Electronic Supplementary Information for

Well-defined mono(η³-allyl)nickel complex ≡MONi(η³-C₃H₅) (M= Si or Al) grafted on silica or alumina: a molecularly dispersed nickel precursor for syntheses of supported small size nickel nanoparticles

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Contents

Experimental section

Fig. S1 | $^1$H and $^{13}$C MAS solid-state NMR spectra of $\equiv$AlONi($\eta^3$-C$_3$H$_5$).

Fig. S2 | Typical STEM images of Ni/SiO$_2$ (a and d), Ni/$\gamma$-Al$_2$O$_3$ (b and e) and Ni$_{ref}$/γ-Al$_2$O$_3$ (c and f) before and after reforming.
Experimental Section

**General consideration:** SiO$_2$ (Aerosil, specific surface area 200 m$^2$/g) and γ-Al$_2$O$_3$ (Aeroxide® Alu C, specific surface area 100 m$^2$/g) were purchased from Evonik Industries, and treated according to the literature method$^1$ to generate SiO$_2$-(500) or γ-Al$_2$O$_3$-(500) ([OH$_{\text{surface}}$]= 0.72 and 0.39 mmol/g for SiO$_2$-(500) and Al$_2$O$_3$-(500), respectively). Ni($\eta^3$-C$_3$H$_5$)$_2$ was prepared according to the literature method.$^2$ Ni$_{\text{ref}}$/\gamma$-Al$_2$O$_3$ (Ni loading, 2.73wt%) was prepared by classic wet impregnation method using Ni(NO$_3$)$_2$ as nickel precursor.$^3$

Elemental analyses were obtained from the service of Mikroanalytisches Labor Pascher (Remagen, Germany). Ni metal dispersion was measured on fresh samples from uptakes of weakly and strongly chemisorbed H$_2$ at 303 K (150–300 mmHg) using an ASAP 2020C chemisorption analyser. Ni dispersion was calculated using 1:1 H:Ni titration stoichiometry. The FTIR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a resolution of 4 cm$^{-1}$ using self-supported sample pellets. Aberration corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a Titan G$^2$ 60-300 CT electron microscope by operating it at the accelerating voltage of 300 kV. Electron gun was used in un-filtered mode and the probe size during STEM analysis was estimated to be about 0.5 nm with beam current of 0.08 nA. The TEM specimens of samples were prepared by depositing a drop of diluted sample solution on a carbon-coated copper grid and then the drop was let dried at room temperature.

**Solid State Nuclear Magnetic Resonance Spectroscopy:** One dimensional $^1$H MAS and $^{13}$C MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 600 MHz for $^1$H NMR and 150 MHz for $^{13}$C NMR, respectively. In all cases, the samples were packed into rotors under inert atmosphere inside the glovebox. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS and adamantane. For $^1$H MAS NMR, a 33 kHz MAS frequency, a 1.5 $\mu$s 90° proton pulse length, a 0.05 s recycle delay and 1000 scans were used. A spin echo was used in order to avoid baseline distortion. For $^{13}$C MAS NMR, the spectra were obtained via direct carbon excitation using spin-echo sequence without decoupling. A 33 kHz MAS frequency, a 2.5 $\mu$s 90° proton pulse length, a repetition delay of 0.1 s and 32k scans were used. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. $^1$H-$^1$H multiple-quantum spectroscopy: Two-dimensional double-quantum (DQ) and triple-quantum (TQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz.
with a conventional double resonance 3.2 mm CP/MAS probe, according to the following
general scheme: excitation of DQ coherences, $t_1$ evolution, $z$-filter, and detection. The spectra
were recorded in a rotor synchronized fashion in $t_1$ by setting the $t_1$ increment equal to one
rotor period. One cycle of the standard back-to-back (BABA) recoupling sequences was used
for the excitation and reconversion period. Quadrature detection in $w_1$ was achieved using
the States-TPPI method. An MAS frequency of 30 kHz was used. The 90° proton pulse
length was 1.5 $\mu$s, while a recycle delay of 0.1 s was used. A total of 128 $t_1$ increments with
256 scans per each increment were recorded. The DQ frequency in the $w_1$ dimension
corresponds to the sum of two single quantum (SQ) frequencies of the two coupled protons
and correlates in the $w_2$ dimension with the two corresponding proton resonances. The TQ
frequency in the $w_1$ dimension corresponds to the sum of the three SQ frequencies of the three
coupled protons and correlates in the $w_2$ dimension with the three individual proton resonances. Conversely, groups of less than three equivalent spins will not give rise to
diagonal signals in this spectrum.

