Alkali and Alkaline Earth Cation-Decorated TiO₂ Nanotube-Supported Rh Catalysts for Vinyl Acetate Hydroformylation

Hongyuan Chuai ¹, Penghe Su ¹, Hongchi Liu ¹, Baolin Zhu ^{1,2}, Shoumin Zhang ^{1,2}, Weiping Huang ^{1,2,3*}

- ^{1.} College of Chemistry, Nankai University, Tianjin 300071, China
- ² The Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China
- ^{3.} Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300071, China
- * Correspondent: hwp914@nankai.edu.cn; Tel: +86-138-2009-6974

Supplementary Figure 1. Size Distributions of Particles in Catalyst Rh0.5/Li-

TNTs-B5



Supplementary Figure 1. Size distributions of particles in catalyst Rh0.5/Li-TNTs-B5 (10 particles selected from Figure 2B and measured by nanomeasure software).

Supplementary Figure 2. XPS Spectra of Mg 1s in Catalyst Rh0.5/Mg-TNTs-

P5



Supplementary Figure 2. XPS spectra of Mg1s in catalyst Rh0.5/Mg-TNTs-P5.

Supplementary Figure 3. FT-IR Spectra of Mg-TNTs



Supplementary Figure 3. FT-IR spectra of Mg-TNTs.

Supplementary Figure 4. Data of GC Analysis

The product of vinyl acetate hydroformylation was analyzed by gas chromatograph and the temperature program was as follows:

Temperature program: 45 ° C, hold for 3 mins; ramp 1, 2 °C/min to 60 °C, hold for 0 mins; ramp 2, 25 °C/min to 250 °C, hold for 5 min. Injection temperature: 260 °C; detector temperature: 265 °C.

Supplementary Figure 3 shows that the GC data of the sample come from the hydroformylation of vinyl acetate over Rh/Li-TNTs-P5 catalyst. The main peaks with different retention time are listed as follows:

Solvent: toluene, RT: 5.059 min;

Product: 2-acetoxy propanal, RT: 5.715 min;

By-product: ethylene, RT: 1.137 min; propanal, RT: 1.340 min; acetic acid, RT: 1.912 Min.

From the GC result, we can find that the substrate vinyl acetate was used up (vinyl acetate, retention time (RT): around 1.75 min) and there was only one main product: 2-acetoxy propanal. Normally, there will be two kinds of aldehyde, 2-acetoxy propanal and 3-acetoxy propanal, generated in the hydroformylation of vinyl acetate. The GC result indicates that the catalyst Rh/Li-TNTs-P5 has high regioselectivity of 2-acetoxy propanal.



Supplementary Figure 4. Gas chromatogram of vinyl acetate hydroformylation after reaction.