Electronic Supplementary Information for

Well-defined mono(η^3-allyl)nickel complex ≡MONi(η^3-C_3H_5) (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

General consideration: SiO_2 (Aerosil, specific surface area 200 m^2/g) and γ-Al_2O_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 $SiO_{2\text{-}(500)}$ or γ-$Al_2O_{3\text{-}(500)}$ ($[OH_{surface}]$= 0.72 and 0.39 mmol/g for $SiO_{2\text{-}(500)}$ and $Al_2O_{3\text{-}(500)}$, respectively). $Ni(\eta^3\text{-}C_3H_5)_2$ was prepared according to the literature method.[2] $Ni_{ref}/\gamma\text{-}Al_2O_3$ (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 ^1H MAS and ^{13}C MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 600 MHz for ^1H 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 ^1H MAS NMR, a 33 kHz MAS frequency, a 1.5 μs 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 μs 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. ^1H-^1H 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.[4] 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 μs, 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.[5] 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 μm) diluted with 50 mg of SiC (150–250 μm) 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 ^oC for 2 h. After that, the reactor was purged by Ar flow (100 ml/min) at 500 ^oC for 20 min and heated up to the desired reaction temperature (600 ^oC). 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(η^3-C_3H_5) (M= Si or Al): 1 g of $SiO_{2-(500)}$ or γ-$Al_2O_{3-(500)}$ was mixed with 15 ml of pentane solution of Ni(η^3-C_3H_5)$_2$ ([Ni]/[$OH_{surface}$]= 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(η^3-C_3H_5) and Ni, 2.11%; C, 1.33 % for ≡AlONi(η^3-C_3H_5), respectively.

Syntheses of nickel nanoparticles Ni/SiO_2 and Ni/γ-Al_2O_3: Surface nickel complexes ≡SiONi(η^3-C_3H_5) and ≡AlONi(η^3-C_3H_5) was treated under H_2 flow (100 ml/min) at 300 ^oC. Finally, brown powder was isolated. Elemental analysis: Ni, 4.02% for Ni/SiO_2 and Ni, 2.07% for $Ni/\gamma\text{-}Al_2O_3$.

References

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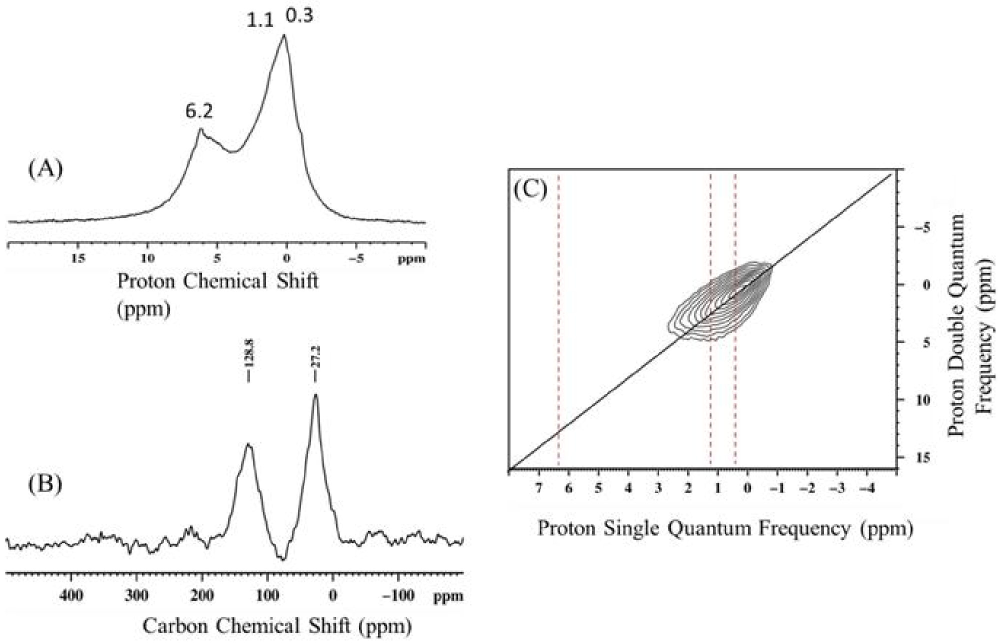

Fig. S1 (A) One-dimensional (1D) ^{1}H MAS solid-state NMR spectrum of ≡AlONi(η^3-C_3H_5) recorded at 600 MHz with a 33 kHz MAS frequency, a repetition delay of 0.05 s and 1k scans, a spin echo being used to avoid baseline distortion. (B) ^{13}C MAS NMR spectrum of ≡AlONi(η^3-C_3H_5) recorded at 150 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(η^3-C_3H_5) recorded with 256 scans per t1 increment, 0.1 s repetition delay, 128 individual t1 increments

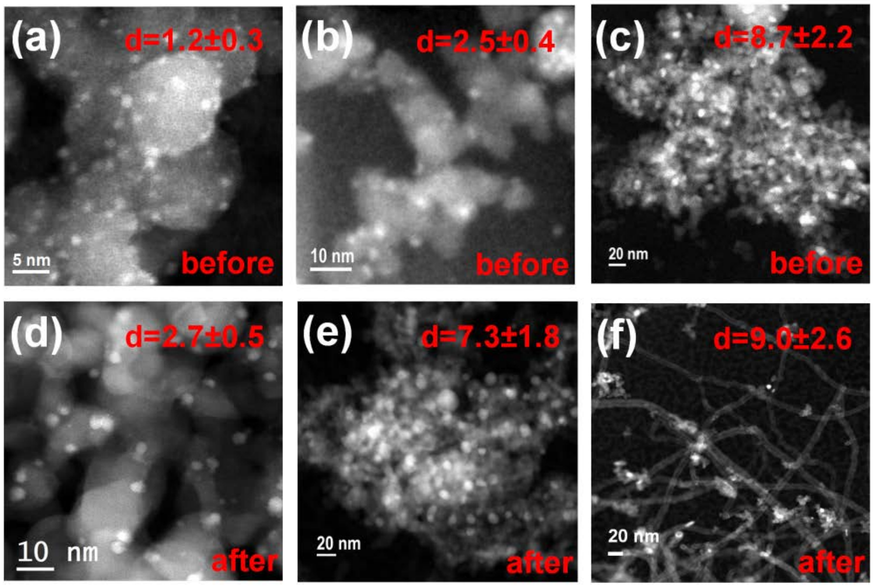

Fig. S2 Typical STEM images of Ni/SiO_2 (a and d), Ni/γ-Al_2O_3 (b and e) and Ni_{ref}/γ-Al_2O_3 (c and f) before and after reforming.