Table S1. Best Fit Results to Rhodium K-edge EXAFS for Various Rhodium-Molybdenum Catalysts Supported in/on FSM-16 and Reference Rh Catalysts

	Rh–O			Rh–C			Rh(–C–)C			Rh–Rh or Rh–Mo			Rh(–O–)Mo			Goodness
Rh wt%	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	of fit
(A) Before Hydroformylation																
$[RhMo_6O_{18}(OH)_6]^{3-}$/FSM-16																
0.22	6.6	1.88	0													12350
	(±3.9)	(±0.15)	(±0.001)													
3.0	6.2	2.014	–0.0011										4.2	3.34	–0.0022	1138
	(±0.3)	(±0.004)	(±0.0003)										(±0.2)	(±0.02)	(±0.0005)	
5.2	7.0	2.030	–0.00030										5.3	3.35	–0.0014	5829
	(±0.6)	(±0.007)	(±0.0006)										(±1.4)	(±0.10)	(±0.0009)	
$[Rh(COD)_2]^+$-$[AlMo_6O_{18}(OH)_6]^{3-}$/FSM-16																
1.6	1.8	2.05	0.0010	8.0[b]	2.092	0[b]	8.0[b]	2.962	0.0001							140
	(±1.2)	(±0.03)	(±0.009)		(±0.004)			(±0.007)	(±0.0003)							
$[Rh(COD)_2]^+$/FSM-16																
1.1	2.0	2.04	0.0020	8.0[b]	2.09	0[b]	8.0[b]	2.99	–0.0053							404
	(±0.8)	(±0.04)	(±0.01)		(±0.01)			(±0.02)	(±0.004)							
(B) After Hydroformylation (433 K, 5h)[a]																
$[RhMo_6O_{18}(OH)_6]^{3-}$/FSM-16																
0.22										8.4	2.679	0.0013				1674
										(±0.2)	(±0.001)	(±0.0002)				
3.0	5.2	2.028	0.0038							1.6	2.709	–0.00008	0.8	3.37	0.0092	48
	(±0.6)	(±0.006)	(±0.0008)							(±0.4)	(±0.001)	(±0.0012)	(±0.7)	(±0.06)	(±0.0077)	
5.2	4.0	2.041	0.0004							1.3	2.676	0.0042	1.0	3.364	–0.0039	187
	(±0.6)	(±0.006)	(±0.0010)							(±0.5)	(±0.004)	(±0.0021)	(±0.2)	(±0.006)	(±0.0010)	
$[Rh(COD)_2]^+$-$[AlMo_6O_{18}(OH)_6]^{3-}$/FSM-16																
1.6										8.2	2.688	–1.7				1567
										(±0.3)	(±0.001)	(±1.7)				
$RhCl_3$/FSM-16																
0.5										7.3	2.686	0.0014				2074
										(±1.0)	(±0.006)	(±0.0031)				
33										7.7	2.685	0.00073				2431
										(±0.5)	(±0.001)	(±0.00023)				
Crystal **1**	6	2.021											6	3.355		Ref. 19
Crystal **3**				8	2.228		8	3.043								Ref. 18

[a] Same reaction conditions as for Table 3.

[b] Equalized to the values for $[Rh(COD)_2]^+[BF_4]^-$ because no loss of COD ligand was found during catalyst synthesis (UV-Visible absorption) and pretreatment (GC).

Table S2. Best Fit Results to Molybdenum K-edge EXAFS for Various Rhodium-Molybdenum Catalysts Supported in/on FSM-16 and Reference Rh Catalysts

