

Supplementary Materials

# The Hydrothermal Stability and the Properties of Non- and Strongly-Interacting Rh Species over Rh/ $\gamma$ , $\theta$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

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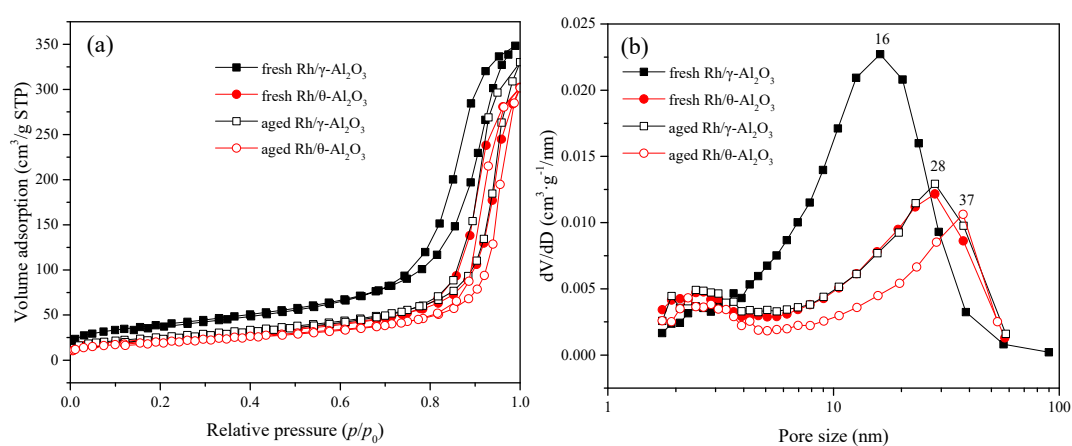
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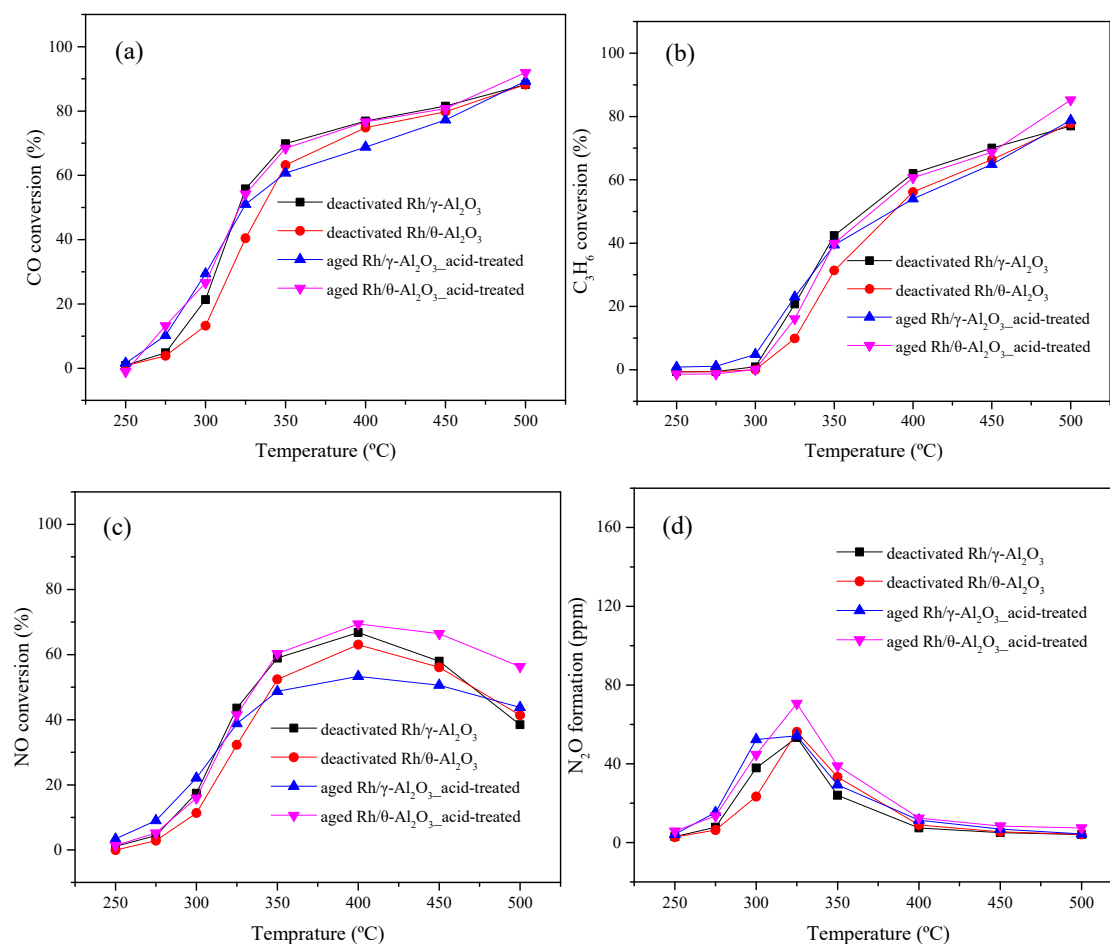
**Figure S1.** The N<sub>2</sub> physical adsorption and desorption analysis results for fresh and aged catalysts: (a) the isothermal plots and (b) pore size distributions.

