Supplementary Information

Metal-Loaded Zeolites in Ammonia Decomposition Catalysis

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XAS

EXAFS - Experimental

EXAFS data analysis was conducted using IFEFFIT with Horae packages (Athena and Artemis). Spectra were calibrated with Ru foil as a reference to avoid energy shifts of the samples. The amplitude reducing parameter was obtained from EXAFS data analysis of the Ru foil, which was used as a fixed input parameter in the data fitting to allow the refinement in the CN of the absorption element.

Sample	Scattering Paths	CN	Radial distance / Å	D-W factor / 10^{-3}	E_0	R-factor	k range	R range
Ru-Y 6.4%	Ru-Ru	9.68 ± 1.19	2.675 ± 0.005	3.8 ± 0.7	-5.42 ± 1.05	1.72	2-13	1-3
Ru-Y (N) 6.4%	**Ru-O**	**4.18 ± 1.70**	**1.99 ± 0.03**	**8.3 ± 5.0**	**-2.00 ± 3.87**	**1.62**	**2-13**	**1-3**
	Ru-Ru	**3.90 ± 1.08**	**2.67 ± 0.01**	**6.2 ± 1.7**	**-4.06 ± 1.77**			
Ru-Y 3.3%	Ru-O	3.10 ± 4.30	1.96 ± 0.09	10.4 ± 17.2	-7.65 ± 13.52	1.48	2-13	1-3
	Ru-Ru	7.01 ± 1.53	2.678 ± 0.008	4.2 ± 1.2	-5.52 ± 1.58			
Ru-Y (N) 3.3%	**Ru-O**	**4.65 ± 1.58**	**2.00 ± 0.02**	**8.1 ± 4.2**	**-2.80 ± 3.34**	**2.59**	**2-13**	**1-3**
	Ru-Ru	**3.35 ± 1.20**	**2.60 ± 0.02**	**7.8 ± 2.5**	**-3.22 ± 2.17**			

Table S.1: Complete EXAFS fitting parameters for Ru-Y catalyst series.

EXAFS - DFT simulations

To ensure consistency, all EXAFS fittings were performed with the same parameters. The R range of 1-4 and k range of 4-12 was considered, with a Hanning k-window at dk = 1 and dR = 0. Fit included all the scattering paths shorter than 4 Å present in the geometry-optimised structure. The background function was fitted without

phase correction. To limit the number of optimised variables, all paths included in the fitting model have been optimised with the same passive amplitude reduction factor (S02) and energy shift parameter (Δ_{E0}). k1, k2, and k3-weighted data are all fitted for reliability, using the Artemis software from the Demeter package.

XANES - DFT simulations

Experimental Ru K-edge XANES for left and right and spectra were calculated and FDMNES codes for Ru_6N_6 clusters. The Green's function multiple-scattering method was used as implemented in the fdmnes code. Calculated spectra in the main panel are shifted vertically for clarity. The XANES region where the largest size effect is observed is zoomed in in the inset.