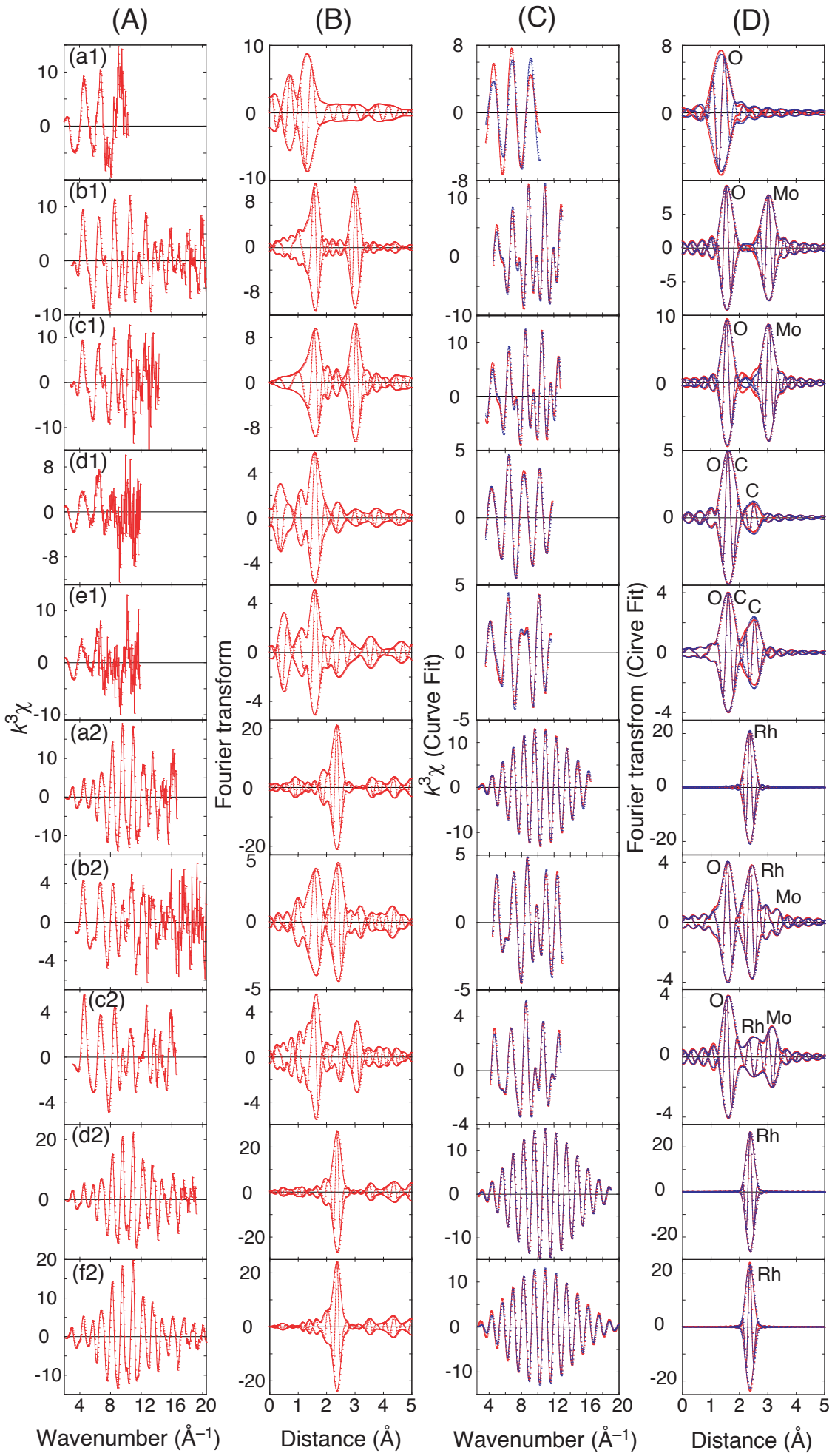
	Mo–O			Mo–O			Mo–Rh			Mo(–O–)Mo or Mo(–O–)Rh			Goodness
Rh wt%	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	*N*	*R*(Å)	$\Delta\sigma^2$(Å^2)	of fit
(A) Before Hydroformylation													
$[RhMo_6O_{18}(OH)_6]^{3-}$/FSM-16													
0.22	6.1	1.60	0.0089	1.3	2.07	0.0015				4.0	3.41	0.0083	1680
	(±2.0)	(±0.09)	(±0.009)	(±0.5)	(±0.02)	(±0.010)				(±2.2)	(±0.11)	(±0.012)	
3.0	0.6	1.67	–0.0022	1.1	2.00	–0.0019				2.5	3.356	–0.0004	1955
	(±0.5)	(±0.02)	(±0.002)	(±0.3)	(±0.05)	(±0.0004)				(±0.5)	(±0.004)	(±0.001)	
$[Rh(COD)_2]^+$-$[AlMo_6O_{18}(OH)_6]^{3-}$/FSM-16													
1.6	1.6	1.664	0.00031	1.9	1.99	0.00071				2.2	3.324	0.00039	425
	(±0.3)	(±0.001)	(±0.0009)	(±0.2)	(±0.02)	(±0.001)				(±0.3)	(±0.001)	(±0.0006)	
(B) After Hydroformylation (433 K, 5h)[a]													
$[RhMo_6O_{18}(OH)_6]^{3-}$/FSM-16													
0.22	1.0	1.664	–2.0	5.3	1.98	0.018	0.9	2.74	2.0	1.4	3.185	–2.4	17
	(±0.8)	(±0.007)	(±5.1)	(±2.1)	(±0.09)	(±0.007)	(±0.7)	(±0.05)	(±3.9)	(±0.5)	(±0.008)	(±2.5)	
3.0	1.8	1.66	–0.0007	2.4	1.99	–0.0007	1.5	2.59	0.0011				3.0
	(±0.1)	(±0.02)	(±0.0023)	(±0.4)	(±0.04)	(±0.0006)	(±0.2)	(±0.02)	(±0.003)				
5.2	0.7	1.67	–0.00030	4.7	1.94	0.010	1.4	2.56	0.0030	0.8	3.35	–0.00018	993
	(±0.5)	(±0.02)	(±0.004)	(±1.2)	(±0.05)	(±0.005)	(±0.1)	(±0.01)	(±0.0008)	(±0.3)	(±0.01)	(±0.002)	
$[Rh(COD)_2]^+$-$[AlMo_6O_{18}(OH)_6]^{3-}$/FSM-16													
1.6	1.7	1.66	0.0013	2.8	1.89	0.012	0.2	2.563	–0.0025	1.3	3.286	0.0024	203
	(±0.2)	(±0.01)	(±0.001)	(±1.4)	(±0.06)	(±0.01)	(±0.2)	(±0.008)	(±0.004)	(±0.2)	(±0.004)	(±0.0004)	
Crystal **1**	4	1.825		2	2.289					3	3.366		Ref. 19

