

Supplementary Material

for the manuscript

**Pd and Pd-Au nanocatalysts supported on exfoliated graphite for  
high throughput dehalogenation by nanocomposite membranes**

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by

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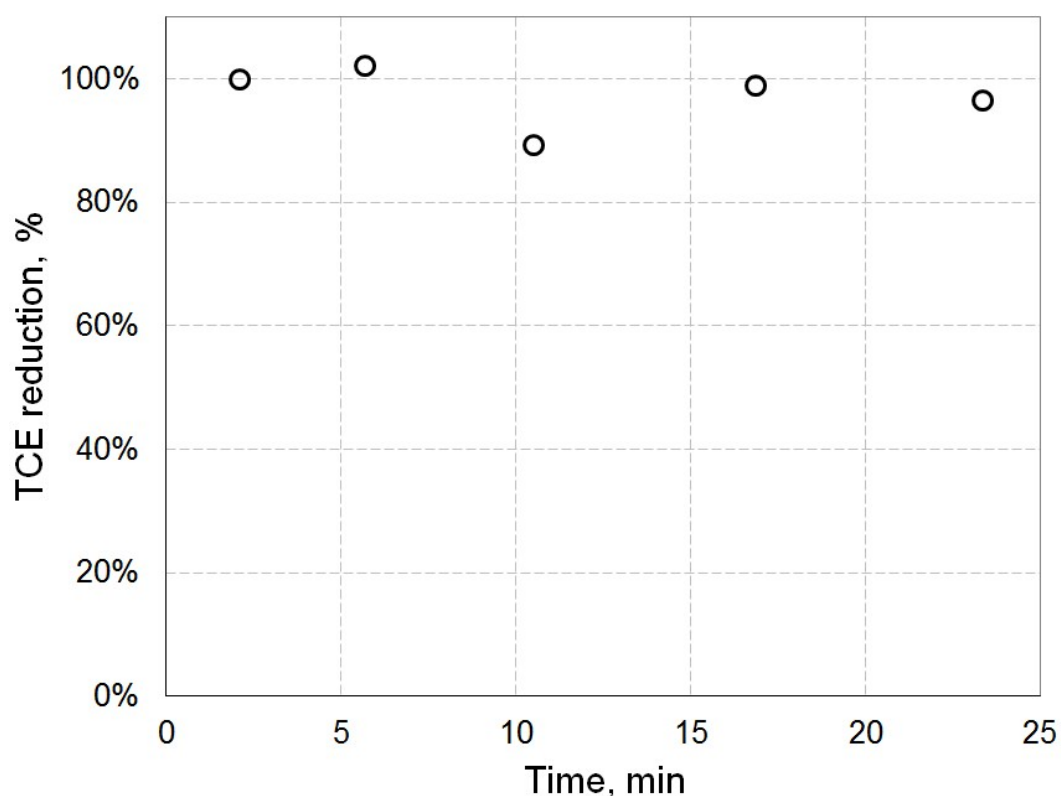
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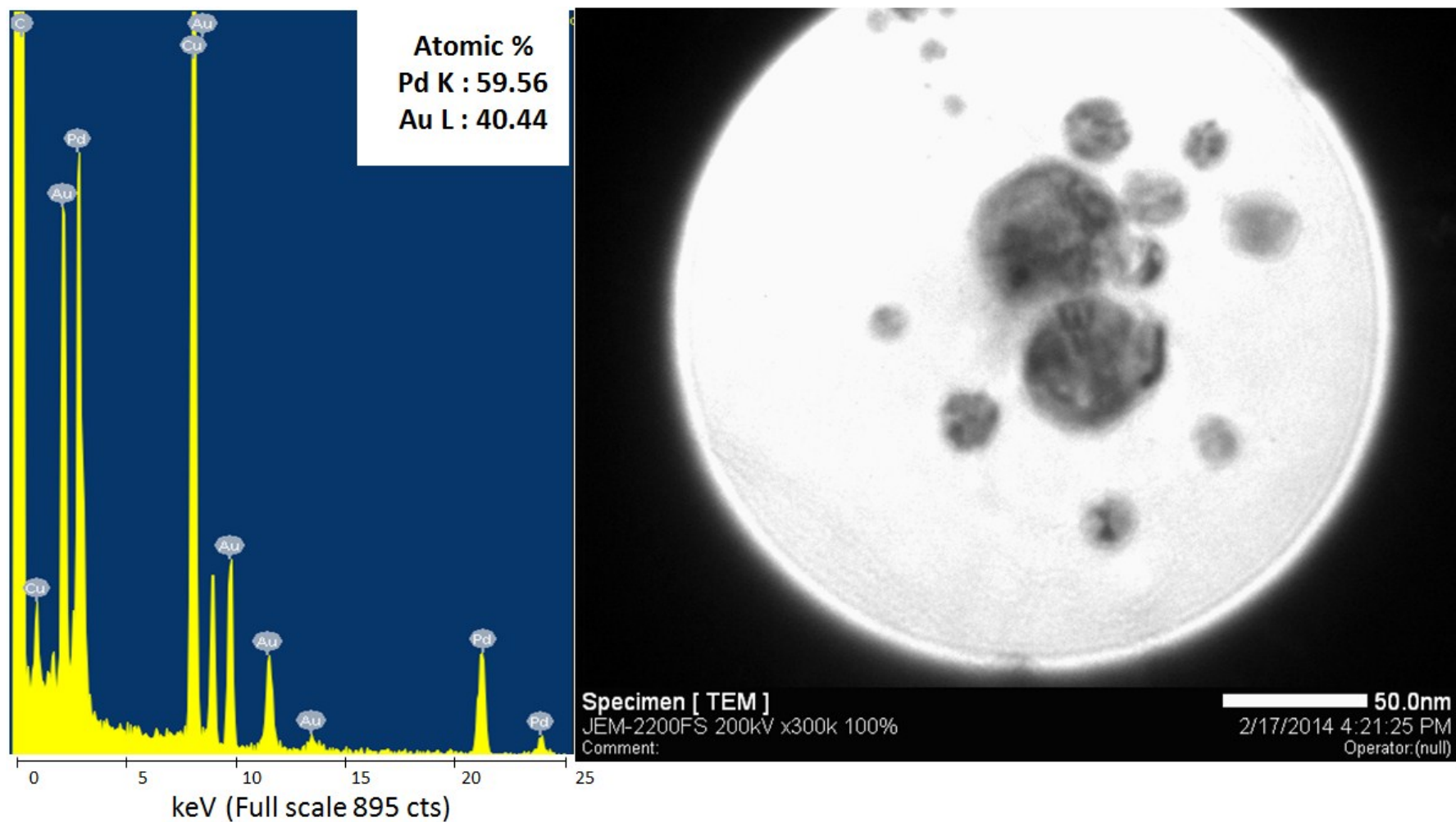
## S1. TCE dechlorination experiments: analytical procedure for measuring TCE

