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Heterogeneous oligomerization of ethylene to liquids on bifunctional Ni-based catalysts: The influence of support properties on nickel speciation and catalytic performance

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ABSTRACT

In this work we present a comparative study of the catalytic performance for the heterogeneous oligomerization of ethylene to liquids of bifunctional catalysts comprising Ni (ca. 5 wt%) impregnated on three aluminosilicate supports exhibiting distinct acidic, textural, and structural properties. Specifically, a nanocrystalline Beta zeolite, a mesostructured Al-MCM-41 sample, and a commercial silica-doped alumina (Siralox-30) were employed as supports. The materials were characterized by ICP-OES, XRD, N_2-physisorption, FTIR-pyridine, ^{27}Al MAS NMR spectroscopy, electron microscopy (HAADF-STEM, TEM), and low-temperature FTIR-CO. The characterization results revealed significant differences in the nickel speciation depending on the support identity. Thus, while isolated Ni^{2+} cations in ion exchange positions were the prevailing species on the zeolitic Ni/Beta catalyst, Ni^{2+} interacting with weakly acidic surface hydroxyl groups (i.e., silanols and aluminols) and under-coordinated Ni^{2+} on the surface of sub-5 nm NiO nanoparticles predominated on Ni/Al-MCM-41 and Ni/Siralox-30 catalysts. In the absence of appreciable deactivation the latter two catalysts displayed significantly higher catalytic activity (related to the Ni sites), thus questioning the general believe that ion exchanged Ni^{2+} cations are the unique active Ni species in Ni-based catalysts. On the other hand, the higher density and strength of the Brønsted acid sites in Ni/Beta determined a higher selectivity to the targeted liquid (C_{5+}) oligomers and a higher degree of branching (i.e., higher octane-number) of the gasoline-range product in comparison to the amorphous catalysts. The C_{5+} productivity, however, was maximum for the most active Ni/Al-MCM-41 catalyst, reaching values as high as 12 mmol/(Kg_{cat} s).

1. Introduction

The oxidative coupling of methane (OCM) to ethylene followed by its oligomerization (OLI) to clean liquid fuels and chemicals is an attractive gas-to-liquid route particularly suited for the valorization of stranded and unconventional (e.g., shale gas) natural gas reserves where the construction of capital-intensive Fischer–Tropsch synthesis or methanol synthesis plants becomes unaffordable [1]. A major challenge in this alternative OCM + OLI route that would speed up its chance for industrial implementation is the replacement of the homogeneous transition metal (i.e., Ni, Co, Cr, Fe, etc.) complexes currently used as catalysts in commercial ethylene oligomerization processes [2] by more robust and "greener" heterogeneous catalysts.

In this respect, bifunctional solid catalysts comprising Ni ions loaded on acidic mesoporous aluminosilicates such as amorphous silica–aluminas [3–5] and ordered Al-MCM-41 [6–8] and Al-SBA-15 [9] materials are regarded as the most promising candidates for catalyzing the oligomerization of ethylene at mild conditions. Conversely to these mesoporous catalysts, Ni loaded on purely microporous zeolites such as X [10], Y [11,12] and MCM-22 [13] typically suffer from a rapid deactivation as bulky oligomers accumulate and remain trapped in the zeolitic micropores blocking the further access of reactants to the active sites. Recently, we have reported a new Ni-zeolite ethylene oligomerization catalysts based on a nanocrystalline zeolite Beta comprising relatively uniform intercrystal mesopores [14]. The absence of large cages in the Beta zeolite and the hierarchical-type porosity combining short-length micropores and interparticle mesopores promoted the fast diffusion of the heavier oligomers resulting in a stable catalytic performance during the oligomerization reaction [14]. In these Ni-containing solid catalysts, the oligomerization of ethylene to liquids

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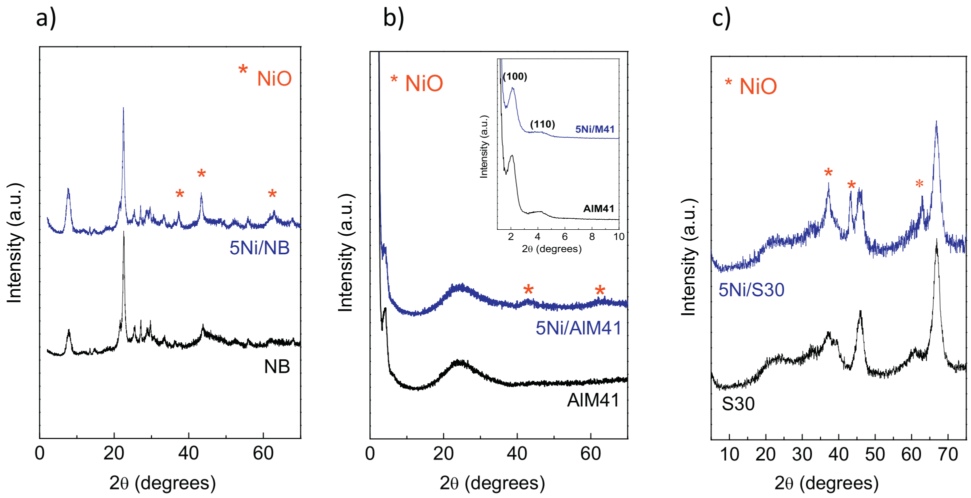

Fig. 1. XRD patterns for the supports and calcined Ni-based catalysts: (a) NB and 5Ni/NB, (b) AlM41 and 5Ni/AlM41 (the low-angle XRD pattern is shown in the inset graph to better appraise the pore ordering of the Al-MCM-41 support), and (c) S30 and 5Ni/S30. The marked peaks correspond to the *fcc*-NiO phase.

