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Removal of cyclopentadiene from 1-octene by transition metal containing zeolites. Part 1: Screening of the adsorption properties

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Abstract

Catalyst activities in olefin (co)polymerisation can be reduced by feed impurities. In the present work, a series of metal exchanged zeolites was tested for the removal of cyclopentadiene from 1-octene. Initial screening was performed at room temperature with a number of (transition) metal exchanged zeolites using 1-octene containing 1000 or 10,000 wt.ppm cyclopentadiene. From these experiments it was concluded that NaX zeolites ion exchanged successively with Ca and Co ions using an intermediate calcination were promising materials. Optimal activation conditions for the CoCaX samples were determined and resulted in the zeolite pretreatment at 500 °C in an oxygen atmosphere. Adsorption isotherms of cyclopentadiene in 1-octene on Ca, Co, and Ag containing NaX zeolites and related materials were recorded, confirming the superior behaviour of a zeolite NaX successively exchanged with Ca and Co ions using an intermediate calcination. Breakthrough experiments using 1-octene feeds containing about 100 wt.ppm cyclopentadiene also demonstrated that this zeolite allowed purification of octene spiked with cyclopentadiene to a concentration below 0.1 wt.ppm.

Keywords: Cobalt; Zeolites; Adsorption; 1-Octene; Cyclopentadiene; Purification

1. Introduction

Olefin polymerisation catalysts require olefin monomer feedstocks of high purity [1–4]. However, monomers used in polymerisation processes often contain impurities, which could poison the catalysts and are difficult to remove adequately by distillation, selective hydrogenation or adsorption. Adsorbents like zeolites exchanged with alkali and alkaline earths, mainly showing Van der Waals interactions between framework and sorbate, are not sufficiently selective for the complete removal of less polar contaminants like dienes, *viz.* cyclopentadiene (CPD) [5]. Separation via more specific interactions between adsorbent and adsorbate, can constitute a promising alternative.

During complexation of unsaturated hydrocarbons by transition metals the metal's d-orbitals can participate in bond-formation with the π-electrons of the ligand [6]. In this respect the removal of unsaturated hydrocarbons with Ag^+ ions is documented [5,10–13]. Moreover, CPD and its derivatives, an important class of ligands in metal-organic chemistry, strongly interact with transition metals through η^1–η^5 bonding modes [7,8]. The formation of an especially strong η^5-cyclopentadienyl-cobalt complex is well-known in literature [9], making Co a promising candidate for CPD removal.

The cation distribution in aluminosilicate zeolites is dependent upon topology and composition. For identical frameworks the maximum number of adsorption sites

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should relate to the number of active transition metal ions and therefore should increase for materials with lower silica/alumina ratio, *viz.* X compared to Y zeolites. To confirm this statement, the evaluation of a series of (transition) metal exchanged zeolites with different topology and Si/Al ratio for their potential to remove CPD from 1-octene is reported in the present work. Co, Ni and Ag exchanged high-alumina zeolites were chosen as candidates for site-specific interaction.

The design of Al-rich zeolite adsorbents requires that a few general rules on cation distribution over hidden and accessible sites including their effects on lattice stability are taken into consideration. In faujasite X and Y-type zeolites, bivalent ions upon dehydration often move from the supercavity (SC) to hidden sites in the centre of hexagonal prisms (SI). The preferred cation positions in dry zeolites are usually in the hexagonal prisms (SI), or close to single six-rings in sodalite cages (SI′) and in supercavities (SII) [14]. The well-known preference of a number of divalent ions for SI is less pronounced with Ni and Co ions, possibly due to the retention of extra-framework oxygen stemming from hydration water hydrolysis and the strong interaction with the single six-rings of zeolites [15,16]. Direct exchange of Na by Co in NaX is known to have a negative effect on the material stability. Co^{2+} has been shown to distort the six-rings of zeolites [16]. Hydrolysis of the hexaquo-complex of Ni and with high probability also Co during exchange leads to de-alumination and eventually destruction of zeolites with high Al content [17–20]. Taking all this into account, a NaX zeolite, with 86 cation sites per unit cell was first exchanged for 50% with Ca ions, calcined to increase stability, and then exchanged with Co [21].