Using a preheated (80°C) 2 mL sample from either the batch or flow-through reactor, a 50  $\mu$ L sample was injected into the gas chromatograph (Perkin-Elmer) using a gas-tight syringe. The TCE peak was observed at 3.0 min, and the area under the curve was extracted for each sample. A 4-point standard calibration curve (10, 100, 1000, and 10,000 ppb) was created to convert areas to mass concentration. The GC was equipped with an electron capture detector, and N<sub>2</sub> was used as the carrier gas. The temperature of the oven was set to 80°C while the detector temperature was 350°C. Control experiments were conducted without H<sub>2</sub> and it was shown that there was no observable adsorption of TCE on xGnP (Figure S1).



**Figure S1.** Results from control experiment conducted with TCE and Pd-Au/xGnP without the reducing agent H<sub>2</sub> present.

## S2. Catalyst characterization by TEM-EDS and AA.



**Figure S2.** TEM EDS results of Pd-Au/xGnP and a TEM micrograph of Pd-Au nanoparticles supported on xGnP.

The Pd and Au nanoparticles were dissolved from the xGnP support, and the solution was filtered and analyzed using AA. AA characterization included the following four steps:

1. A sample of Pd/xGnP or Pd-Au/xGnP was weighed and heated in aqua regia at the boiling point for 1 h.
2. After heating, the suspension was sonicated (Aquasonic 50T, VWR Scientific) for 3 h.
3. The sonicated suspension was filtered through a 0.45  $\mu\text{m}$  mixed cellulose ester filter (Millipore).
4. The filtrate was diluted with DI water and analyzed for Pd and Au content using AA. Because not all Au was leached from Au-xGnP, the cake on the surface of the filter was analyzed for gold content. To do that the filter was dried in a fume hood for 12 h, then was weighed, suspended in fresh aqua regia and subjected to the sequence of treatment steps 2 to 4 three times. At the end, the gold concentration in the filtrate was less than 2% of the total leached Au concentration.

