



Activated takovite catalysts for partial hydrogenation of ethyne, propyne, and propadiene

Sònia Abelló^a, Danny Verboekend^a, Blaise Bridier^a, Javier Pérez-Ramírez^{a,b,*}

^a Institute of Chemical Research of Catalonia (ICIQ), Avinguda Països Catalans 16, 43007 Tarragona, Spain

^b Catalan Institution for Research and Advanced Studies (ICREA), Passeig Luïís Companys 23, 08010 Barcelona, Spain

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ABSTRACT

The gas-phase hydrogenation of ethyne, propyne, and propadiene was investigated over partially reduced Ni–Al mixed oxides derived from takovite, a hydrotalcite-type compound. The unique attributes of the hydrotalcite route leads to more active and selective catalysts compared to conventional Ni/Al₂O₃ prepared by impregnation. Tuning calcination and reduction conditions of the catalyst precursor is essential to optimize the hydrogenation performance. The best catalyst, calcined and reduced at 773 K, rendered stable propene yields up to ca. 65% and consisted of a Ni(Al)O_x solid solution with 55% of the total bulk nickel in reduced form and surface enrichment by aluminum. Sintering of NiO and crystallization of NiAl₂O₄ at high calcination temperature induce lower activity. The alkyne or diene conversion increases with the percentage of metallic Ni in the samples, while an optimal degree of nickel reduction maximizes the monoalkene selectivity. Below the optimum, oligomer formation is favored and above the optimum, alkane production increases. A similar pattern was found for the H₂/HC ratio. The alkene selectivity experiences a dramatic increase in early stages of the reaction, which correlated with the build-up of C-containing species on the catalyst (sub-)surface. These selectivity-enhancing species are formed at specific reaction temperatures, highlighting the relevance of the testing procedure on assessing hydrogenation catalysts. The catalytic performance is strongly influenced by the hydrocarbon substrate. In contrast to propyne and propadiene, ethyne hydrogenation led to a C₂H₄ yield of only 6%.

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1. Introduction

An important segment of commercial catalytic hydrogenations in the petrochemical and fine (specialty) chemical industries is the selective transformation of organic compounds with conjugated or cumulative double bonds and/or triple bonds into the corresponding monoalkene [1–5]. Supported palladium (<0.1 wt% Pd on low-surface-area alumina) is the preferred catalyst for semi-hydrogenation of alkyne (e.g. ethyne, propyne) and alkadiene (e.g. propadiene, butadiene) impurities to olefins in C₂–C₅+ fractions of steam crackers [2,4,6–8]. ‘Bare’ Pd catalysts experience over-hydrogenation to the alkane and formation of higher hydrocarbons by oligomerization (green oil). Accordingly, modification of monometallic Pd systems by promoters and/or additives is essential to increase the alkene selectivity and lifetime [3,5,8,9]. A representative example of modified palladium catalyst for partial hydrogenation of triple bonds in the fine chemical industry is the Lindlar system, consisting of 5 wt% Pd supported on CaCO₃ promoted by lead diacetate and quinoline [10]. Compared to palladium catalysts,

supported nickel catalysts prepared by impregnation are more selective to the alkane while displaying extensive oligomerization [7, 8,11,12]. In fact, nickel is frequently used for alkene hydrogenation or total alkyne hydrogenation [1,3]. Besides, nickel requires higher operating temperatures (up to 623 K) than palladium (323–353 K) [1]. Strategies to prevent total hydrogenation over nickel catalysts include promotion by additional metals (e.g. Cu, Re, Pb, Ag, Bi, Mo) [7,13,14], partial presulfiding, and continuous dosing of small H₂S amounts to the reactor [1].

Pd has monopolized recent open-literature publications on hydrogenation of alkynes, dienes, and alkenes [5,15–19], which was traditionally focused on supported nickel (on alumina or pumice), Raney nickel, and nickel boride catalysts [20–26]. Supported gold nanoparticles also attract recent attention due to the superior thermodynamic selectivity with respect to palladium [27]. In the nineties, Monzón et al. [28] prepared Ni/NiAl₂O₄ by coprecipitation of Ni₁–Al₂ precursors (22 wt% Ni) followed by calcination at 1173 K and reduction at 773 K. Tests in ethyne hydrogenation at 423 K led to very low ethene yields (ca. 6%) and an extremely high coking rate (up to 7.5 g_{coke} g_{cat}⁻¹ h⁻¹). Incorporation of Zn, Cr, and/or Fe in the base Ni₃–Al₁ hydrotalcite increased the ethene yield to 13% [29,30].

