Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Information

Insight into the Interdependence of Ni and Al in Bifunctional Ni/ZSM-5 Catalysts at Nanoscale

Hue-Tong Vu,[a]† Iztok Arčon,[b,c]† Danilo Oliveira de Souza,[d] Simone Pollastri, [d] Goran Dražić, [a] Janez Volavšek,[a] Gregor Mali,[a] Nataša Zabukovec Logar [a,b] and Nataša Novak Tušar [a,b*]

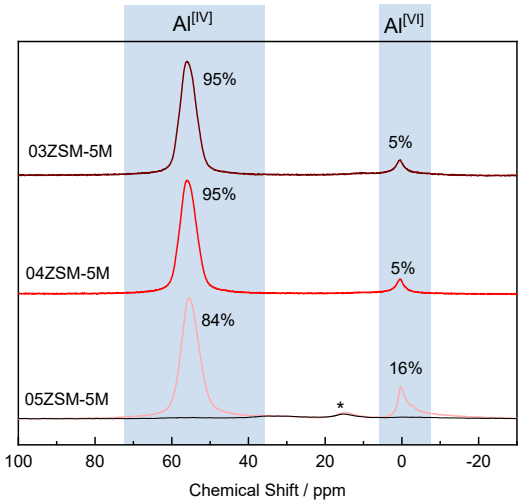

Figure S.1. ^{27}Al-NMR spectra of ZSM-5 zeolites, i.e., 03ZSM-5, 04ZSM-5 and 05ZSM-5, with the fraction of tetrahedral Al (Al$^{[IV]}$) and octahedral Al (Al$^{[VI]}$). Black line and asterisk mark the instrumental background.

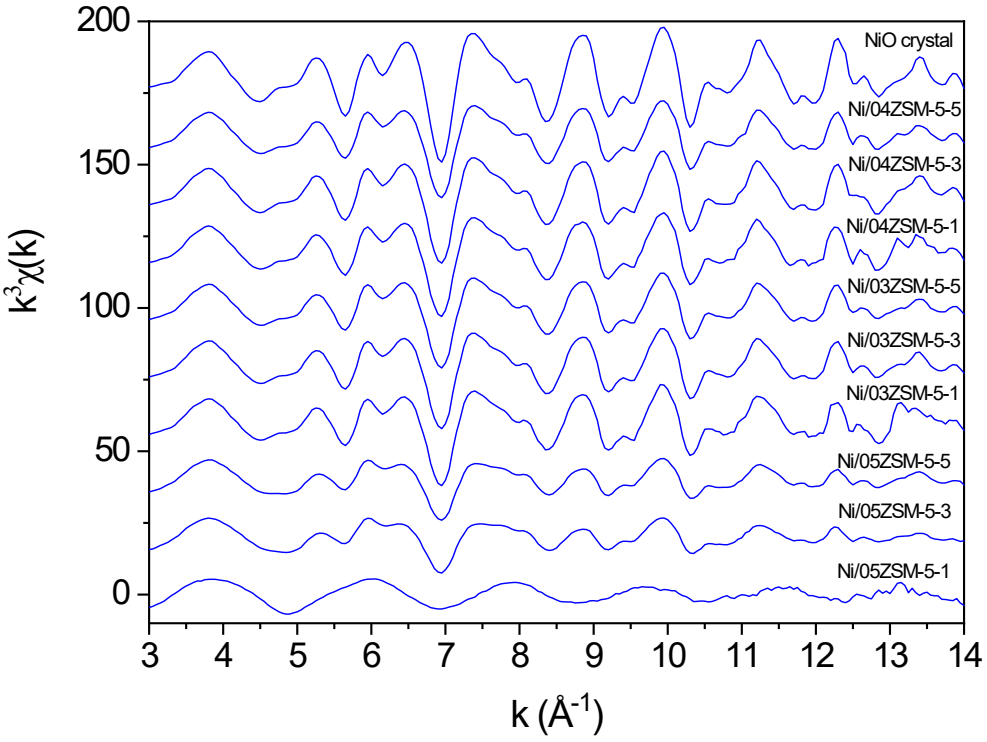

Figure S.2. The k^3-weighted Ni K-edge EXAFS spectra of the Ni functionalized ZSM-5 zeolite samples. The spectrum of the reference crystalline NiO is added for comparison.

