Supporting Information

Life Cycle of Single Atom Catalysts: A Mössbauer Study of Degradation and Reactivation of Tetrapyrrolic Fe-N-C Powders

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Experimental Section

Preparation of Zn-N-C, Fe_2O_3@Fe-N-C and NDC-Fe-HT-X

The samples were prepared similarly to what previously reported.[7] In a typical synthesis, 0.7 g of 1,2-dicyanobenzene were mixed with 7 g of LiCl/$ZnCl_2$ mixture (60 mol% LiCl) in an Ar-filled glovebox. The resulting powder was heated with a heating rate of 10 K/min to 800 °C in a tube furnace with a constant Ar flow and let at this temperature for 1 h. The obtain material was ground, washed with 0.1 M HCl for several hours and dried (Zn-N-C). Zn-N-C was degassed at 250 °C under vacuum, transferred inside an Ar-filled glovebox and mixed with a eutectic mixture of LiCl/$FeCl_3$ in a Schlenk tube. The closed tube was heated up to 170 °C for 5 hours in order to melt the salt mixture and exchange Zn with Fe. Afterwards, the sample was let to cool down to room temperature and washed with deionized water to remove the salt mixture. Finally, it was washed with 0.1 M HCl for several hours and dried (Fe_2O_3@Fe-N-C). NDC-Fe-HT-0 (air free state) was prepared from Fe_2O_3@Fe-N-C after further washing it with 1 M HCl at 80 °C. The dried sample was placed in an alumina crucible and pushed inside a tube furnace pre-heated at 1000 °C under Ar atmosphere. After 10 minutes the furnace was turned off and opened to quickly cool down the sample to room temperature. The sample was then transferred as quick as possible to an Ar-filled glovebox. NDC-Fe-HT-X were obtained after exposing NDC-Fe-HT-0 to air for X days.

Characterizations

Mössbauer measurements were performed at T = 4.2 K on a transmission spectrometer using a sinusoidal velocity waveform with both the source of ^{57}Co in rhodium and the absorber in the liquid He bath of a cryostat. In order to refer the measured isomer shifts to α-Fe at ambient temperature, 0.245 mm s^{-1} was added to the measured values. The spectra were fitted with Lorentzian lines grouped into electric quadrupole doublets and sextets arising from magnetic hyperfine splitting.

N_2-sorption measurements were carried out on a Quantachrome Autosorb iQ2. Prior to the measurements, the samples were outgassed at 250 °C under vacuum overnight. Brunauer–Emmett–Teller (BET) theory was employed to determine the specific surface area using the Micropore BET Assistant supplied by the instrument software. Pore size distributions were calculated with the quenched-solid density functional theory (QSDFT) method (slit/cylindrical pores, adsorption branch).

TGA-MS was performed on a Mettler Toledo TGA/DSC 1 instrument connected to a Pfeiffer Vacuum Thermostar mass spectrometer in Ar atmosphere. The employed heating rate was 10 K/min. Two isothermal steps (150 °C and 250 °C for 20 and 45 minutes, respectively) were performed in order to ensure the complete outgas of the samples.

Electrochemical measurements

Electrochemical measurements were performed in a three-electrode glass cell using 0.1 M $HClO_4$ as electrolyte, an Au wire as counter electrode and a freshly calibrated RHE as reference electrode. Catalyst inks were prepared by dispersing 5 mg of catalyst in 840 µL of N,N-dimethylformamide and 50 µL of 5 wt% Nafion suspension, followed by sonication. To obtained a catalyst loading of 290 µg/cm^2, 10 µL of ink was drop-cast onto a well-polished glassy carbon electrode and dried. An Autolab PGSTAT302N (Metrohm) potentiostat was employed for the measurements. The solution resistance was determined by electrochemical impedance spectroscopy. The ORR curves were corrected for capacitive currents by subtracting the curves recorded in Ar-saturated electrolyte from the curves recorded in O_2-saturated electrolyte.

Figure S1. Summary of the percentage of the different components in the Mössbauer spectra over time. Spectra are measured at T = 4.2 K.