[a] Same reaction conditions as for Table 3.

(Supporting Materials, Figures)

Figure S1. Rh K-edge EXAFS data for (a – c) $[RhMo_6O_{18}(OH)_6]^{3-}$/FSM-16 [0.22 (a), 3.0 (b), and 5.2 wt% Rh (c)], (d) $[Rh(COD)_2]^+$-$[AlMo_6O_{18}(OH)_6]^{3-}$/FSM-16, (e) $[Rh(COD)_2]^+$/FSM-16, and (f) $RhCl_3$/FSM-16 catalyst (33 wt% Rh). a1 – e1: before catalysis. a2 – f2: after propene hydroformylation at 433 K for 5h. (A) k^3-weighted EXAFS χ function, (B) its associated Fourier transform, and curve-fit results in *k*-space (C) and *R*-space (D). Solid and dotted lines are experimental and calculated, respectively, in C and D.

Figure S2. Mo K-edge EXAFS data for (a – c) $[RhMo_6O_{18}(OH)_6]^{3-}$/FSM-16 catalysts [0.22 (a), 3.0 (b), and 5.2 wt% Rh (c)] and (d) $[Rh(COD)_2]^+$-$[AlMo_6O_{18}(OH)_6]^{3-}$/FSM-16. a1 – d1: before catalysis. a2 – d2: after propene hydroformylation at 433 K for 5h. (A) k^3-weighted EXAFS χ function, (B) its associated Fourier transform, and curve-fit results in *k*-space (C) and *R*-space (D). Solid and dotted lines are experimental and calculated data, respectively, in C and D.