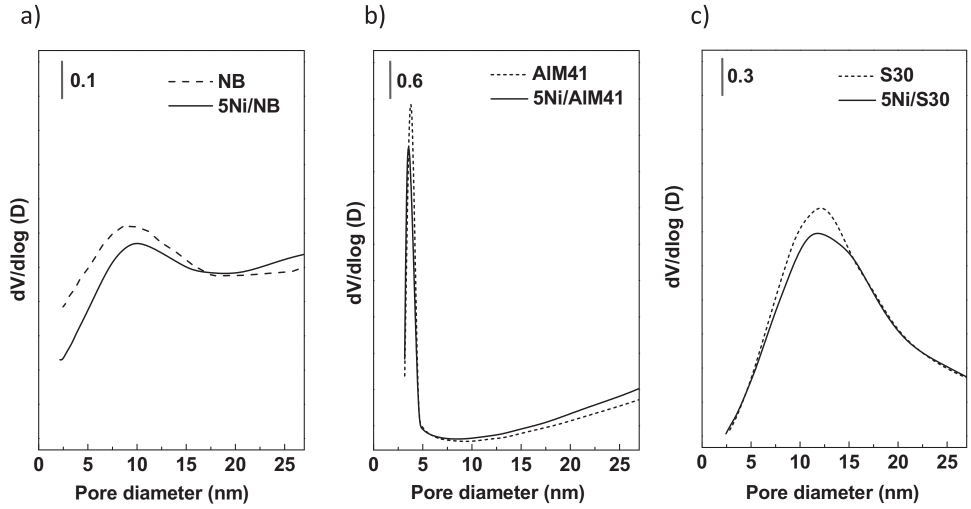

Fig. 2. Pore size distributions for the supports and corresponding catalysts derived from N_2-physisorption by applying the BJH-KJS method (see Section 2).

occurs through a cascade-type reaction where ethylene is first activated and oligomerized to short-chain linear α-olefins with an even number of carbon atoms on the Ni sites. The Ni-catalyzed oligomerization (so-called *true oligomerization*) is believed to occur through a coordination-insertion mechanism similar to that proposed for homogeneous organo-nickel systems [15]. In this line, Andrei et al. have recently proposed a mechanism involving the formation of metallacyclic intermediates that accounts for the product distribution observed in Ni-Al-SBA-15 catalysts [9]. Then, the primary C_{4+} olefins formed on the Ni sites are reacted on the Brønsted acid sites of the aluminosilicate carrier promoting the formation of liquid (C_{5+}) oligomers with increased degree of branching. Depending on the reaction conditions and catalyst acidity a certain amount of odd carbon numbered oligomers may also form via cracking of heavier olefins. The acid-catalyzed oligomerization is usually referred to as *hetero-oligomerization* route.

According to the above cascade-type reaction sequence, the activity (i.e., ethylene conversion) of the heterogeneous Ni-acid catalysts would be determined by the amount of accessible active Ni sites while the density and strength of the Brønsted acid sites and the porosity of the solid acid carrier would mostly govern the carbon-number distribution and structure of the final oligomers. Regrettably, the precise nature of the active Ni species is not exempt of controversy [16]. Thus, isolated Ni ions occupying exchange positions are generally proposed as the active sites for the Ni-catalyzed ethylene oligomerization whatever the acidic support used while bulk NiO particles are suggested to be inactive for the reaction [8,6] The most controversial issue in the previous literature concerns the oxidation state of the active Ni ions. In this respect, monovalent Ni^+ ions, which were detected in thermo-activated catalysts by means of room-temperature (RT) FTIR spectroscopy of adsorbed CO [5,17–19] and EPR measurements [17,18,20], have been generally assigned the role of active Ni sites. More recently, based also on RT FTIR-CO spectroscopic data, Lallemand et al. proposed both Ni^+ and dehydrated Ni^{2+} ions as catalytic active sites in ethylene oligomerization on Ni-exchanged Al-MCM-41 and Y materials [21]. However, in our earlier work on Ni/Beta we demonstrated that the formation of Ni^+ occurs by reduction of Ni^{2+} with CO during the RT FTIR-CO experiments and that Ni^{2+} species were the only ones detected when lowering the CO adsorption temperature from RT to −20 °C [14]. In addition, co-adsorption CO-ethylene experiments followed by FTIR lead us to definitively assign Ni^+ ions in Ni/Beta the role of mere spectators [14]. On the other hand, the concentration of paramagnetic Ni^+ species detected by EPR (diamagnetic Ni^{2+} ions are silent to this technique) barely represented ca. 1–2% of the total Ni present in the investigated catalysts [20]. Therefore, in our

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