* Corresponding author at: Institute of Chemical Research of Catalonia (ICIQ), Avinguda Països Catalans 16, 43007 Tarragona, Spain. Fax: +34 977 920 224.

E-mail address: jperez@icq.es (J. Pérez-Ramírez).

In general, hydrogenation studies of acetylenics and dienes over nickel catalysts used a fixed condition for activation of the precursor material (calcination and reduction) and catalytic tests have been typically conducted with ethyne [12,20,26,31,32]. Comprehensive relationships between the catalyst synthesis, structure, procedure for catalyst evaluation, and the resulting hydrorefining performance have not been derived. Besides, studies assessing the sensitivity to the hydrocarbon in terms of chain length (e.g. ethyne and propyne) and type of insaturation (e.g. propyne and propadiene) have not been reported. Monzón et al. [28] showed that the degree of nickel reduced can be controlled by the reduction temperature of the Ni–Al oxide, but the influence thereof on ethyne hydrogenation was not examined. Phillipson et al. [25] observed that the isomer selectivity in the hydrogenation of 1,3-butadiene is affected by the reduction temperature of Ni/Al₂O₃. Apart from reduction conditions, well established is also that the calcination of nickel oxide impacts on the reduction properties, as early shown by Benton and Emmett [33]. Consequently, the possibility rises to design rules for more efficient nickel-based hydrogenation catalysts by proper selection of the synthesis and activation conditions.

Herein, we have investigated *unpromoted* reduced Ni–Al mixed oxides derived from takovite (Ni–Al hydrotalcite) in the gas-phase hydrogenation of ethyne, propyne, and propadiene. The hydrotalcite route makes it possible to obtain multimetallic mixed oxides combining high metal loadings, high metal (inter)dispersion, and high surface area [34–36]. Structure–performance relationships associated with the activation of the takovite precursor have been derived by detailed characterizations and catalytic tests in a continuous fixed-bed reactor at different temperatures and hydrogen-to-hydrocarbon ratios. *Operando* infrared spectroscopy monitored the formation of carbon-containing species on the catalyst surface under reaction conditions, which has been correlated with changes in alkene selectivity.

2. Experimental

2.1. Catalyst preparation and activation

Ni–Al hydrotalcite with a nominal Ni/Al molar ratio of 3, known as takovite, was synthesized by continuous coprecipitation using the ILDP method [37]. Briefly, aqueous solutions of 0.75 M Ni(NO₃)₂·6H₂O and 0.25 M Al(NO₃)₃·9H₂O and the precipitating agent (NaOH + Na₂CO₃, 1 M of each) were pumped into a 6 ml-microreactor attached to a high-shear homogenizer rotating at 13,500 rpm. The pH of the slurry was measured and controlled by an in-line probe directly at the outlet of the precipitation chamber. The synthesis was carried out at constant pH 10 with an average residence time of 18 s. The product slurry was collected in a glass vessel and aged at 313 K for 12 h under stirring, followed by filtration, washing, and drying at 353 K for 12 h. The as-synthesized sample, denoted as ‘AS,’ was calcined in static air at different temperatures (623, 773, or 1173 K) for 15 h using a ramp of 5 K min⁻¹. Previous to catalytic tests (Section 2.3), the calcined samples were treated in He at 623 K for 30 min and cooled or heated in the same gas to the desired prereluction temperature (423, 623, or 773 K), which was done in a mixture of 5 vol% H₂ in He during 30 min. Occasionally, a 5 h-reduction treatment was carried out. The ramp used in the temperature programs was 5 K min⁻¹. Along the manuscript, the samples are designated as ‘Cx–Ry,’ where ‘x’ and ‘y’ stand for the calcination and reduction temperatures, respectively.

2.2. Catalyst characterization

The chemical composition of the as-synthesized Ni–Al hydrotalcite was determined by X-ray fluorescence in a Philips PW 2400

spectrometer. Before analysis, the sample was mixed with Li₂B₄O₇ and Lil as tensoactive agent, and the mixture was fused at 1423 K in a Perle’X-3 radiofrequency furnace.