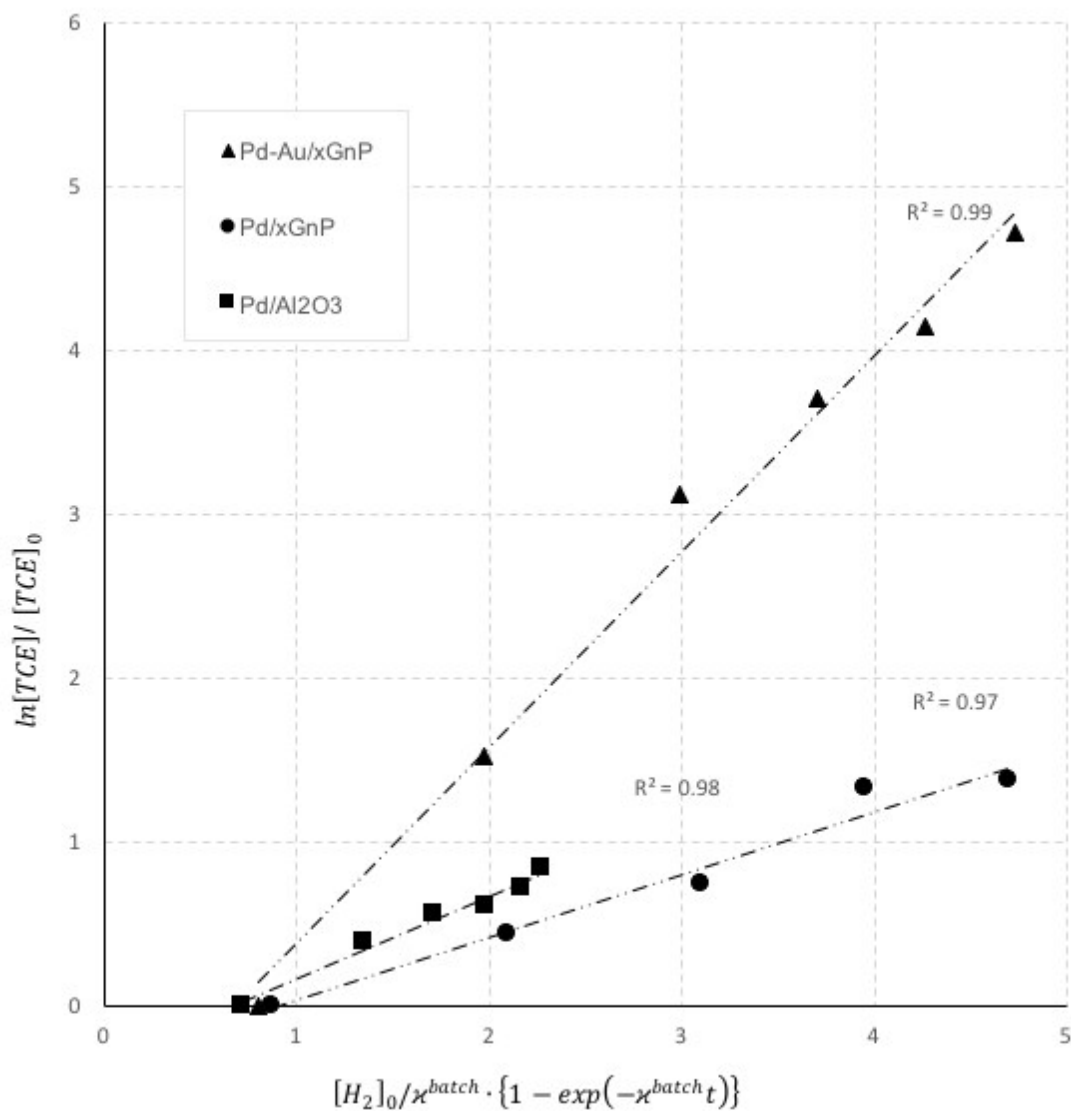
**Table S1.** Atomic adsorption spectroscopy results of Pd and Au concentration on graphene normalized by the mass of xGnP.

