The role of different Ni sites in supported nickel catalysts for butene dimerization under industry-like conditions

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ABSTRACT

An industrial 20% NiO/SiO$_2$–Al$_2$O$_3$ catalyst and model systems prepared by impregnation of two differently acidic SiO$_2$–Al$_2$O$_3$ supports with Ni(Cp)$_2$ or Ni(COD)$_2$ have been analyzed by spectroscopic in situ studies and catalytic CSTR tests during butene oligomerization under industrially relevant conditions. Active and selective sites for linear C$_8$ target olefins are single Ni^{n+} species (n = 1 and/or 2) which form during conditioning by oxidative addition of Brønsted sites to Ni^0 precursor species. This is connected with a switch from an acid-catalyzed ionic mechanism to a metal-catalyzed coordinative mechanism, which shifts the product composition from strongly branched olefins to more linear olefins. Deactivation at extended times on stream is due to reaggregation of the active Ni single sites to Ni^0 clusters. Operando EPR performed for the first time in flowing butenes at 20 bar clearly shows that such clusters are not active. Brønsted sites play a crucial role in stabilizing the Ni single sites.

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1. Introduction and objective

Since about 60 years [1], even more than a decade before the detection of the so-called "nickel effect" by Ziegler, nickel-containing catalysts are being used for the oligomerization of n-butenes in both homogeneous and heterogeneous catalytic processes. While the homogenous DIMERSOL™ process is performed over nickel complexes in the presence of organo-aluminium activators as catalysts, the heterogeneous OCTOL™ process is performed over supported NiO/Al$_2$O$_3$–SiO$_2$ catalysts at reaction temperatures of 343 to 393 K in the liquid phase using the C$_4$ fraction from the steam cracker (raffinate III) as feedstock [2]. The product composition strongly depends on the surface acidity of the catalysts. Highly acidic catalysts with a low Ni/Al ratio preferentially produce undesired strongly branched products such as dimethylhexenes and higher oligomers via a carbenium ion mechanism, while materials with a lower acidity (higher Ni/Al ratio) show a high selectivity to the target products n-octenes and methylheptenes [3].

Over optimized catalysts, on which a Ni-catalyzed coordinative mechanism is predominant, typical C$_8$ selectivities of ≈80% are obtained at a conversion of ≈45% to 47%, and the C$_8$ fraction consists typically of 13% n-octenes, 62% methylheptenes and 25% dimethylhexenes [2]. However, it has also been shown that the behaviour of the supported NiO/Al$_2$O$_3$–SiO$_2$ catalysts is strongly dynamic, espe-

cially within the first several hours on stream. The product composition in the initial reaction period reflects a predominating carbenium ion mechanism with a high dimethylhexene selectivity which is gradually replaced by a metal-catalyzed mechanism leading to far more linear products in due course [4]. This suggests that during the conditioning period the nature of the active sites may change too, yet little is known about this change.

The product composition over optimized supported NiO/Al$_2$O$_3$–SiO$_2$ catalysts is very similar to that obtained in the homogeneous butene dimerization process [4]. This suggests that the reaction mechanism and the properties of active Ni sites might also be similar in both cases. In general, a Ni$^+$–H species is considered to be the active site in the homogeneous olefin oligomerization process in which two butene molecules are inserted subsequently and the final olefin product is eliminated by β-H elimination which is assumed to restore the active Ni$^+$–H species [5–8].

For heterogeneous catalysts, the structure and valence state of the active nickel sites as well as the mechanism of their formation from precursor species are still not well understood. In early studies of supported NiO/Al$_2$O$_3$–SiO$_2$ catalysts, a layered nickel aluminosilicate was suggested as the active phase with coordinatively unsaturated Ni^{2+} as the active sites [9]. In Ni-exchanged Y zeolites, Ni$^+$ and superparamagnetic Ni^0 species were detected by EPR spectroscopy after interaction of the zeolite with 1-butene [10], from which it was concluded that either Ni$^+$ or both these species could be the active sites in olefin oligomerization. EPR-active Ni$^+$ sites were also detected in prereduced NiCaY zeolites, and a linear relation was

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found between their concentration and the conversion in ethylene oligomerization [11]. In situ EPR studies of NiCaX and Ni/SiO$_2$ catalysts in the presence of C$_2$–C$_6$ linear olefins have shown that the latter adsorb on Ni$^+$, shifting the parallel component of the g tensor to values below 2.0 [12]. This was also found for a supported 10 mol% NiO/Al$_2$O$_3$–SiO$_2$ catalyst after pretreatment in vacuum and adsorption of up to 80 kPa of different butenes at 470 K. The resulting EPR signals were assigned to Ni$^+$–butene complexes. Based on these results, Ni$^+$ was claimed to be the active site in butene oligomerization [13]. Reduction to Ni$^+$ was also detected in supported NiSO$_4$/γ-Al$_2$O$_3$ both after evacuation at 873 K and after interaction of the prereduced catalysts with ethylene or propylene at room temperature. Interestingly, no Ni$^+$ was detected upon interaction with 1-butene, therefore Ni$^+$ was excluded as the active site for butene oligomerization [14]. Finally, it should be mentioned that highly dispersed Ni^0 was also suggested as the active site in oligomerization of ethylene over NiY catalysts [15].

It is the aim of this work to shine light upon the way of the formation of Ni$^+$ and Ni^0 sites in supported nickel catalysts and their role in the heterogeneous n-butene oligomerization process. Therefore, the catalytic reaction has been studied in a continuous stirred tank reactor (CSTR) containing the bare support, while the active catalyst was created in situ by stepwise dosage of the Ni component. For the first time, operando high-pressure EPR measurements of working catalysts have been performed under reaction conditions as close as possible to those of the industrial process to monitor the behaviour of Ni^0 clusters, while Ni$^+$ was analyzed in catalysts quenched after different times on stream at 77 K. Moreover, the influence of acidic sites on the structure of Ni species was analyzed by in situ FTIR spectroscopy. By integrated evaluation of catalytic and spectroscopic results, detailed knowledge on the desired and detrimental properties of these catalysts should be obtained, which can help to improve their catalytic performance, in particular, the selectivity to linear C$_8$ products.