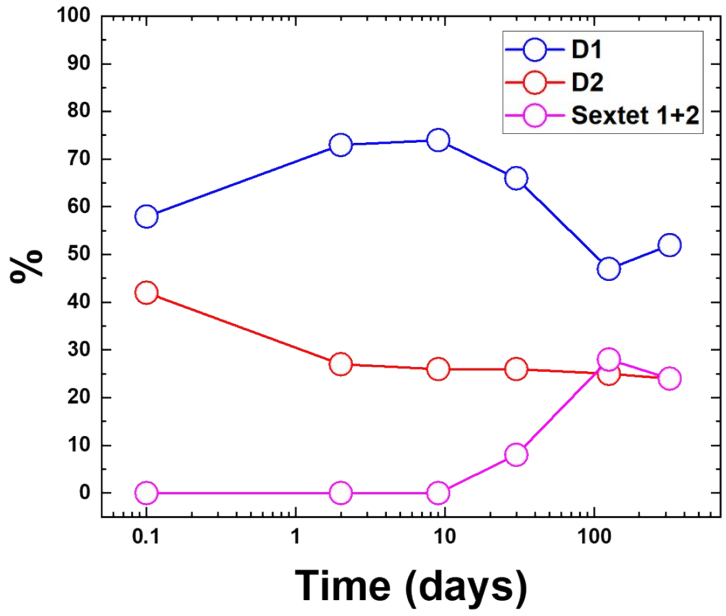

Table S1. Fitting parameters of the different components obtained from the Mössbauer measurements of NDC-Fe-HT-X at 4.2 K; isomer shift (IS, mm s^{-1}) with respect to α-iron at 4.2 K, quadrupole splitting (QS, mm s^{-1}), magnetic hyperfine field (H, Tesla) and percentage of the spectral area (%). The inferior statistics of the NDC-Fe-HT-320-Reactivated spectra do not allow for a precise evaluation of Mössbauer parameters.

Sample	D1 (IS; QS; %)	D2 (IS; QS; %)	Sextet (IS; H; %)	Sextet (IS; H; %)
NDC-Fe-HT-0	0.27; 1.54; 58	0.63; 2.89; 42	-	-
NDC-Fe-HT-2	0.25; 1.24; 73	0.60; 2.90; 27	-	-
NDC-Fe-HT-9	0.24; 1.13; 74	0.58; 2.91; 26	-	-
NDC-Fe-HT-30	0.24; 1.13; 66	0.58; 2.91; 26	0.3; 47.5; 4	0.28; 43.6; 4
NDC-Fe-HT-125	0.24; 1.13; 47	0.58; 2.91; 25	0.22; 47.4;14	0.25; 40.8; 14
NDC-Fe-HT-320	0.24; 1.13; 52	0.58; 2.90; 24	0.22; 47.7; 13	0.20; 42.5; 11
NDC-Fe-HT-320 Reactivated	0.15; 1.16; 69	1.12; 2.66; 15	0.13; 49.8; 16	

Table S2. Structural values obtained from N_2-sorption porosimetry measurements for NDC-Fe-HT. For the surface area (SA), both the value obtained by applying the Brunauer–Emmett–Teller theory (SA_{BET}) and the one from quenched solid density functional theory calculation with slyt and cylindrical pores (SA_{QSDFT}) are reported. For the pore volume (PV), both the value from QSDFT (PV_{QSDFT}) and the one measured at $P/P_0 \approx 0.99$ (TPV) are reported. Micro indicates pores ≤ 2 nm and meso pores between 2 nm and 33 nm (upper value of the employed model).

Sample	SA_{BET} (m^2/g)	TPV (cc/g)	SA_{QSDFT} (m^2/g)			PV_{QSDFT} (cc/g)		
			micro	meso	total	micro	meso	total
NDC-Fe-HT-2	1247	1.90	954	368	1322	0.331	1.037	1.368
NDC-Fe-HT-320	922	0.89	716	251	967	0.250	0.479	0.729