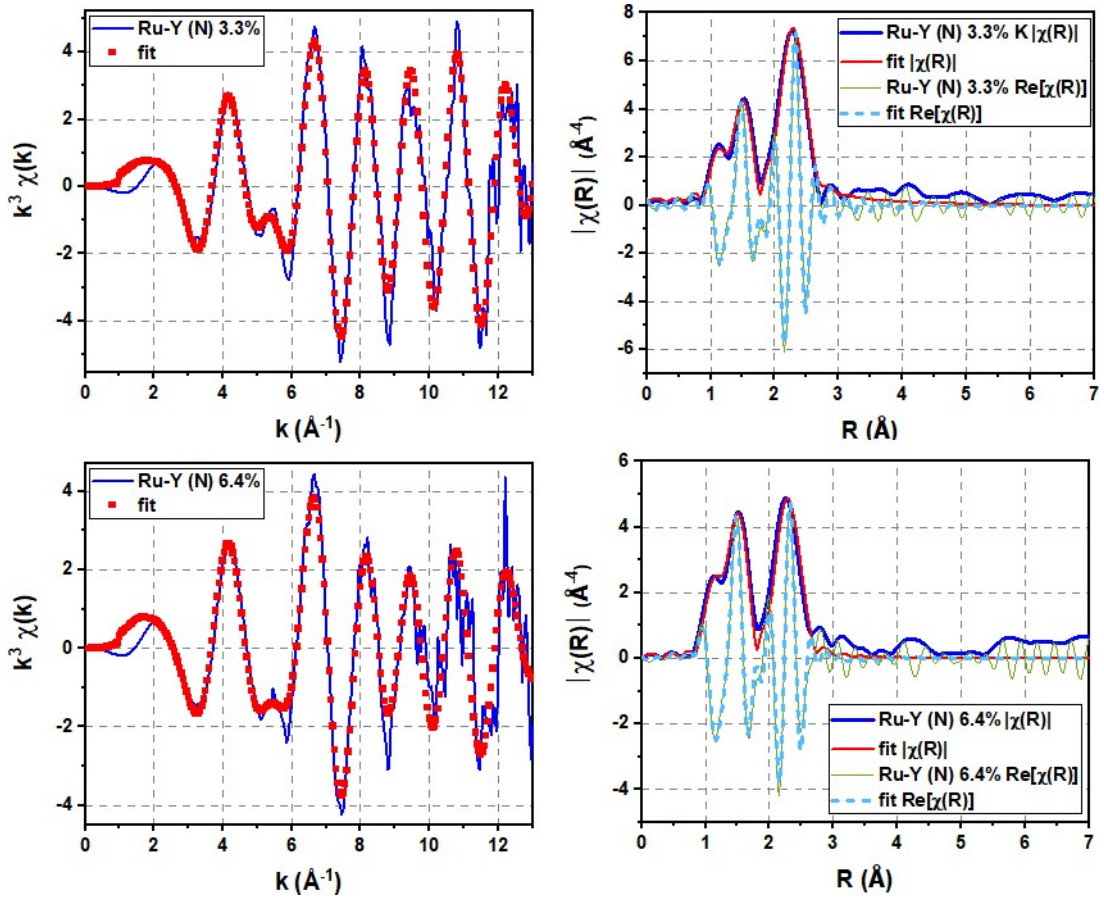

Figure S.1: EXAFS fitting curves of Ru-Y (N) 6.4% and Ru-Y (N) 3.3% in R-space and k-space.

Model	1st shell	CN	R_{fit} (Ru-N)$_1$ [Å]	σ [Å]	ΔR_{fit} (N)	2nd shell	CN	R_{fit} [Å]	σ [Å]	ΔR_{fit} (Ru)	R-value
Ru_6N_6	Ru-N	1	1.93	0.002 ± 0.002	0.176 ± 0.017	Ru-Ru	2	2.33	0.005±0.001	-0.113 ± 0.004	1.24%
							1	2.7			
							2	3.566			

Model	1st shell	CN	R_{fit} (Ru-N)$_1$ [Å]	σ [Å]	ΔR_{fit} (N)	2nd shell	CN	R_{fit} [Å]	σ [Å]	ΔR_{fit} (Ru)	R-value
Ru_6N_6	Ru-N	1	1.93	0.006 ± 0.005	0.145 ± 0.031	Ru-Ru	2	2.33	0.005±0.001	0.113 ± 0.004	2.05%
							1	2.7			
							2	3.566			

Table S.2: Complete DFT calculation parameters for Ru_6N_6 fitting to the EXAFS spectra of Ru-Y (N) 3.3% (top) and Ru-Y (N) 6.4% (bottom). σ is the Debye-Waller factor; R_{fit} is the fitted bond length; ΔR_{fit} is the deviation of the fitted bond length. k_{wt} = 1-3, k-range = 4-12.

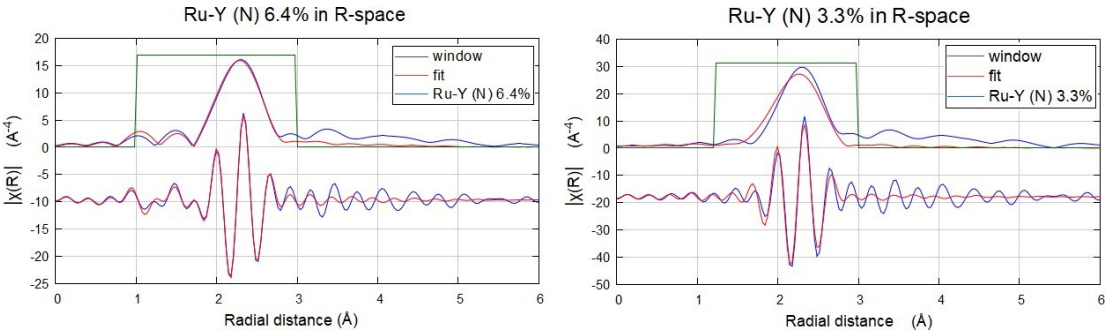

Figure S.2: Fourier-transformed magnitudes of Ru K-edge EXAFS spectra of Ru-Y (N) 6.4% and Ru-Y (N) 3.3%. The best simulated fitting results using this thesis' proposed Ru_6N_6 cluster model is shown in red.