(A)
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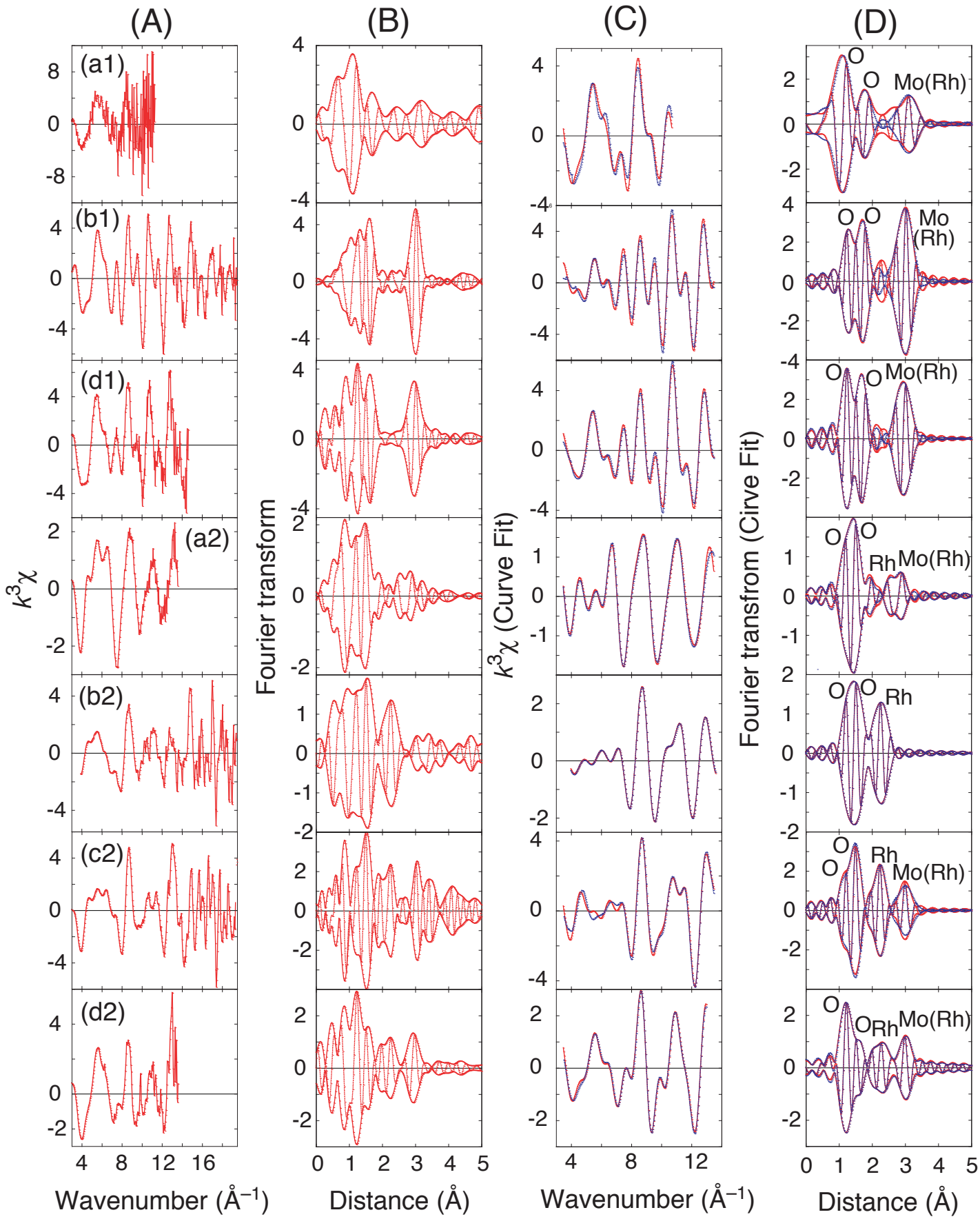
Wavenumber (Å^{-1})
Distance (Å)


(A)
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$k^3\chi$
Fourier transform
$k^3\chi$ (Curve Fit)
Fourier transfrom (Cirve Fit)
Wavenumber (Å^{-1})
Distance (Å)
O
Mo(Rh)
Mo
(Rh)
Rh