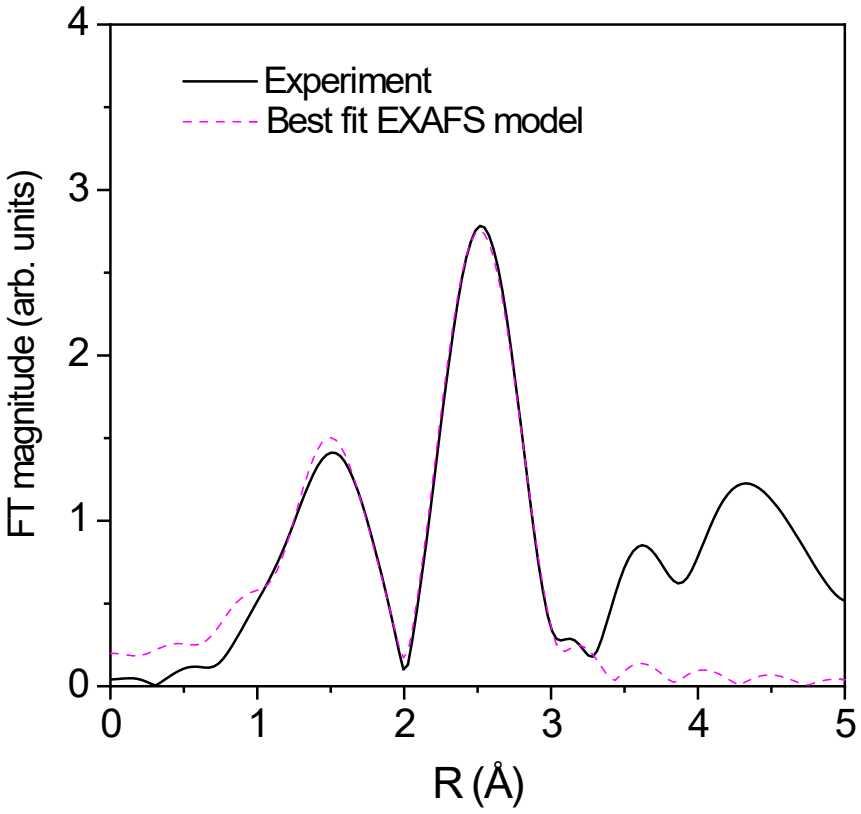

Figure S.3. Fourier transform magnitude of k^3 - weighted Fe EXAFS spectrum of the reference sample with NiO nanoparticles on CeO_2 support, calculated in the k range of 3–11 $Å^{-1}$. Experiment (black solid line), best-fit EXAFS model in the R range of 1.2–3.3 Å.

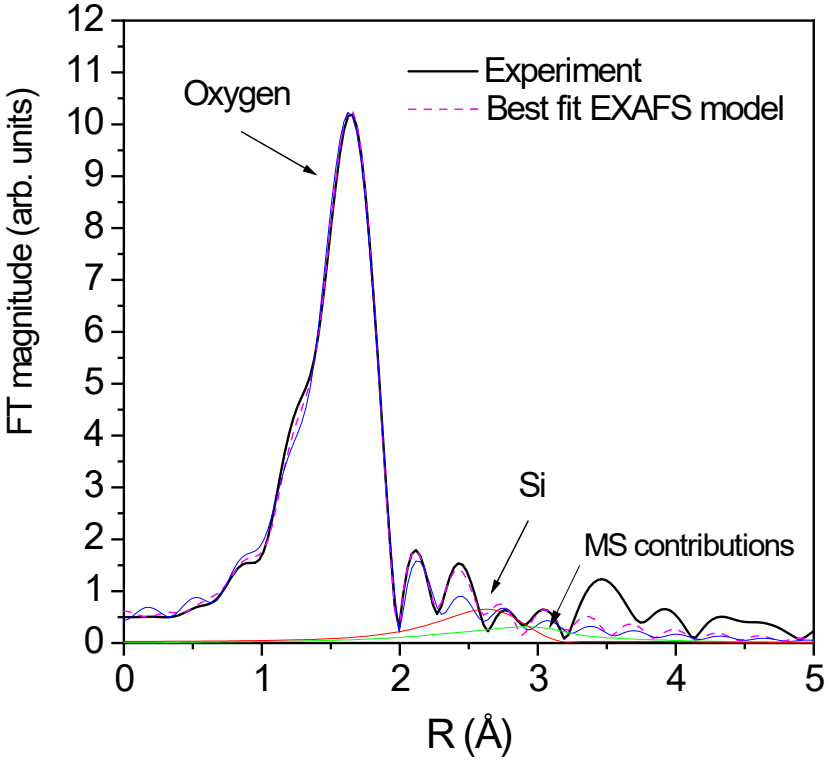

Figure S.4. Fourier transform magnitude of k^3 - weighted Fe EXAFS spectrum of the Ni/05ZSM-5-1 sample, calculated in the k range of 3–14 $Å^{-1}$. Experiment (black solid line), best-fit EXAFS model in the R range of 1.2–3.2 Å (magenta dashed line), and single scattering contribution of Oxygen (blue line) and Si neighbors (red line), and contributions of multiple scatterings within the octahedra of nearest oxygen neighbors (green line).

Table S.1. Parameters of the nearest coordination shells around Ni cations in the crystalline NiO reference sample: coordination number N, distance (R), and Debye-Waller factor (σ^2). Uncertainty of the last digit is given in parentheses. A best fit is obtained with the amplitude reduction factor $S_0^2 = 0.90(5)$ and the shift of the energy origin ΔE_o = -2(1) eV. The R-factor (quality of fit parameter) is listed in the last column.