Catalyst	Metal concentration normalized by xGnP mass				
	Sample A1	Sample B1	Sample C1	AVE	CI, 90%
Pd/xGnP					
Pd	6.54%	7.62%	4.91%	6.36%	$\pm 1.30\%$
Pd-Au/xGnP					
Pd	6.54%	7.62%	7.62%	7.26%	$\pm 0.59\%$
Au	7.59%	7.30%	6.20%	7.03%	$\pm 0.70\%$

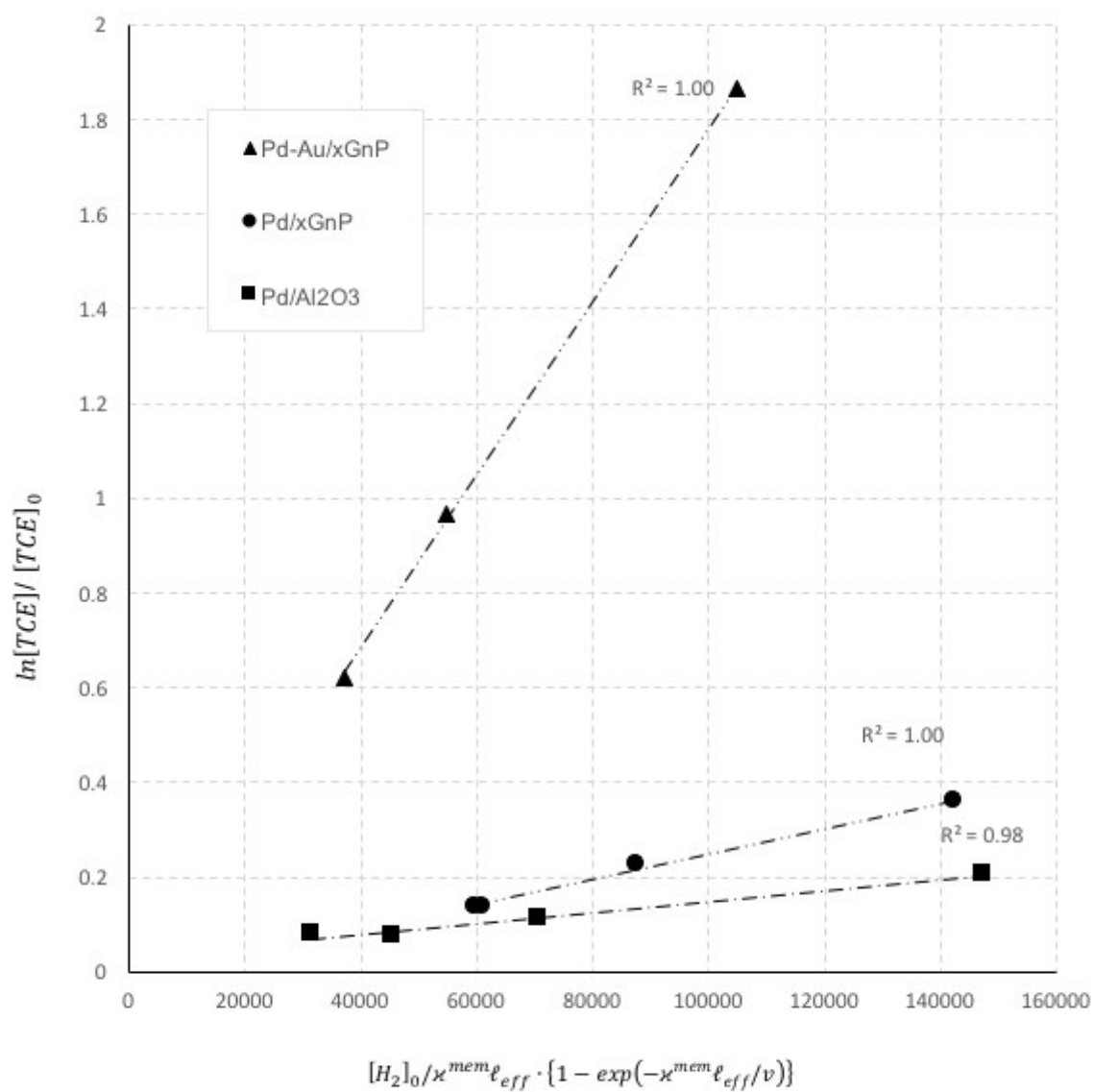
### S3. Comparison of 1<sup>st</sup> order and 2<sup>nd</sup> order reaction kinetics.

