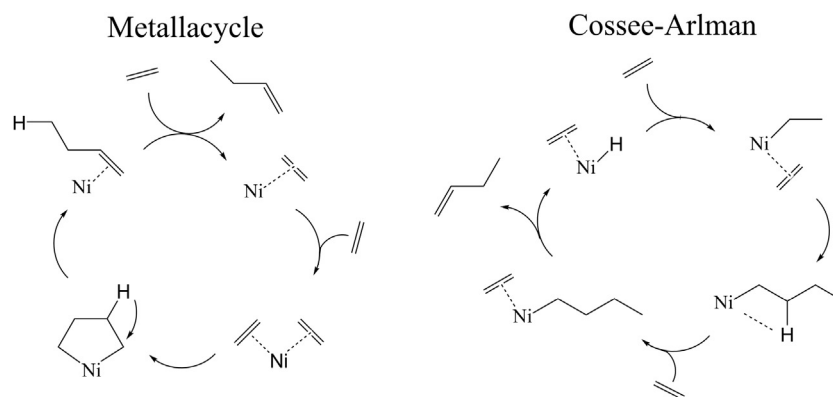
Nickel containing inorganic porous materials such as amorphous silica-alumina [6,7], ordered mesostructured materials [8–10] and Ni-zeolites [11–13] are regarded as the most promising candidates among the reported catalysts. Notably, all these catalysts are active without the use of a co-catalyst. The mesoporous catalysts are reported to perform better than microporous catalysts, which typically suffer from rapid deactivation due to blocking of micropores by alkenes formed during the reaction [12]. An exception is the nanocrystalline Ni-H-Beta zeolite, investigated at 120 °C and P_{ethene} = 26 bar, which was resistant to deactivation. The Ni-H-Beta catalysts were prepared by ion exchange of protons with Ni²⁺. For these catalysts, the activity was reported to increase linearly with increasing Ni loading until almost all of the acid sites were exchanged. Furthermore, for catalysts with Ni content ≤ 2% (i.e. with significant amounts of Brønsted acid sites remaining), approximately 93% selectivity towards even numbered alkenes with

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Scheme 1. The two widely recognized reaction mechanism for the homogeneously catalyzed oligomerization of ethene.

Schulz-Flory type distribution was observed, suggesting that the acid sites have negligible activity for oligomerization under these conditions. However, the observed branching among the even numbered products was ascribed to the acid sites [13].

A detailed kinetic study of the ethene oligomerization reaction was recently published by Toch et al. [14] who investigated Ni-SiO₂-Al₂O₃ catalyst between 170 and 230 °C and P_{ethene} from 1.5 to 3.5 bar. They observed that the catalyst was resistant to deactivation during 8 h on stream and due to the absence of strong acid sites, they concluded the catalytic activity to be solely from the nickel ion sites. The catalyst showed a Schulz-Flory type product distribution with about 90% selectivity towards butenes, while thermodynamic distribution was observed among the linear butenes. By combining experimentally obtained data with single event microkinetic modelling, they concluded the Cossee-Arlman mechanism to be more likely than the metallacycle mechanism because of the Schulz-Flory product distribution, without excluding the metallacycle mechanism completely [14].

Recently, Brogaard and Olsbye utilized molecular modelling to investigate the reaction mechanism of ethene oligomerization catalyzed by Ni-SSZ-24 zeolite, as well as the formation of the active site. After comparing three possible catalytic cycles, they concluded the most probable reaction path to be the Cossee-Arlman mechanism and that the support could be involved in the active site formation [15].

The metallacycle mechanism has recently been proposed for ethene oligomerization by Andrei et al. over Ni-ALSBA-15. The authors suggested two types of mechanisms: the metallacycle mechanism for oligomerization of ethene and a second mechanism based on acid catalysis for isomerization of products. The Cossee-Arlman mechanism was concluded as unlikely because of the absence of co-catalysts in these reactions [16].