2. Experimental

2.1. Materials origin, modification and nomenclature

Powder samples of zeolite NaX and NaY from Chemie Uetikon AG (CU), with the following anhydrous unit cell (UC) composition, respectively:

$Na_{86}Al_{86}Si_{106}O_{384}$ $Na_{54}Al_{54}Si_{138}O_{384}$

were used as starting materials. A number of experiments were performed with zeolite NaA (type 3A) from CU and zeolite KL from the former Union Carbide Corp. (Antwerp) with the following anhydrous UC composition, respectively:

$Na_{24}Al_{11.4}Si_{12.8}O_{48}$ $K_9Al_9Si_{27}O_{72}$

The parent zeolites were stored at room temperature in a desiccator over a saturated aqueous NH_4Cl solution, ensuring equilibration with water vapour at saturated humidity, thus avoiding water vapour sorption when handling samples in the open atmosphere.

Aqueous chloride solutions of transition metals (0.05 M) were used during the ion exchange procedure to avoid structural damage of the zeolite matrix and introduction of acidity through hydrolysis of the transition metal ion hydration complex at pH values <6 [20]. After ion exchange, the samples were washed till chloride-free, air dried at 60 °C and stored in inert atmosphere. Subsequent ion exchanges were performed in the same conditions after calcination of the dried sample at 500 °C under flowing oxygen.

A typical sample denoted as CoCaX50 indicates that NaX zeolite was first exchanged with a volume of a 0.1 M aqueous $CaCl_2$ solution to obtain a 50% degree of Ca^{2+} for Na^+ exchange, assuming complete Ca uptake. The CaNaX50 sample thus obtained was washed till Cl^- free, dried at 60 °C and calcined at 500 °C for 20 h, using a linear increase of sample temperature of 1 °C per minute. The CaNaX50 sample was exchanged with such a volume of 0.05 M aqueous $CoCl_2$ so as to obtain 50% exchange of the cation exchange capacity (CEC), then washed and dried at 60 and 150 °C. It was stored in inert atmosphere and transferred water-free to the sorption unit(s). Samples denoted as CoNaX100 and CoNaY100 were only exchanged for about 70% of the CEC using adequate amounts of a solution of 0.05 M $CoCl_2$. Samples of TS-1 and Ti-MCM were synthesised according to established methods [22,23].

The cation content of the samples was measured with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after dissolution of the zeolite samples in concentrated sulphuric acid. Phase purity and degree of crystallinity of all samples was estimated by X-ray diffraction (XRD) by comparison the peak intensities to those of reference samples. Cation distribution over hidden en accessible sites was obtained according to literature (Table 1). For CoCaX50, the position of Ca^{2+} and Co^{2+} ions was determined via Rietveld analysis of X-ray powder diffraction data.

2.2. Fourier transform infrared (FTIR) spectroscopy

Adsorption of CO at room temperature on CoCaX50, CoNaX25, CoNaX50 and CoNaX100 samples precalcined at 500 °C was studied in a flow cell, positioned in the sample compartment of a Nicolet 730 FTIR spectrometer. Self-supporting wafers containing 5 ± 1 mg/cm^2 were suspended in the IR cell, perpendicular to the IR beam. All sample pretreatments were done *in situ* in this cell. Measurements were also performed on a CoCaX50 sample predried at 500 °C in flowing nitrogen and on a CoCaX50 sample precalcined at 400 °C in flowing air. IR spectra were collected at room temperature under a continuous flow of 0.1 vol.% CO in N_2. Errors on integrated peak areas in the 2000–2400 cm^{-1} range (via repeated experiments) were determined to be below ±5%.

2.3. Thermogravimetric analysis

The weight change of a CoCaX50 sample subjected to different pretreatment conditions was monitored in a TGA Q500 thermoanalyzer. In a first step, moisture equil-