The reactivity of newly synthesized nanoparticles fit a 2<sup>nd</sup> order model (eq. (7) in the main manuscript) better than 1<sup>st</sup> order model (e.g. ) because of the disappearance of

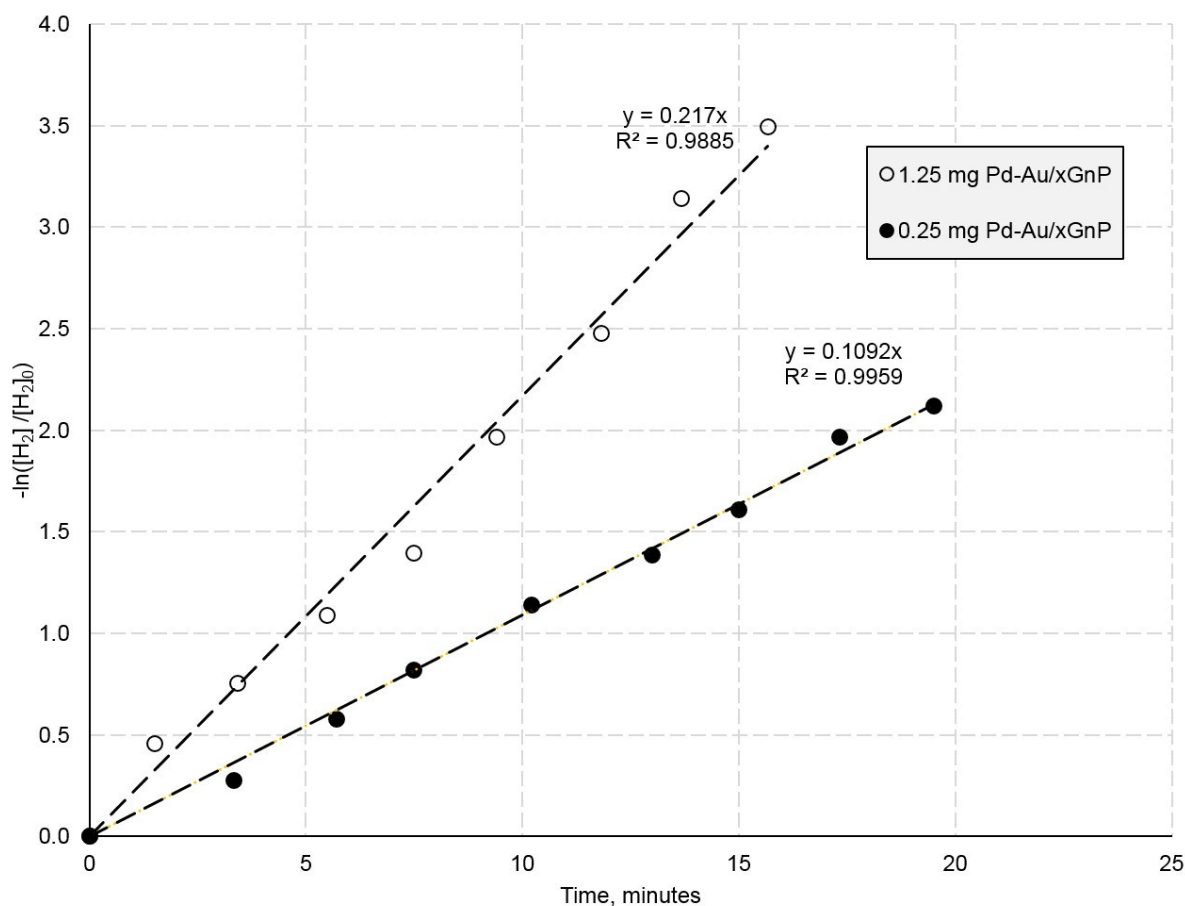
H<sub>2</sub> with time. The 2<sup>nd</sup> order fits of batch (Figure S3) and flow-through (Figure S4) reaction data yielded R<sup>2</sup> values of 0.92 and 0.96, which was significantly higher than corresponding R<sup>2</sup> values (0.73 and 0.91) obtained for to 1<sup>st</sup> order models.



