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Comparison of differently synthesized Ni(Al)MCM-48 catalysts in the ethene to propene reaction

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ABSTRACT

MCM-48 has been prepared by four synthesis routes varying in hydrothermal treatment, pH, surfactant and silica source. These materials have been functionalized with nickel and aluminum via incipient wetness impregnation (IWI) and template ion exchange (TIE). The support and the final catalysts were characterized using nitrogen physisorption, powder X-ray diffractometry (PXRD) and ICP-OES. Textural analysis showed that the definite structure of the support was retained with IWI and was partly affected by TIE. Upon IWI small nickel oxide particles on the surface were formed, whereas with TIE no nickel-related crystalline phases could be detected. The optimal nickel and aluminum loadings were found for IWI- and TIE-MCM-48 concerning the catalytic activity in the ethene to propene reaction (ETP). With ethene conversion of over 40% propene selectivity of up to 56% could be reached with IWI and TIE catalysts. The preparation method of the MCM-48 had more influence on the activity of the TIE catalysts than of the IWI ones.

1. Introduction

Propene is after ethene the second most important basic organic chemical. The demand of propene is constantly increasing due to the growing need of polypropylene and propylene oxide. Propene is mostly obtained as byproduct during steam cracking of naphtha to ethylene and catalytic cracking of crude oil into petroleum fractions in refineries [1]. A more sustainable route for the production of propene would be the conversion of biomass to propene using ethanol as a feedstock, which can be easily transferred to ethene. The challenging step would be the reaction from ethene directly to propene. For this process heterogeneous catalysts like SAPO-34 [2–5], ZSM-5 [6] and alumina supported tungsten hydride [7] have been studied. Furthermore, MCM-41 functionalized via template ion exchange (TIE) [8–11] or equilibrium adsorption [12] catalyzes the ETP reaction. Feeding ethanol, results using Ni-MCM-41 (TIE) [13] and Ni-FSM-16 (TIE) [14] are as well published. The reaction pathway for nickel on MCM-41 was postulated by Iwamoto and Kosugi [8] to consist of ethene dimerization to 1-butene, which isomerizes to *cis*- and *trans*-2-butene. The last step would comprise then the olefin metathesis reaction of ethene with 2-butene to form propene. Using SAPO-34 and ZSM-5, the reaction mechanism was concluded to occur presumably via ethene oligomerization and consecutive cracking to propene due to shape selectivity of the pores [3].

The focus in the present study is set on Ni/MCM-48. MCM-48 was discovered in the early nineties and is part of the M41S family which is in the following way classified: a hexagonal (MCM-41), a cubic (MCM-48) and a lamellar phase (MCM-50) [15]. MCM-48 could be assigned to the space group *Ia3d* with a 3d network containing channels running along [111] and [100] [16]. MCM-48 synthesized after different preparation methods was functionalized via template ion exchange (TIE) and incipient wetness impregnation (IWI). These materials were characterized via nitrogen physisorption, powder X-ray diffractometry (PXRD) and optical emission spectroscopy with inductively coupled plasma (ICP-OES). Catalytic activity in the ETP reaction was determined and compared with respect to the applied preparation techniques and to the obtained characterization results.

2. Experimental section

2.1. Synthesis

V-MCM-48 synthesis [17]: A solution of 21.1 g of HDTMABr (hexadecyltrimethyl-ammonium bromide) (Merck), 0.3 g of sodium chloride (Merck) and 67.5 g of deionized water were mixed with 17 g of ethanol (Merck) and 1.0 g of concentrated hydrochloric acid (Merck). The mixture was stirred for 30 min and a solution, consisting of 20.5 g of sodium silicate (Merck) and 20.5 g of deionized water, was added and stirred for 15 to 30 min. The resulting gel was aged for 72 h at 100 °C, filtered, washed with water and tried at room temperature. Finally, the material was calcined at 550 °C for 7 h in synthetic air (Westfalen Gas, purity: 99.9%).

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H-MCM-48/D-MCM-48 synthesis: 9.32 g of potassium hydroxide (Merck) were solved in 372 mL of deionized water. This solution was mixed with 74 mL of TEOS (tetraethyl orthosilicate) (Merck) and was stirred for 10 min. 78.8 g of HDTMABr or CTMABr (cetrimonium bromide) (Merck) was added und the resulting suspension was stirred for another 30 min at room temperature. The gel was aged for 72 h at 95 °C, filtered and washed with water. The recovered solid was calcined at 550 °C for 6 h in synthetic air.

S-MCM-48 synthesis [18]: 2.6 g of HDTMABr was added to a mixture of 50 mL of technical ethanol, 15 mL of concentrated ammonia (Merck) and 120 g of deionized water. The suspension was stirred heavily for 10 min. 3.4 g of TEOS was inserted and stirred for 6 h at room temperature. The solid was filtered, washed with water and calcined at 550 °C for 6 h in synthetic air.

Impregnation: nickel/aluminum nitrate (Merck, Riedel-de Haën) was solved in water and this solution was slowly added to the support. The material was dried at 120 °C over night and calcined at 550 °C for 6 h in synthetic air. Nickel citrate was synthesized with following method [19–20]. Nickel carbonate (Alfa Aesar) was mixed with water and heated under reflux to 100 °C. Then, citric acid (Merck) was added in the molar ratio to nickel carbonate of 3–2. The solution was cooled to room temperature and was used for impregnating MCM-48.