2. Experimental

2.1. Catalysts

An industrial NiO/SiO$_2$–Al$_2$O$_3$ catalyst with 20 wt.% NiO (NiO/SiAl-1) prepared by the precipitation of nickel carbonate on an acidic silica-alumina support (SiAl-1, Si:Al $\sim$ 6) followed by subsequent calcination in a N$_2$ flow at 873 K was obtained from Oxeno. The same SiAl-1 support as well as a silica–alumina support with a lower acidity (SiAl-2, Si:Al $\sim$ 20) was used for the in situ formation of the active catalyst during the CSTR tests by stepwise dosage of solutions of bis-cyclopentadienyl nickel, Ni(Cp)$_2$, or bis-cyclooctadienyl nickel, Ni(COD)$_2$, as well as for the preparation of catalysts for spectroscopic studies. For in situ EPR studies, the support materials were pressed into tablets, crushed, and sieved to obtain particle fractions of 0.3 to 0.8 mm diameter, which were heated for 2 h in dry H$_2$ and for further 3 h in dry air flow at 873 K to remove impurities. The thus-pretreated supports were transferred into a glove box, impregnated with solutions of Ni(Cp)$_2$ or Ni(COD)$_2$ in dry heptane to achieve Ni loadings of 0.05 to 6.0 wt.% and dried by volatilization of the solvent overnight at room temperature. The thus-prepared catalysts are labelled in due course as xNi/SiAl–y(C), where x denotes the Ni loading in wt.%, y = 1 or 2 refers to the kind of the support and C=Cp or COD indicates the nickel source. For in situ FTIR studies, self-supporting wafers of the supports pretreated at 873 K in H$_2$ and air flow were heated again for 10 min in vacuum at 673 K within the FTIR cell. The cell was then transferred to the glove box, and the wafers were removed and impregnated with the Ni complex solution. After drying in

the glove box at room temperature for a short period , the wafers were remounted into the FTIR cell. Prior to the respective experiments, the residual heptane was removed by evacuation of the FTIR cell at room temperature.

2.2. CSTR experiments

Twenty-five grams of the powdered Ni-free support were dispersed in about 200 ml of butane in a completely flooded CSTR. The catalyst was retained by a fine filter membrane installed so close to the stirrer blades that the formation of a filter cake was prevented by the high shear. The liquid phase was exchanged at a rate of 5 ml/min resulting in a residence time of about 40 min. Ideal CSTR behaviour of the equipment had been verified previously by monitoring with alkane exchange. As feedstock dry raffinate III was used (typical composition: 0.1% isobutene, 19.6% n-butane, 30.5% trans-butene, 14.2% cis-butene, 35.2% 1-butene and 0.19% isobutene). Ni(Cp)$_2$ or Ni(COD)$_2$ solutions (1% in heptane) were dosed into the feed stream in 8 ml portions every 10 min via a dosage slope. The composition of the effluent was analyzed every 30 or 60 min for oligomerisates by liquid dosage to a hydrogenating GC equipped with a DB-1 capillary column (Agilent Nr. 127-1013-E, 10 m × 0.1 mm) and a Pt catalyst in the injector section. For C4 analysis, the stream was evaporated and injected into a 30 m × 0.25 mm HP-Al/S capillary column as a gas to prevent column plugging by highly boiling components.

2.3. EPR measurements

Operando EPR measurements were performed using ca. 100 mg of catalyst particles placed in a tubular quartz plug-flow reactor having a 2.5-mm inner diameter and 1.5-mm wall thickness which was directly implemented in the cavity of a Bruker ELEXSYS 500-10/12 cw-EPR spectrometer and connected by Swagelok fittings to a liquiflow meter at the inlet and a pressure controller at the outlet for maintaining a pressure of 20 bar inside the reactor. Heat was transferred to the reactor by a preheated stream of nitrogen [16]. The catalyst was heated in a dry N$_2$ flow for 10 min at 353 K before pressurizing at this temperature with 20 bars of the reactant mixture.

The same raffinate III mixture as in the CSTR tests was also used as the reactant feed in the operando EPR experiments. This mixture was passed over molecular sieve 5 A to remove traces of moisture before allowing it to enter into the reactor. In a typical run, 1.9 to 2.0 g/h of raffinate III was passed over 80 to 100-mg catalyst particles at 353 K for several hours, and spectra were recorded at this temperature after different time intervals. The product mixture leaving the reactor was expanded to normal pressure and passed through a cold trap at 273 K. The C$_4$ hydrocarbons not condensed in the cold trap were analyzed by on-line GC. The C$_8$ olefins were collected in the cold trap for distinct periods of time and analyzed off-line. The same conditions as for the analysis of the CSTR products have been used.

For detecting Ni$^+$ species, the reaction was stopped after different periods of time by cooling to room temperature and expanding to normal pressure. The reactor was transferred to the glove box, and the catalysts were filled into normal EPR tubes, sealed and measured at 77 K using a finger dewar filled with liquid nitrogen.

Computer simulation of EPR spectra was performed with the program SIM14S of Lozos et al. [17] using the spin Hamiltonian

$$H = \mu_B \cdot S \cdot g \cdot B_0 \tag{1}$$

where μ_B is the Bohr magneton, S is the electron spin operator, g is the g tensor and B_0 is the magnetic field vector.