**Catalytic test:** The catalytic tests were carried out in a fixed-bed quartz reactor (inner
diameter, 4 mm) under atmospheric pressure. For each test, 10 mg of catalyst (150–250 $\mu$m)
diluted with 50 mg of SiC (150–250 $\mu$m) was introduced into a quartz reactor. Quartz wools
were used to hold the catalyst bed in a fixed position. Prior to reaction, the catalyst was
reduced *in situ* under H$_2$/Ar flow (H$_2$, 10 vol%; flow rate, 100 ml/min) at 500 °C for 2 h.
After that, the reactor was purged by Ar flow (100 ml/min) at 500 °C for 20 min and heated
up to the desired reaction temperature (600 °C). The reactant gases (CH$_4$/CO$_2$/N$_2$= 1/1/8, P= 1
atm) were introduced to the reactor at a total flow of 100 ml/min (WHSV= 600 L h$^{-1}$ g cat$^{-1}$).
Reactants and products were continuously monitored by gas chromatography (Varian 450-
GC).

**Syntheses of surface nickel complexes **≡MONi($\eta^3$-C$_3$H$_5$) (M= Si or Al): 1 g of
SiO$_2$-(500) or $\gamma$-Al$_2$O$_3$-(500) was mixed with 15 ml of pentane solution of Ni($\eta^3$-C$_3$H$_5$)$_2$
([Ni]/[OH$_{\text{surface}}$]= 1:1) and the mixture was stirred at room temperature for 24 h. After
filtration, washing with pentene (3×20 ml) and drying under vacuum, off-white powder was
isolated. Yields: 95%. Elemental analysis: Ni, 3.76%; C, 2.35% for ≡SiONi($\eta^3$-C$_3$H$_5$) and Ni,
2.11%; C, 1.33 % for ≡AlONi($\eta^3$-C$_3$H$_5$), respectively.

**Syntheses of nickel nanoparticles Ni/SiO$_2$ and Ni/$\gamma$-Al$_2$O$_3$:** Surface nickel
complexes ≡SiONi($\eta^3$-C$_3$H$_5$) and ≡AlONi($\eta^3$-C$_3$H$_5$) was treated under H$_2$ flow (100 ml/min)
at 300 °C. Finally, brown powder was isolated. Elemental analysis: Ni, 4.02% for Ni/SiO₂ and Ni, 2.07% for Ni/γ-Al₂O₃.

References
Fig. S1 (A) One-dimensional (1D) $^1$H MAS solid-state NMR spectrum of $≡$AlONi($\eta^3$-C$_3$H$_5$) recorded at 600 MHz with a 33 kHz MAS frequency, a repetition delay of 0.05 s and 1k scans, a spin echo being used to avoid baseline distortion. (B) $^{13}$C MAS NMR spectrum of $≡$AlONi($\eta^3$-C$_3$H$_5$) recorded at 150 MHz with a 33 kHz MAS frequency, a repetition delay of 0.1 s and 32k scans, via direct carbon excitation using spin-echo sequence without decoupling. (C) Two-dimensional (2D) $^1$H-$^1$H double-quantum (DQ)/single-quantum (SQ) spectrum of $≡$AlONi($\eta^3$-C$_3$H$_5$) recorded with 256 scans per t1 increment, 0.1 s repetition delay, 128 individual t1 increments.

Fig. S2 Typical STEM images of Ni/SiO$_2$ (a and d), Ni/$\gamma$-Al$_2$O$_3$ (b and e) and Ni$_{red}$/γ-Al$_2$O$_3$ (c and f) before and after reforming.