Powder X-ray diffraction was studied in a Bruker-AXS D5005 θ – θ diffractometer equipped with a Bruker-AXS MRI high-temperature chamber and a diffracted beam graphite monochromator using CuK α radiation. A thin layer of sample (ca. 30 mg) was mounted on the Pt₉₀–Rh₁₀ heater strip by placing a few droplets of a suspension of finely ground sample in ethanol followed by drying under ambient conditions. The as-synthesized and calcined samples were measured at 298 K in N₂ (100 ml STP min⁻¹). *In situ* XRD patterns during reduction of the Ni–Al oxides were recorded in 5 vol% H₂ in N₂ (100 ml STP min⁻¹) at 423, 623, 773, and 1173 K after 30 min equilibration at each temperature. The heating rate between each temperature step was 5 K min⁻¹. Data were collected at $2\theta = 10^\circ$ – 70° with a step size of 0.05° and a counting time of 1 s per step.

Thermal analysis was performed in a Mettler Toledo TGA/SDTA851e microbalance. Analyses were performed in air (50 ml STP min⁻¹), ramping the temperature from 298 to 1173 K at 5 K min⁻¹.

N₂ isotherms at 77 K were measured in a Quantachrome Autosorb-1 MP analyzer. Before analysis, the samples were degassed in vacuum at 393 K for 12 h.

Temperature-programmed reduction with hydrogen (H₂-TPR) was measured in a Thermo TPDRO 1100 unit equipped with a thermal conductivity detector. Ca. 50 mg of Ni–Al oxide obtained by calcination of takovite at 623, 773, and 1173 K were loaded in the quartz microreactor (11 mm i.d.), pretreated in N₂ (20 ml STP min⁻¹) at 623 K for 1 h, and cooled to 323 K in the same atmosphere. The analysis was carried out in a mixture of 5 vol% H₂ in N₂ (20 ml STP min⁻¹), ramping the temperature from 323 to 1173 K at 10 K min⁻¹. H₂-TPR was also carried out over prerelucted samples. For this purpose, the calcined samples were *in situ* reduced in 5 vol% H₂ in N₂ (42 ml STP min⁻¹) at different temperatures (423, 623, and 773 K) and times (30 min and 5 h) previous to the analysis.

X-ray photoelectron spectroscopy (XPS) measurements were obtained using a VG-Microtech Multilab 3000 spectrometer equipped with a MgK α ($h\nu = 1253.6$ eV) excitation source, a nine-channel-tron detection system, and a hemispheric electron analyzer. The sample was outgassed overnight at room temperature in a UHV chamber ($<5 \times 10^{-8}$ Torr). In some cases, before XPS measurements, the specimen was transferred to a high-pressure reaction cell (10^{-3} Torr) attached to the analysis chamber of the spectrometer and pretreated in H₂ at 773 K. Reduced samples were immediately transferred to the analysis chamber. All binding energies were referenced to the C 1s line at 284.6 eV, and the integrated intensities were corrected by atomic sensitivity factors [38].

2.3. Catalytic tests

The gas-phase hydrogenation of propyne, propadiene, and ethyne was studied at ambient pressure in a MicroActivity Reference setup (PID Eng&Tech). The catalyst (0.15 g, sieve fraction 200–400 μ m) was loaded in the 12 mm i.d. quartz microreactor, heated in He at 623 K for 30 min, and prerelucted in 5 vol% H₂ in He (42 ml STP min⁻¹) as described in Section 2.1. The catalysts were tested isothermally at intervals of 50 K in the range 373–523 K using a typical feed mixture of (alkyne or alkadiene)/H₂/He = 2.5/7.5/90 and a total flow of 42 ml STP min⁻¹ (weight hourly space velocity, WHSV = 16,800 ml h⁻¹ g⁻¹). The tests were run starting at the highest or lowest temperature, with a holding time of 5 h at each temperature. The influence of the hydrogen-to-propyne ratio (1–5) was studied over selected catalysts at 523 K. For this purpose, the inlet hydrocarbon concentration was kept at 2.5 vol% and the hydrogen concentration was decreased from 12.5 to 2.5 vol%

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