Direct Synthesis of Propene Using Supported Bifunctional Nickel Catalysts – Preparation and Potential

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Summary

A number of catalyst systems have been prepared for the direct conversion of ethene to propene. The catalysts were comprised of nickel species on mesoporous MCM-41. Different nickel precursors and preparation methods were employed. The catalysts were analyzed using XRD, TEM, EDX, BET, TPR and ICP. Additionally, catalytic tests were conducted. The best catalyst system exhibited an ethene conversion of 51 % and a propene yield of 23 %.

Keywords

Rational design of catalysts.

Unlike ethene, propene is merely a side product when it comes to huge industrial processes like steam cracking or catalytic cracking. The availability and production capacity of propene is therefore to a large extent directly coupled with the demand for ethene. However, the demand for propene has been constantly growing in past years since propene is used for the production of a number of large volume chemicals (e. g. polypropylene). This growth – outpacing a similar development for ethene – led to a considerable gap between propene supply and demand[1]. In this context intensive research for new syntheses is currently underway. An alternative process is based on the metathesis of ethene with butene in order to yield propene. This process has already been realized industrially[2]. Relevant catalyst systems for low temperatures are based on Re_2O_7 supported on γ-Al_2O_3[3]. Molybdenum and tungsten complexes (also supported on typical SiO_2 or Al_2O_3 materials) are used at higher temperatures up to 400 °C.

Another attractive opportunity is the direct conversion of the cracker main product ethene to propene employing supported bifunctional nickel catalysts. It is reported in the literature that the reaction may proceed via three consecutive reaction steps[4]. A possible sequence of reaction steps is shown in Fig. 1. First of all, ethene dimerizes to 1-butene followed by a double bond shift to 2-butene. Subsequent metathesis between ethene and 2-butene affords propene. The catalyst system is comprised of a nickel species on MCM-41.
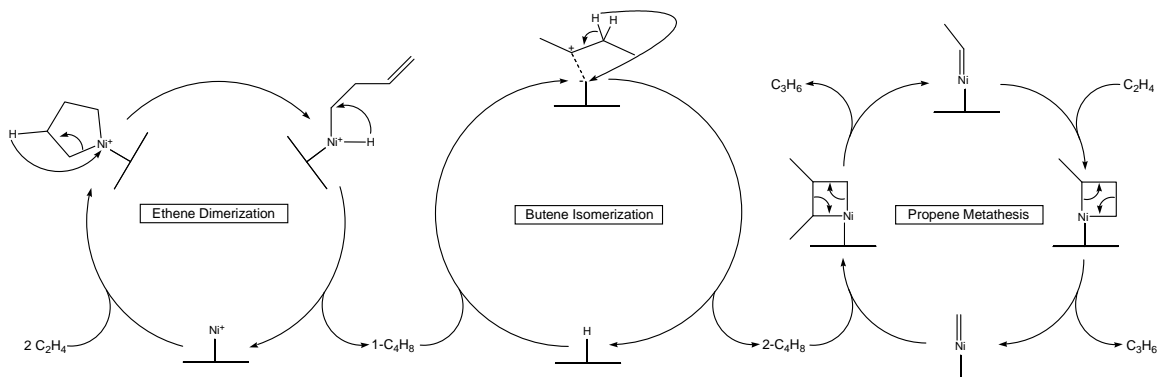

Fig. 1: Possible catalytic cycle of the direct synthesis of propene

This contribution presents the results of a comprehensive experimental study dealing with the preparation and the characterization of supported bifunctional nickel catalysts. Different preparation strategies have been applied in order to obtain an active catalyst for the above reaction. Commercially available MCM-41 (Sigma) was used as support and underwent an equilibrium adsorption treatment with different nickel precursors. Moreover, MCM-41 was synthesized hydrothermally and treated by template ion exchange[4]. Nickelnitrate, -acetate, -acetylacetonate and -citrate solutions with different concentrations were used to elucidate the influence of nickel dotation and dispersion. Fig. 2 depicts propene selectivity and ethene conversion in a temperature range between 50 and 450 °C. Significant ethene conversion can already be observed at temperatures as low as 50 °C. At this temperature, ethene consumption corresponds mainly to the formation of 1-butene via dimerization. Between 250 and 300 °C the isomerization of 1-butene to 2-butene as well as the metathesis of 2-butene with additional ethene sets in. For the catalyst prepared with nickel citrate the maximal propene selectivity of 51 % is reached at 400 °C. Combined with a conversion of 44 %, this leads to a remarkable propene yield of 23 %. Therefore, the catalyst prepared with nickel citrate employing equilibrium adsorption was classified as auspicious. Consequently, the catalyst system was thoroughly analyzed by using XRD, TEM, EDX, BET, TPR and ICP. Moreover, catalytic tests were performed to investigate the influence of residence time and initial ethene concentration. Long-time activity measurements revealed that the conversion decreased by approximately 10 % in 60 h. Propene selectivity remained almost constant.
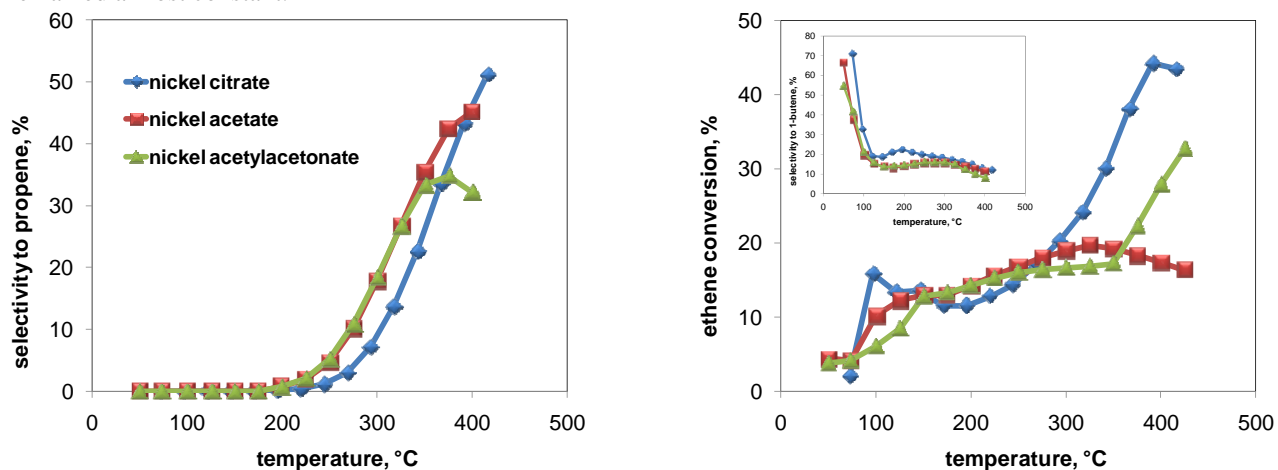

Fig. 2: Propene selectivity and ethene conversion as a function of temperature for three selected nickel precursors ($x_{C2H4}^{in} = 5$ %; $W/F_{total} = 0.5$ kg h/m³)

Based on the experimental results, the direct conversion of ethene to propene using supported bifunctional nickel catalysts shows promising potential to partially close the gap between propene demand and supply (based on traditional sources like steam cracking) in the future.

References

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