**Figure S3.** Example fits of batch reaction kinetics data to the 2<sup>nd</sup> order reaction model.



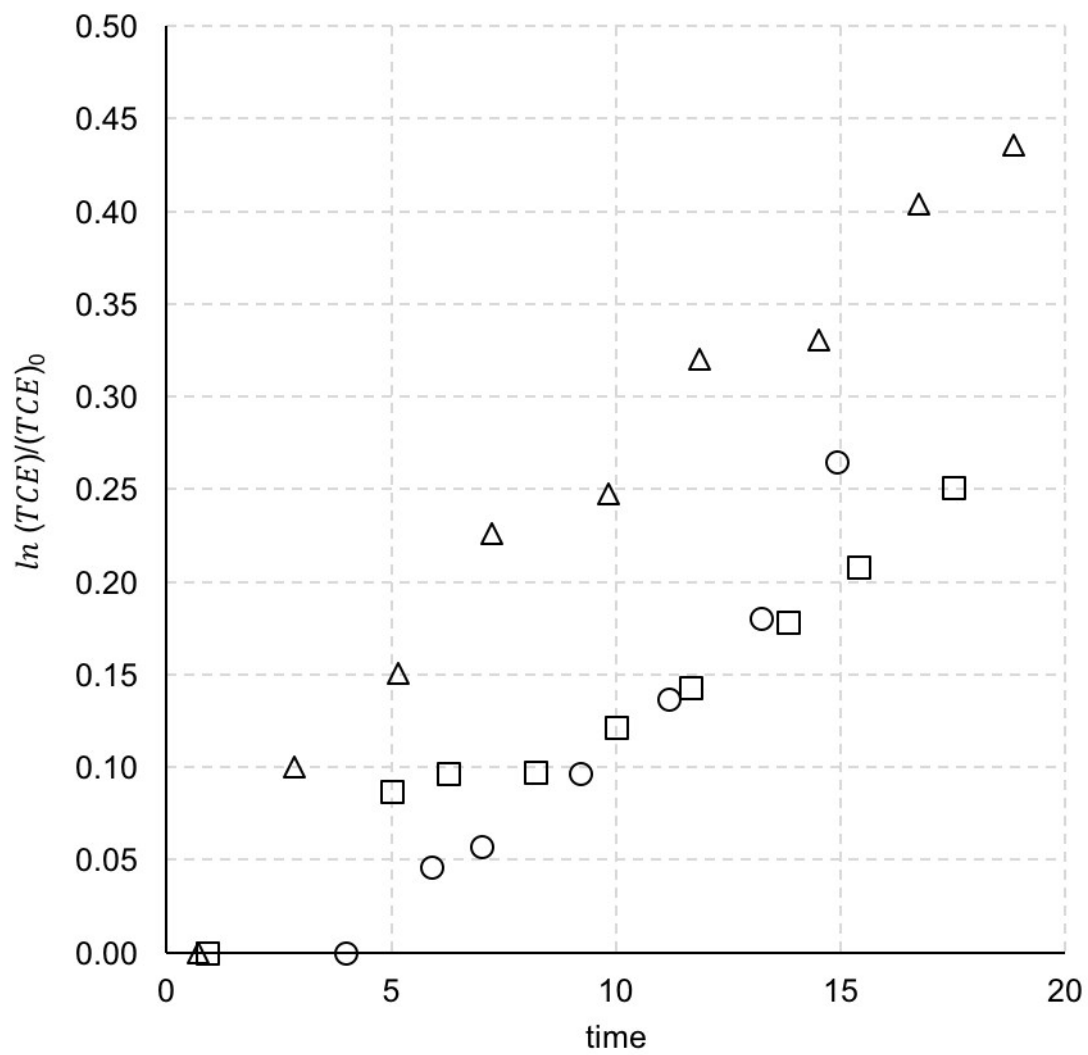
**Figure S4.** Example fits of flow-through reaction kinetics data to the 2<sup>nd</sup> order reaction model.



**Figure S5.** Example fits of H<sub>2</sub> decomposition kinetics data to the 1<sup>st</sup> order reaction model for TCE dehalogenation experiments with Pd-Au/xGnP catalyst at regular (1.25 mg) and low (0.25 mg) loadings.