**Table S1.** The physical properties of fresh and aged Rh/γ, θ-Al<sub>2</sub>O<sub>3</sub> catalysts.

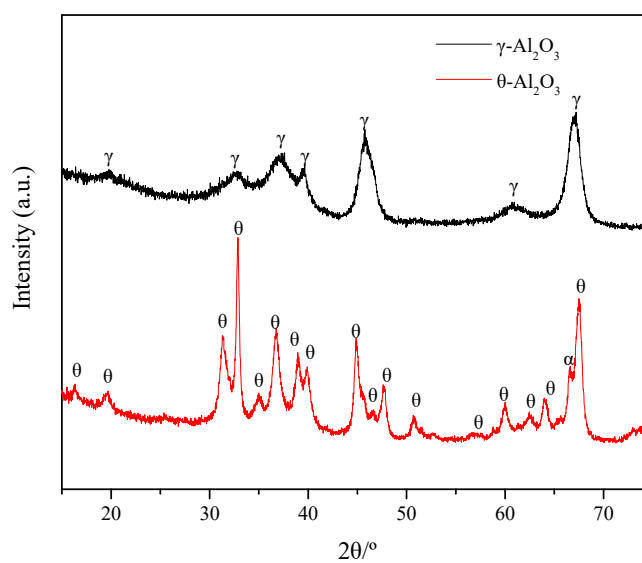
| Samples                             | BET (m <sup>2</sup> /g) |      | Pore volume (cm <sup>3</sup> /g) |      |
|-------------------------------------|-------------------------|------|----------------------------------|------|
|                                     | Fresh                   | Aged | Fresh                            | Aged |
| Rh/γ-Al <sub>2</sub> O <sub>3</sub> | 139                     | 91   | 0.54                             | 0.48 |
| Rh/θ-Al <sub>2</sub> O <sub>3</sub> | 83                      | 72   | 0.47                             | 0.44 |

**Table S2.** Quantification of Rh (3d<sub>5/2</sub>) signals of Rh/γ, θ-Al<sub>2</sub>O<sub>3</sub> catalysts.

| Samples                                         | Binding energy of Rh 3d <sub>5/2</sub><br>(eV) |                  |                  | Rh <sup>0</sup> /Rh<br>(%) | Rh <sup>3+</sup> /R<br>(%) | Rh <sup>4+</sup> /Rh<br>(%) |
|-------------------------------------------------|------------------------------------------------|------------------|------------------|----------------------------|----------------------------|-----------------------------|
|                                                 | Rh <sup>0</sup>                                | Rh <sup>3+</sup> | Rh <sup>4+</sup> |                            |                            |                             |
| fresh Rh/γ-Al <sub>2</sub> O <sub>3</sub>       | 307.4                                          | 309.4            | 310.4            | 11.9                       | 56.4                       | 31.7                        |
| fresh Rh/θ-Al <sub>2</sub> O <sub>3</sub>       | 307.4                                          | 309.3            | 310.5            | 15.5                       | 50.0                       | 34.5                        |
| deactivated Rh/γ-Al <sub>2</sub> O <sub>3</sub> | -                                              | -                | 310.4            | 0                          | 0                          | 100                         |
| deactivated Rh/θ-Al <sub>2</sub> O <sub>3</sub> | -                                              | -                | 310.3            | 0                          | 0                          | 100                         |



**Figure S2.** The profiles of (a) CO, (b) C<sub>3</sub>H<sub>6</sub>, (c) NO conversion, and (d) N<sub>2</sub>O formation over deactivated and aged Rh/γ, θ-Al<sub>2</sub>O<sub>3</sub> after acid-treated (HCl-KBr) under TWC reaction condition. Feed stream: 1% CO, 1000 ppm HCs (C<sub>3</sub>H<sub>6</sub>:C<sub>3</sub>H<sub>8</sub> = 2:1), 1000 ppm NO, 0.917% O<sub>2</sub>, 12% CO<sub>2</sub>, 3% H<sub>2</sub>O, N<sub>2</sub> balance.



**Figure S3.** XRD patterns of catalyst supports.