Template ion exchange: 20 mL of a 0.01–0.05 M nickel nitrate solution were added to 1 g of uncalcined MCM-48. The suspension was stirred at 80 °C for 1 h, aged without stirring for 24 h at 100 °C and filtered. The solid was washed with water and dried. To 1 g of this recovered solid, 6 mL of a 0.01–0.05 M aluminum nitrate solution were inserted, stirred at 80 °C for 1 h, aged for 24 h at 105 °C and filtered. The material was washed with water, dried and calcined at 550 °C in synthetic air.

2.2. Characterization

Nitrogen physisorption analysis was accomplished at −196 °C with a Nova4000e Surface Area & Pore Size Analyzer set-up from Quantachrome Instruments. Prior to measurement the solids were outgassed at 250 °C in vacuo. Surface areas, pore diameters and volumes of the materials were calculated using standard BET and DFT theory, respectively.

Powder X-ray diffractometry (PXRD) was performed using a Philips X'Pert 3040 MPD Pro DY 1467. Cu-K_α radiation with a wavelength of 1.54 Å was applied.

For optical emission spectroscopy with inductively coupled plasma (ICP-OES) a SpectroFlame FTMOA81A from Spectro Analytical Instruments was used for determining the nickel content of the samples.

2.3. Catalytic testing

The ETP reaction was performed at atmospheric pressure in a single-pass fixed bed reactor (quartz tube, inner diameter: 1 cm, length of catalyzed bed: 1.4 cm). The reactor was loaded with 400 mg of catalyst, which was pelletized into 350–500 μm pellets. Each catalyst was heated in helium flow to 500 °C in 3 h and held at this temperature for at least 2 h. Then, the catalyst was cooled to the reaction temperature of 350 °C. The reaction feed was composed of 3% ethene (Westfalen Gas, purity: 99.5%) and 97% helium (Westfalen Gas, purity: 99.999%) with a total flow rate of 13 mL/min. All experimental data were obtained after 4 h of continuous services. The products were analyzed on-line in a gas chromatograph (Shimadzu GC-14B).

The conversion of ethene (X), the yields (Y) and the selectivity (S) of the products were calculated using the following equations:

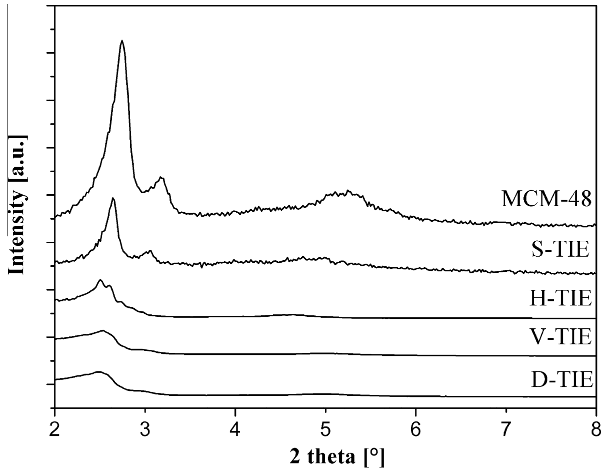

Fig. 1. Representative low angle X-ray diffraction patterns of MCM-48 and TIE-MCM-48.

$$X = \frac{\dot{n}_{\text{ethene},0} - \dot{n}_{\text{ethene}}}{\dot{n}_{\text{ethene},0}} \quad Y = \frac{\dot{n}_{\text{product}} - \dot{n}_{\text{product},0}}{\dot{n}_{\text{ethene},0}} \cdot \frac{|\nu_{\text{ethene}}|}{|\nu_{\text{product}}|} \quad S = \frac{Y}{X}$$

with n is the amount [mol] and ν the stoichiometric coefficient.

3. Results and discussion

3.1. Characterization of MCM-48

MCM-48 was prepared using four different synthesis instructions [17–18]. They differed in duration and temperature of hydrothermal treatment, silica source (TEOS or sodium silicate), chosen pH value (acidic or basic) and structure directing surfactant (HDTMABr or CTABr). The quality and structural ordering of these as-synthesized MCM-48 materials were obtained via powder X-ray diffraction and nitrogen physisorption. Each calcined silica sample exhibited the same characteristic low angle XRD pattern (Fig. 1), in which the four diffraction peaks (2 1 1), (2 2 0), (4 2 0) and (3 3 2) [21] can be clearly distinguished. Nitrogen physisorption data are listed in Table 1 and sorption isotherms are shown in Fig. 2. All samples possess a narrow pore size distribution and lack any noticeable hysteresis in the type IV isotherms (IUPAC classification [22]). Between p/p_0 0.20–0.35 a well-defined step occurs, caused by spontaneous filling of the mesopores due to capillary condensation. The BET surface areas for all samples were over 1000 m^2/g and the pore diameter was in the range of 3.4–3.6 nm.

3.2. Impregnated MCM-48

All calcined MCM-48 materials were impregnated with different amounts of nickel nitrate and aluminum nitrate. Nitrogen physisorption analysis indicated a minimal shrinkage of the BET surface area, pore diameter and pore volume (Table 1) during incipient wetness impregnation. No destruction of the well-defined pore structure occurred. In Fig. 3 the sorption isotherms of H-IWI impregnated with different amounts of nickel nitrate are shown. The steps shrank with higher nickel loading due to the decrease of BET surface area. After calcination of the impregnated materials small nickel oxide particles are formed inside and outside the pore system of the support reflecting physisorption analysis. The structural integrity of the IWI-MCM-48 was also proved with low angle XRD measurements. The nickel oxide particle size (nickel loadings over 1 wt.%) can be measured with PXRD (Fig. 4). As Lensveld et al. [19–20] have demonstrated with MCM-41 as support, the nature of the nickel precursor influences the dispersion, average particle