

Hydrogen-etched TiO_{2-x} as Efficient Support of Gold Catalysts for Water-Gas

Shift Reaction

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Table S1. Physical properties of Au-TiO₂ and Au-TiO_{2-x} catalysts

| Catalysts | Au loading (wt. %) ^a | Dispersion (%) ^b | TOF at 240 °C (s ⁻¹) | TOF at 200 °C (s ⁻¹) |
|--------------------------|------------------------------------|--------------------------------|-------------------------------------|-------------------------------------|
| Au-TiO ₂ -N | 3.9 | 15.1 | 1.23 | 0.37 |
| Au-TiO _{2-x} -N | 3.9 | 12.4 | 2.16 | 0.73 |

a Measured by ICP-OES.

b Measured by TEM.

Table S2 Comparison of water-gas shift rates of Au-TiO_{2-x}-N catalysts with literature data.

| Catalysts | Conditions | T (°C) | Ea (kJ/mol) | TOF (s ⁻¹) | Ref. |
|---------------------------------|---|--------|----------------|---------------------------|--|
| 4 wt. %Au-TiO _{2-x} -N | 6.25% CO, 50% H ₂ O, 43.75% N ₂ | 200 | 56.4±1.8 | 0.73 | This work |
| 4 wt. %Au-TiO _{2-x} -N | 6.25% CO, 50% H ₂ O, 43.75% N ₂ | 240 | 56.4±1.8 | 2.16 | This work |
| 0.51 AuP25_UV_L | 11% CO, 26% H ₂ O, 7% CO ₂ , 26% H ₂ in He | 200 | 45.2 | 0.2 | <i>J. Am. Chem. Soc.</i> 2013 , 135, 3768-3771. |
| Au/TiO ₂ (DP, 3.4%) | 1% CO, 2% H ₂ O, He (balance) | 100 | 46 | 0.00079 | <i>Chem. Commun.</i> 1997 , 271-272. |
| 1.5 wt.% | 4.76%CO, 10.06% CO ₂ , 28.46% | 300 | | 0.18 | <i>Int. J. Hydrogen Energ.</i> |

| | | | | | | |
|---|---|-----|--------|--------|--|--|
| Au-TiO ₂ | H ₂ , 35.38% H ₂ O, 21.34% N ₂ | | | | | 2016 , 41, 4670-4681. |
| Pt/Na-TiO ₂ | 2.83% CO, 5.66% H ₂ O, 37.74% H ₂ , 53.77% He | 250 | 80 | 1.39 | | <i>J. Catal.</i> 2011 , 278, 123-132. |
| 0.5% Pt/CaO-TiO ₂ | 3% CO and 10% H ₂ O (balance He) | 220 | 72.8 | 0.38 | | <i>Appl. Catal. B-Environ.</i> 2011 , 101, 738-746. |
| 30Na:Pt/Al ₂ O ₃ | 7% CO, 11% H ₂ O, 9% CO ₂ , 37% H ₂ , 10% Ar, balance He | 250 | 77 | 0.35 | | <i>J. Catal.</i> 2016 , 339, 163-172. |
| Pt/Ce _{0.75} Zr _{0.25} O ₂ | 5% H ₂ , 15% CO, 5% CO ₂ , 20% H ₂ O, and balance N ₂ plus 50 ppm of H ₂ S | 200 | 47 ± 6 | 0.0337 | | <i>J. Catal.</i> 2016 , 341, 1-12. |
| 3.7% Pt/MoO ₂ C | 11% CO, 21% H ₂ O, 6% CO ₂ , 43% H ₂ , 19% N ₂ | 240 | 49 ± 4 | 0.72 | | <i>J. Catal.</i> 2015 , 330, 280-287. |
| 0.01 wt.% Ir/FeO _x | 2% CO, 10% H ₂ O in He | 300 | 50 | 2.31 | | <i>J. Am. Chem. Soc.</i> 2013 , 135, 15314-15317. |
| 5Ni5Cu/CeO ₂ | 7% CO, 22% H ₂ O, 10% CO ₂ , 20% H ₂ , balance He | 350 | 41.3 | 0.013 | | <i>J. Catal.</i> 2014 , 314, 32-46. |