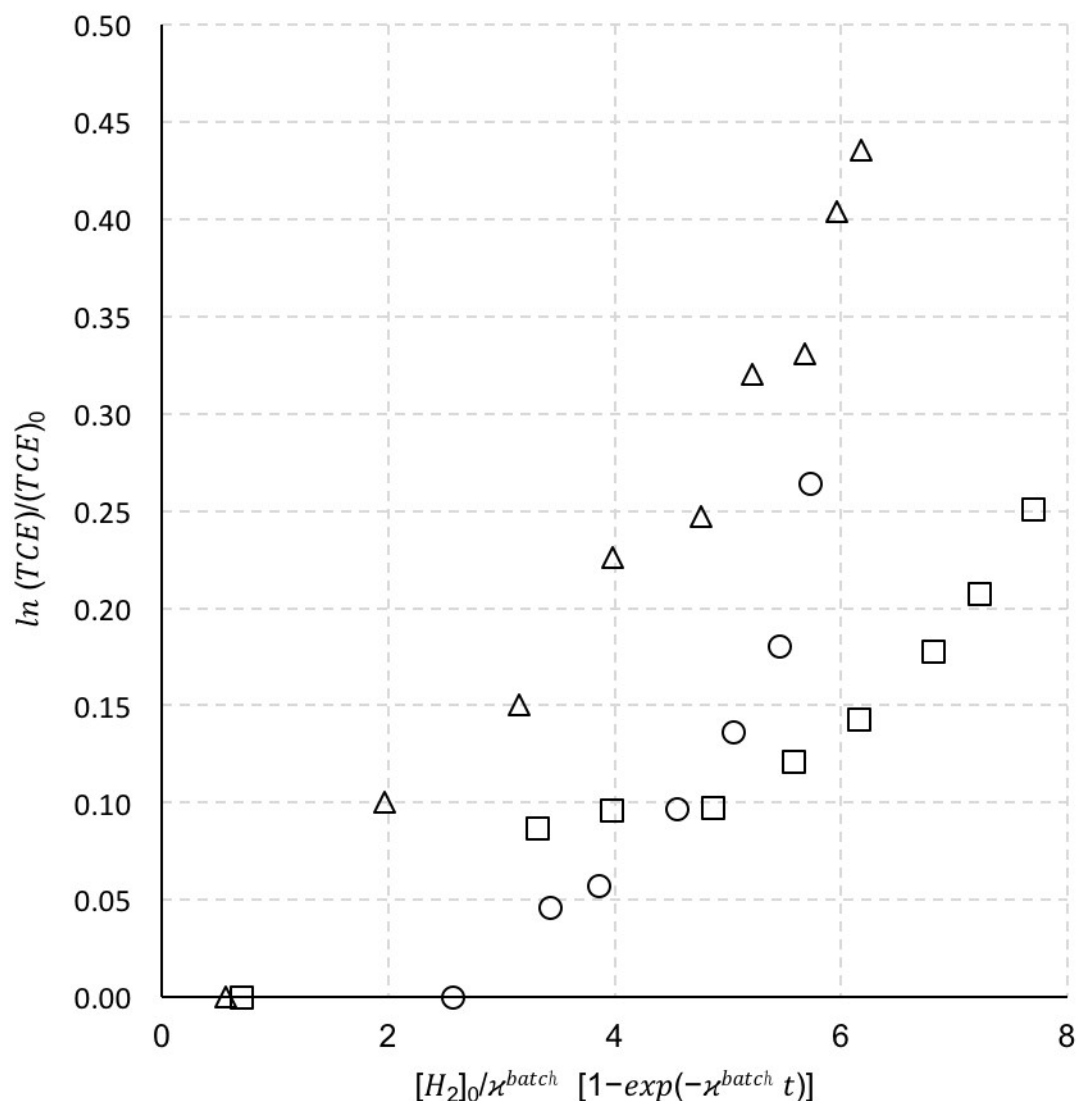
#### **S4. TCE dechlorination experiments using low concentrations of Pd-Au/xGnP**

For dechlorination experiments with low Pd-Au/xGnP loadings, the protocol was identical to the procedure described in section 2.4.1 except that 5 times lower (0.25 mg) loading of the catalyst (Pd-Au/xGnP) was used. We decreased the loading in order to explore the reaction kinetics when TCE conversion was low. Based on these experiments, it was shown that TCE conversion batch reactions fit a 1<sup>st</sup> order model better than a 2<sup>nd</sup> order although the improvement was not statistically significant: the R<sup>2</sup> statistics were  $0.971 \pm 0.015$  and  $0.925 \pm 0.059$  ( $p = 0.05$  and  $n = 3$ ), respectively.



