Supporting Online Information

Enhanced Catalytic Properties of Rhodium Nanoparticles Deposited on Chemically Modified SiO₂ for Hydrogenation of Nitrile Butadiene Rubber

Peng Cao^a, Yanqiang Ni^a, Rui Zou^a, Liqun Zhang^{a,b}, Dongmei Yue^{a,b*}

^a State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

^b Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing 100029, China



Fig. S1. Images of (a) $Rh(III)/SiO_2 \mathbf{3}$ and (b) $Rh(III)/MSiO_2 \mathbf{1}$.



Fig. S2. SEM images of (a) SiO_2 , (b) $MSiO_2$, (c) $Rh(II)/SiO_2$ **3** and (d) $Rh(II)/MSiO_2$ **1**.



Fig. S3. Nitrogen adsorption/desorption isotherms of (a) SiO₂ and (b) MSiO₂.



Fig. S4. XPS survey scan of (a) SiO₂ and (b) MSiO₂.



Fig. S5. Degree of hydrogenation of NBR under different reaction conditions with Rh(III)/MSiO₂ **1** as catalyst. Reaction conditions: (a) concentration of NBR solution=3 wt%, W_{PPh3}/W_{cat} = 0.5, P_{H2} =3.0 MPa, and T=120 °C; (b) concentration of NBR solution=3 wt%, W_{cat}/W_{NBR} =0.05, W_{PPh3}/W_{cat} =0.5, P_{H2} =3.0 MPa, and t=8 h; (c) concentration of NBR solution=3 wt%, W_{cat}/W_{NBR} =0.05, W_{PPh3}/W_{cat} = 0.5, T=120 °C, and t=8 h; (d) concentration of NBR solution=3 wt%, W_{cat}/W_{NBR} = 0.5, W_{PPh3}/W_{cat} = 0.5, t=8 h, and T=120 °C.



Fig. S6. Catalytic performance of recycled catalyst for hydrogenation of NBR.



Fig. S7. SEM micrographs of Rh(III)/MSiO₂1: (a) before reaction and (b) after 3rd cycle.



Fig. S8. (a) XPS survey spectra $Rh(III)/SiO_2$ and used $Rh(III)/MSiO_2$; (b) XPS Rh 3d spectra for $Rh(III)/SiO_2$ and used $Rh(III)/MSiO_2$.



Fig. S9. FTIR spectra of $Rh(III)/SiO_2$ and used $Rh(III)/MSiO_2$.



Fig. S10. Effect of various supports catalysts on degree of hydrogenation. Reaction conditions: NBR solution (200 mL, 3 wt%), supported catalyst (0.12 g, 2 wt%), and triphenylphosphine (0.06 g, 1 wt%) were heated at 120 °Cand H₂ pressure of 3.0 MPa for 6 h.



Fig. S11. Effect of different metal catalysts on degree of hydrogenation. Reaction conditions: NBR solution (200 mL, 3 wt %), supported catalyst (0.12 g, 2 wt %), and triphenylphosphine (0.06 g, 1 wt %) were heated at 120°C and H₂ pressure of 3.0 MPa for 6 h.

Table S1. Surface area, pore volume, and average pore diameter from BJH absorption calculation

Materials	S _{BET} ^a (m ² /g)	V_{P^b} (cm ³ /g)	D _{BJH} ^c (nm)
SiO ₂	152.44	0.73	19.40
MSiO ₂	115.30	0.39	15.21

^aBET surface area, ^bpore volume, and ^caverage pore diameter from BJH absorption.

Table S2. Results from XPS Si 2p spectrum of SiO₂ in Fig. 4a

Species	Position (eV)	Contribution (%)
Si ⁴⁺	103.72±0.1	97.66±0.2
Si-OH	105.92±0.1	2.34±0.2

Table S3. Results from XPS Si 2p spectrum of MSiO₂ in Fig. 4b

Species	Position (eV)	Contribution (%)
Si ⁴⁺	103.49±0.1	99.92±0.01
Si-OH	105.69±0.1	$0.08{\pm}0.01$

Table S4. Results from XPS N 1s spectra of MSiO₂ in Fig. 4d

Species	Position (eV)	Contribution (%)
"free"-NH ₂	399.8±0.2	76.73±0.3
hydrogen bonded -NH ₂	401.3±0.2	23.27±0.3

Table S5. Degree of hydrogenation for Rh(III)/MSiO₂ 1 prepared by using different solvents

Solvents	Water	Water/Ethanol	Ethanol
HD (%)	96.68	95.87	96.88

Reaction conditions: NBR solution (200 mL, 3 wt%), supported catalyst $Rh(III)/MSiO_2 1$ (0.30 g, 5 wt%), and PPh₃ (0.15 g, 0.25 wt%) were heated at of 120 °C under H₂ pressure of 3.0 MPa for 8 h.

Table S6. Degree of hydrogenation for $Rh(III)/MSiO_2 1$ with different particle sizes of SiO_2

Particle sizes of SiO ₂ (µm)	0.04	1	10	48	150
HD (%)	72.92	77.86	76.66	65.23	62.40
Separation	No	No	Hard	Formal	Formal

Reaction conditions: NBR solution (200 mL, 3 wt %), supported catalyst (0.12 g, 2 wt %), and PPh₃ (0.06 g, 1 wt %) were heated at 120 °C under H₂ pressure of 3.0 MPa for 6 h.

Table S7. Comparison of degrees of hydrogenation and compositions of fresh and used catalysts

Recycle	1	2	3
HD (%)	98.53	90.35	67.61
Content of Rh (%)	1.18	1.03	0.98