Table S3 Microstructure parameters of monoclinic TiO₂ in various TiO₂ supports and Au-TiO₂ catalysts.

| Sample | Monoclinic TiO ₂ | | | | | | |
|--------------------------|-----------------------------|---------------|------------------------|---------|--------|--------|---------------------|
| | 2theta (°) | d-spacing (Å) | Microstrain (Δd/d) (%) | a (Å) | b (Å) | c (Å) | V (Å ³) |
| TiO ₂ -N | 14.168 | 6.246 | 0.702 | 12.1751 | 3.7551 | 6.5433 | 285.466 |
| TiO _{2-x} -N | 14.246 | 6.212 | 0.720 | 12.2007 | 3.7532 | 6.5212 | 285.141 |
| Au-TiO ₂ -N | 14.126 | 6.264 | 0.802 | 12.1782 | 3.7550 | 6.5286 | 285.006 |
| Au-TiO _{2-x} -N | 14.159 | 6.250 | 0.812 | 12.1605 | 3.7532 | 6.5302 | 284.252 |

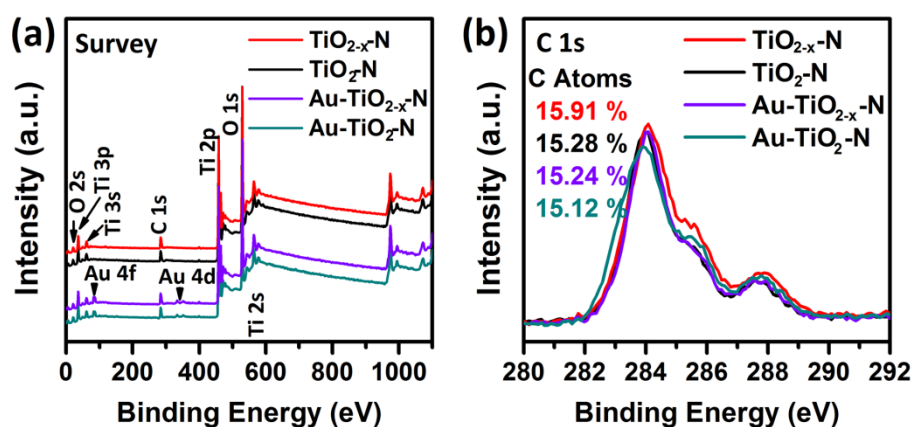


Figure S1. XPS spectra of various TiO₂ supports and Au-TiO₂ catalysts.

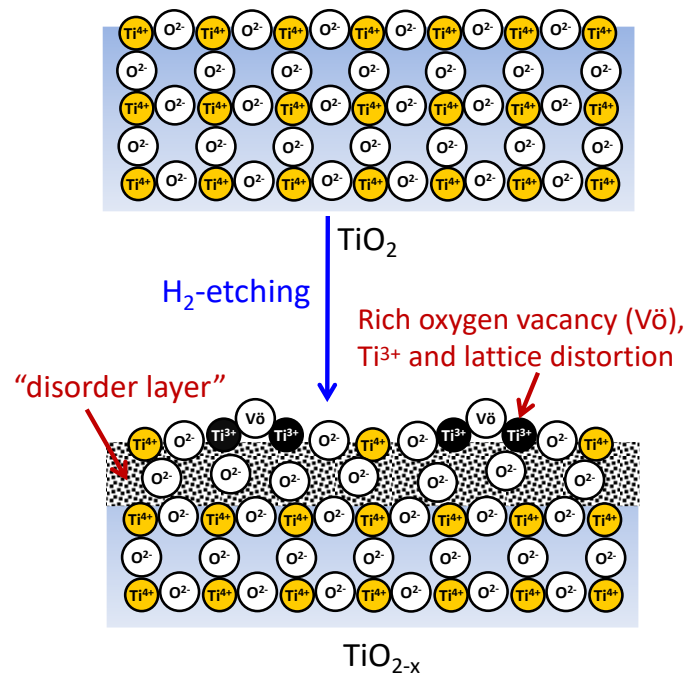


Figure S2. Schematic structure of white and blue black TiO₂.