Ni neighbor	N	R [Å]	σ2 [Å2]	R-factor
NiO crystal				
O	6	2.080(5)	0.0047(5)	0.0016
Ni	12	2.952(2)	0.0053(5)	
O	8	3.42(2)	0.009(2)	

Table S.2. Parameters of the nearest coordination shells around Ni cations in the reference sample with NiO nanoparticles on CeO_2 support: average coordination number N, distance (R), and Debye-Waller factor (σ^2). Uncertainty of the last digit is given in parentheses. A best fit is obtained with the amplitude reduction factor $S_0^2 = 0.90(5)$ and the shift of the energy origin ΔE_o = -2(1) eV. The R-factor (quality of fit parameter) is listed in the last column.

Ni neighbor	N	R [Å]	σ2 [Å2]	R-factor
NiO crystal				
O	6.0(8)	2.05(2)	0.008(1)	0.0028
Ni	11(1)	2.94(2)	0.008(2)	
O	7(1)	3.39(5)	0.009(2)	

Table S.3. Parameters of the nearest coordination shells around Ni in Ni/05ZSM-5-1 sample: coordination number N, distance (R), and Debye-Waller factor (σ^2). Uncertainty of the last digit is given in parentheses. A best fit is obtained with the amplitude reduction factor $S_0^2 = 0.90(5)$ and the shift of the energy origin ΔE_o = -2(1) eV. The R-factor (quality of fit parameter) is listed in the last column.

Ni neighbor	*N*	*R* [Å]	σ² [Å²]	*R*-factor
Ni/05ZSM-5-1				
O	6.0(5)	2.053(4)	0.0061(5)	0.0032
Si	2(1)	3.17(6)	0.017(4)	

Table S.4. Parameters of the nearest coordination shells around Ni in Ni/ZSM-5 zeolite samples: average number of neighbor atoms (N), distance (R), and Debye-Waller factor (σ^2). Uncertainty of the last digit is given in parentheses. A best fit is obtained with the amplitude reduction factor $S_0^2 = 0.90(5)$ and the shift of the energy origin $\Delta E_o = -2(1)$ eV. The R-factor (quality of fit parameter) is listed in the last column.

Ni neighbor	***N***	***R* [Å]**	**σ^2 [Å^2]**	***R*-factor**
Ni/05ZSM-5-3				
O	6.0(4)	2.063(5)	0.0066(5)	0.0015
Ni	4.2(5)	2.959(4)	0.0065(6)	
O	2(1)	3.46(3)	0.009(2)	

Ni neighbor	***N*N$_{rel}$***	***R* [Å]**	**σ^2 [Å^2]**	***R*-factor**
Ni/05ZSM-5-5				
O	6.0(6)	2.063(5)	0.0061(5)	0.0021
Ni	4.9(5)	2.957(4)	0.0063(6)	
O	3(1)	3.45(3)	0.009(2)	

Ni neighbor	***N*N$_{rel}$***	***R* [Å]**	**σ^2 [Å^2]**	***R*-factor**
Ni/04ZSM-5-1				
O	6.0(6)	2.072(5)	0.005(5)	0.0034
Ni	8.7(5)	2.961(4)	0.0058(6)	
O	6(1)	3.47(3)	0.009(2)	

Ni neighbor	***N*N$_{rel}$***	***R* [Å]**	**σ^2 [Å^2]**	***R*-factor**
Ni/04ZSM-5-3				
O	6.0(6)	2.071(5)	0.0052(9)	0.0024
Ni	9.0(6)	2.956(4)	0.0055(6)	
O	6(1)	3.45(3)	0.009(2)	

Ni neighbor	N^*N_{rel}	*R* [Å]	σ^2 [Å^2]	*R*-factor
Ni/04ZSM-5-5				
O	6.0(6)	2.070(5)	0.006(5)	0.0011
Ni	8.6(5)	2.957(4)	0.0062(6)	
O	4(1)	3.55(3)	0.009(2)	

Ni neighbor	N^*N_{rel}	*R* [Å]	σ^2 [Å^2]	*R*-factor
Ni/03ZSM-5-1				
O	6.0(6)	2.066(4)	0.0061(7)	0.0006
Ni	8.5(6)	2.952(3)	0.0060(4)	
O	4(1)	3.43(3)	0.009(2)	

Ni neighbor	N^*N_{rel}	*R* [Å]	σ^2 [Å^2]	*R*-factor
Ni/03ZSM-5-3				
O	6.0(6)	2.071(4)	0.0058(7)	0.0010
Ni	9.0(5)	2.958(3)	0.0063(4)	
O	4(1)	3.46(3)	0.009(2)	

Ni neighbor	N^*N_{rel}	*R* [Å]	σ^2 [Å^2]	*R*-factor
Ni/03ZSM-5-5				
O	6.0(6)	2.069(4)	0.0064(7)	0.0009
Ni	8.5(5)	2.956(3)	0.0063(4)	
O	4(1)	3.46(3)	0.009(2)	