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A Ternary Rh Complex Catalyst Highly Active and Stable in Hydrogenation of Acrylonitrile-Butadiene Rubber

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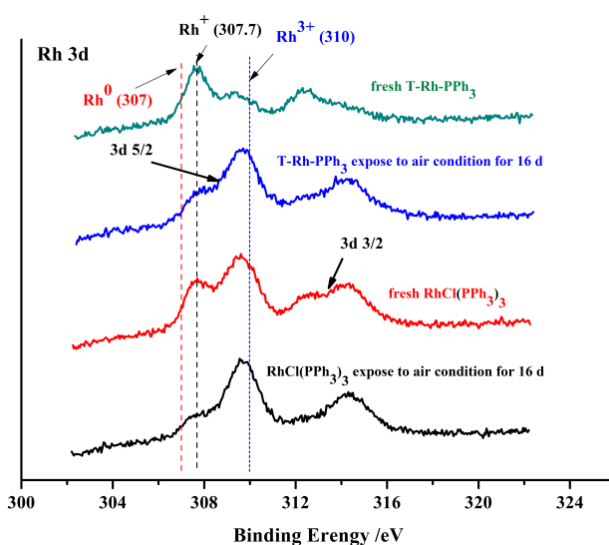


Fig. 1. X-ray photoelectron spectra of the Rh 3d region for various Rh catalysts.

The X-ray photoelectron spectra of the Rh 3d_{5/2} of various Rh catalysts are shown in Fig. 1. The spectrum of Rh 3d_{5/2} electrons for both catalysts was decomposed in two peaks: one at low binding energy centered at 307.7 eV and other at higher binding energy at 309.2-309.5 eV. Rh 3d_{5/2} electrons with binding energy of 307.6-309.6 eV (mean: 308.8 eV) have been usually assigned to Rh⁺ species^{1,2}, while the component appearing at 308.8-311.3 eV (mean: 308.8 eV) can be associated with Rh³⁺ species^{1,2}. For fresh T-Rh-PPh₃, the major signal of Rh 3d_{5/2} was observed at 307.7 eV, which was identical with that of the value of the state of Rh⁺. However, spectra for fresh RhCl(PPh₃)₃ shows two relatively sharp Rh 3d_{5/2} peaks at binding energies of 307.7 and 309.3 eV, respectively. Compared with previous literature reports^{1,3,4}, the Rh 3d_{5/2} peaks for fresh RhCl(PPh₃)₃ observed in the range of 307.7-309.3 eV can be assigned to cationic Rh^{δ+} (δ~1) species. After exposing to air condition for 16 d, only a major signal of Rh 3d_{5/2} for RhCl(PPh₃)₃ was observed at 309.5 eV, indicating the few portion of

Rh^+ was oxidized. The similar spectrum was observed for T-Rh- PPh_3 . The reason for the indistinguishable difference in the Rh $3d_{5/2}$ binding energies (~ 309.5 eV) for the two catalysts is that only a few Rh^+ transferred to Rh^{3+} after a relatively short oxidation time of 16 d.

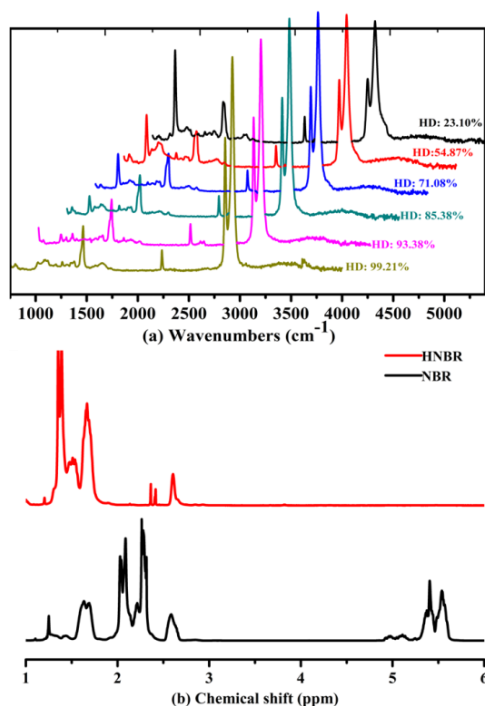


Fig. S2 (a) FTIR spectra of different degrees of hydrogenation of NBR, (b) ^1H NMR spectra of NBR and HNBR

Fig. S2 (a) shows the FTIR spectra of HNBR samples with different degrees of hydrogenation. The main peaks are at 2237 cm^{-1} (assigned to $-\text{CN}$ stretching vibration), 2928 cm^{-1} (assigned to $-\text{CH}_2-$ symmetric stretching vibration), 2857 cm^{-1} (assigned to $-\text{CH}_2-$ asymmetric stretching vibration), 1463 cm^{-1} (assigned to $-\text{CH}_2-$ deformation vibration), 968 cm^{-1} (assigned to $-\text{CH}=\text{CH}-$ (1,4 cis- and trans-unit)), and 724 cm^{-1} (assigned to $-\text{CH}_2-$ vibration).

