



Alumino-mesostructured Ni catalysts for the direct conversion of ethene to propene



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ABSTRACT

Ni/MCM-41 and Ni/AlMCM-41 were synthesized at different Si/Al ratios and tested in the direct conversion of ethene to propene (ETP-reaction). It was intended to evaluate the effect of modifying the catalyst acidity on the ETP-reaction rather than optimizing its performance. All catalysts were characterized by powder XRD, N₂-physisorption, ²⁹Si and ²⁷Al MAS NMR, TEM, NH₃-TPD, pyridine-DRIFTS, H₂-TPR, and TPO. Ni/MCM-41 showed low catalytic activity due to its low acidity. Ni/AlMCM-41 catalyst with a Si/Al ratio of 60 had high catalytic activity. Characterization results revealed that the catalyst structure does not have effect on the catalytic activity. Al could be incorporated into the MCM-41 framework up to Si/Al ratio of 16. Two different Ni-composites on the surface of the MCM-41 and AlMCM-41 were observed. Deeper characterization is required to know the Ni state. Important deactivation was observed at 450 °C. The nature of the carbonaceous species and reaction mechanism require deeper characterization.

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1. Introduction

The chemical industry is based mainly on ethene and propene as block-building chemicals. Both compounds are produced as co-products in the steam cracking of different hydrocarbon steams and in the refinery-based catalytic cracking. The petrochemical industry is presently facing a major squeeze in propylene availability as a result of the growth in propene derivatives, especially polypropylene [1]. Owing to this strong global demand, there is concern that the supply of propene from its traditional sources will not be sufficient to keep pace with demand [1,2]. Consequently, to meet the increasing demand for the production of propene, the on-purpose technologies will be of great interest. Several strategies have been proposed for propene production, the dehydrogenation of propane [2], the catalytic cracking of C₄ alkenes to propene [3,4] and the metathesis of ethene and 2-butene [3,5]. The dehydrogenation of propane requires relatively large capital investments as well as high operating costs. The catalytic cracking of C₄ alkenes produces a broad spectrum of by-products and it is difficult to implement [6], and the metathesis process requires 2-butene and ethylene in equal quantities. Also, Sugiyama et al., and Iwamoto et al., have shown that it is possible to obtain propene directly from

ethanol by using Ni-doped MCM-41 and FSM-16 catalysts [7,8] which open a new alternative to produce propene from renewable sources.

Recently, the direct conversion of ethene to propene without any addition of other hydrocarbons (ETP-reaction) was found to offer an attractive alternative. This reaction was observed, at first, in a few early papers on olefin metathesis catalysts, over supported molybdenum and tungsten catalysts [9,10]. Recently, Iwamoto et al. [11–13] found that Ni ions loaded on MCM-41 prepared by template ion exchange catalyze the direct conversion of ethene to propene in the presence of water vapor. Because MCM-41 is not stable in presence of water [14], the long-term stability of the catalyst is questionable. Taoufik et al., have reported the direct transformation of ethene into propene over a tungsten hydride supported on alumina [15], but the conversion was low after 10 h on stream, reaching around 10% of conversion. Oikawa et al. [16] and Lin et al., showed that silicoaluminophosphate microporous molecular sieve, SAPO-34, and H-ZSM-5 zeolite are highly active for the ETP-reaction, but they present a serious deactivation with time on stream [17,18]. More recently, intensive work has been done in order to understand the nature of the catalytic active sites and the reaction mechanism of the ETP-reaction on Ni/MCM-41 catalysts [19–21], and the nature and mechanism of formation of the active sites on Ni/MCM-41 are being subject of discussion [22,23].

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