The aim of the current study was to compare the performance of Ni-based catalysts based on zeolite supports and dense, mesoporous supports, respectively, under similar reaction conditions. A further aim of the study was to characterize the active sites of zeolite-based catalysts by FTIR spectroscopy and elucidate mechanistic details of the ethene oligomerization reaction through contact time variation experiments.

2. Experimental

2.1. Catalyst preparation

Microcrystalline NH₄-Beta zeolite ((Si/Al) = 19) was obtained from Zeolyst (CP-814C). The NH₄-Beta sample was calcined at 550 °C for 6 h using a heating rate of 1.5 °C/min to obtain the protonated form. The resulting material is denoted H-Beta(m).

Nanocrystalline Na-Beta zeolite (Si/Al = 13) was obtained from PQ. The Na-Beta sample was calcined at 550 °C for 3 h using a heating rate of 1 °C/min (denoted Na-Beta(n)) before ion exchange. The catalyst was

subjected to three consecutive ion exchanges with 1 M NH₄NO₃ at 70 °C for 2 h using a liquid to solid ratio of 20 cm³/g, then dried overnight. The exchange was then followed by calcination at 550 °C for 8 h, using a heating rate of 5 °C/min to obtain the protonated form. The resulting material is denoted H-Beta(n).

The nickel ion exchanged zeolite samples were prepared as described by Martinez et al. [13]. The zeolite sample was subjected to four consecutive ion exchanges with intermediate drying steps at 100 °C. The exchanges were carried out with 0.1 M aqueous solution of Ni(NO₃)₂ at 70 °C for 4 h using a liquid-to-solid-ratio of 10 cm³/g. Subsequently, the material was calcined at 550 °C for 3 h using a heating rate of 1 °C/min. The material obtained by ion exchange and calcination of H-Beta(m) is denoted Ni-H-Beta(m). The material obtained by ion exchange and calcination of Na-Beta(n) is denoted Ni-H(Na)-Beta(n)(2), while the material obtained by ion exchange and calcination of H-Beta(n) is denoted Ni-H-Beta(n) and Ni-H-Beta(n)(2) with 2 and 4 wt% Ni, respectively.

2 wt.% NiSO₄-SiO₂-Al₂O₃ and 2 wt.% NiSO₄-Al₂O₃ catalysts were prepared as previously described in detail by Lu et al. [17]. SiO₂-Al₂O₃ and γ-Al₂O₃ supports were impregnated with an aqueous solution of nickel sulfate (NiSO₄) followed by drying over night at 105 °C and calcination in air at 400 °C for 2 h.

2.2. Catalyst characterization

The phase identification of the zeolite samples was performed by X-ray powder diffraction (PXRD) measurements. A Bruker D8 Discover diffractometer was employed, using Cu K_α radiation (λ = 1.5406 Å). The textural properties of the samples were derived from N₂ adsorption isotherms, measured at -196 °C, using a BELSORP-mini II instrument. All samples were outgassed in vacuum for 1 h at 80 °C and 3 h at 300 °C, and then measured. The catalyst pore volumes and surface areas were determined using the t-plot and BET methods. Scanning electron microscopy (SEM) was performed by using a Hitachi SU8230 microscope; the characterization parameters are included in the images. Elemental analysis was performed on Agilent 4100 MP-AES instrument after dissolving the catalyst in 1 mL 15 wt% HF.

The nature of the active sites was investigated by FTIR spectroscopy. The experiments were carried out in transmission mode using a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with a mercury cadmium telluride (MCT) cryodetector working with 2 cm⁻¹ resolution. Thin self-supporting wafers of each sample (H-Beta(m) and Ni-H-Beta(m)) were placed inside a flow IR cell designed to allow high temperature treatment under gas flow and ex-situ low-temperature IR measurements. Prior to adsorption experiments, samples were thermally treated in He flow (50 mL/min) up to 300 °C and left at this temperature for 3 h, in order to mimic the activation conditions used in the catalytic tests. In order to investigate the role of Ni sites in the oligomerization reaction, in one experiment Ni-H-Beta(m) sample was

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