**Figure S6.** Fits of batch reaction kinetics data to the 1<sup>st</sup> order reaction model.

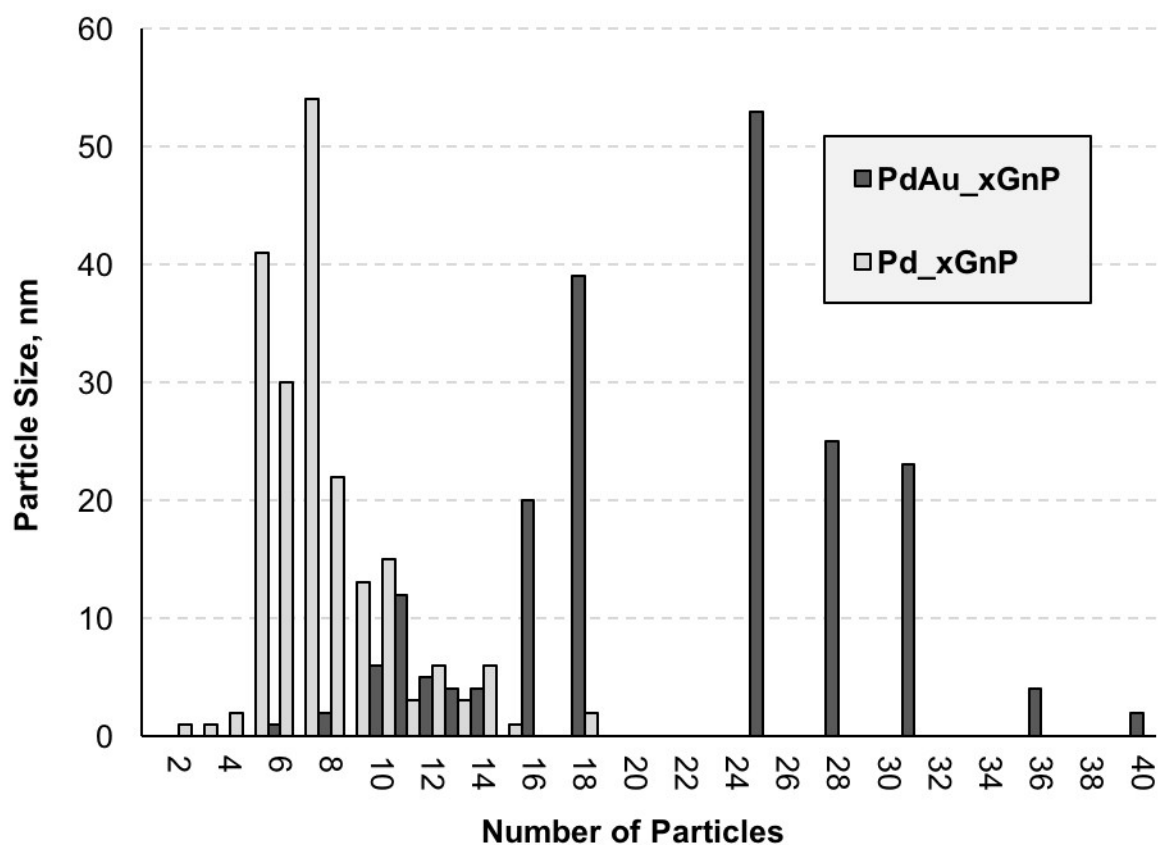




**Figure S7.** Fits of batch reaction kinetics data to the 2<sup>nd</sup> order reaction model.

#### **S4. Particle size distribution of Pd and Pd-Au nanoparticles on xGnP supports**

From TEM images, we could estimate the particle size distribution of Pd and Pd-Au nanoparticles using imageJ software (version java 1.6.0\_65) (Figure S8). The distributions were calculated by randomly measuring the diameters of 200 nanoparticles on xGnP supports. Pd nanoparticles ranged in size from 2 to 20 nm, while ~ 87 % of these particles ranged in size from 5 to 0 nm. Pd-Au nanoparticles ranged in size from 6 to 40 nm, and 85% of these particles ranged in size from 10 to 30 nm.



**Figure S8.** Size distribution of Pd and Pd-Au nanoparticles on xGnP supports. Each distribution was calculated based on 200 randomly selected nanoparticles.