Fig. S2 (b) illustrates the ^1H NMR spectra of HNBR and NBR. The main peaks are assigned as follows: 5.3-5.4 ppm ($-\text{CH}=\text{CH}-$, 1,4-cis and trans structural units); 2.5 ppm ($-\text{CH}-\text{CN}$, acrylonitrile structural units); 1.2-1.4 ppm ($-\text{CH}_2-\text{CH}-$, methylene structure unit); 1.5-1.6 ppm ($-\text{CH}_2-$, methylene structure); 0.8-0.9 ppm ($-\text{CH}_3$, methyl structure).

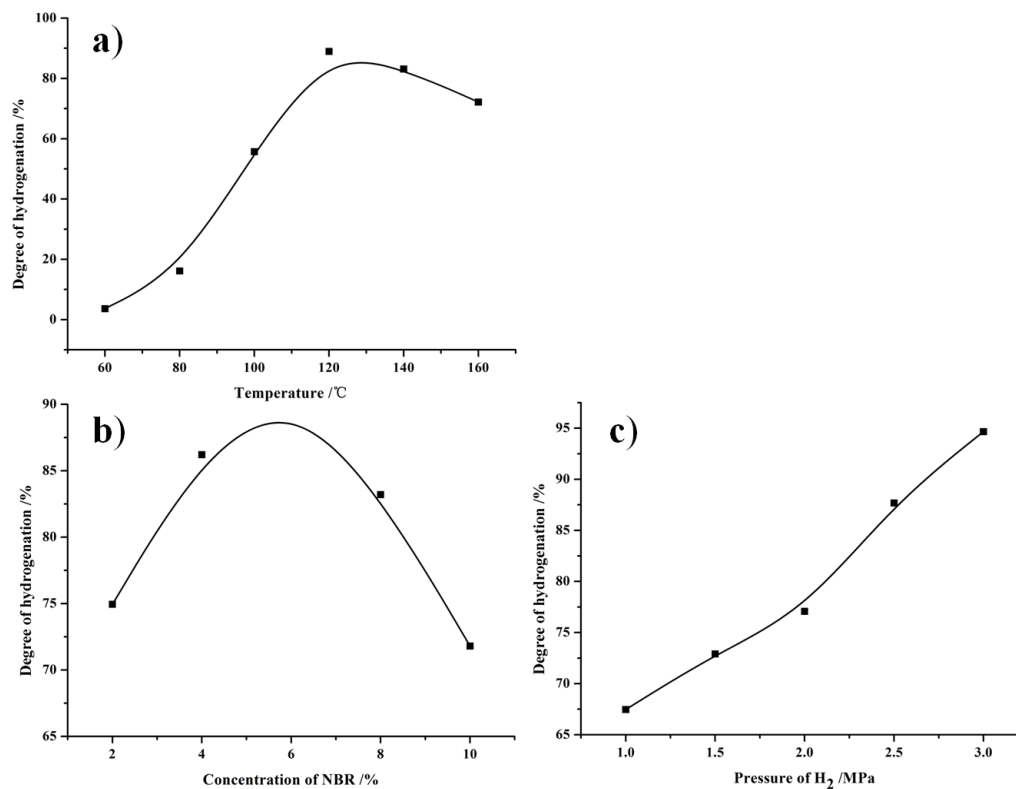


Fig. S3 Hydrogenation of NBR using catalyst of T-Rh-PPh₃: (a) P_{H₂}=2.5 MPa, W_{cat.}/W_{NBR}=0.1%, concentration of NBR=6%, t=8 h; (b) P_{H₂}=2.5 MPa, W_{cat.}/W_{NBR}=0.1%, T=120 °C, t=8 h; (d) W_{cat.}/W_{NBR}=0.1%, concentration of NBR=6%, t=8 h, T=120 °C.

References:

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