

Direct methylation of N-Methylaniline with CO₂/H₂ catalyzed by gold nanoparticles supported on alumina

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1. In situ XRD patterns of the Al₂O₃ obtained by different calcination temperatures

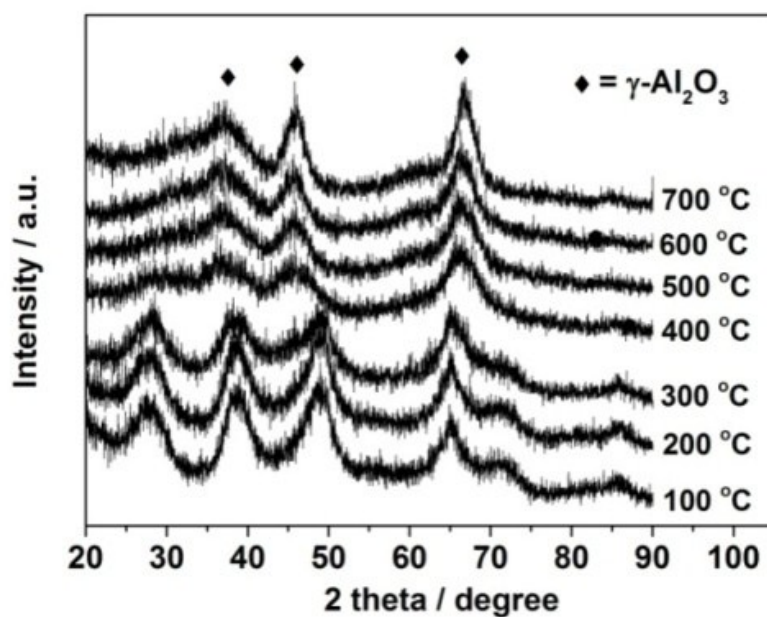
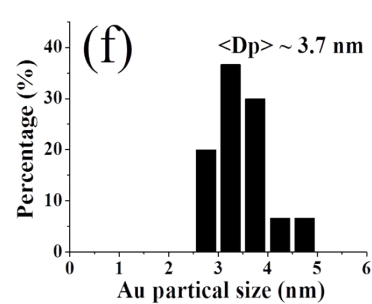
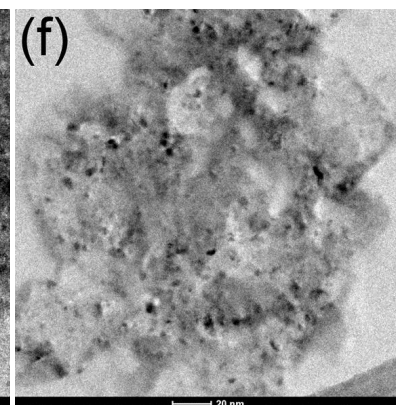
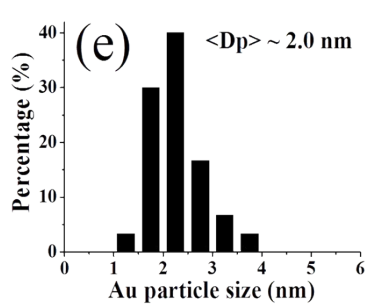
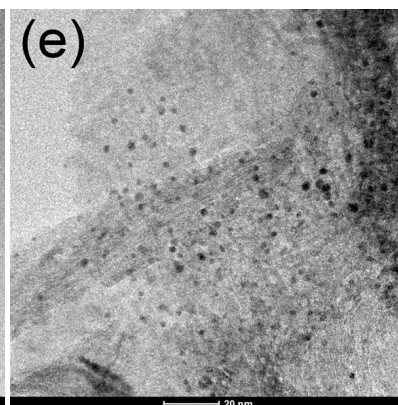
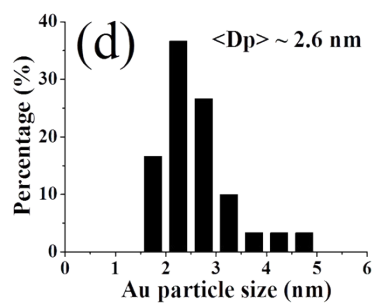
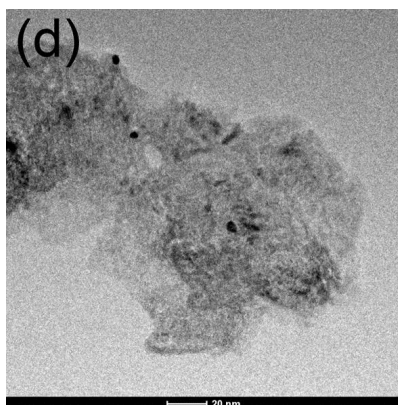
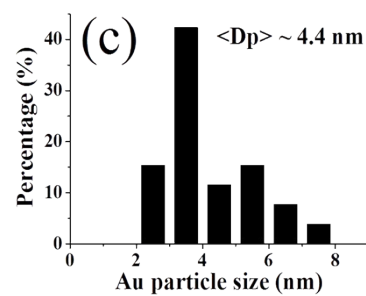
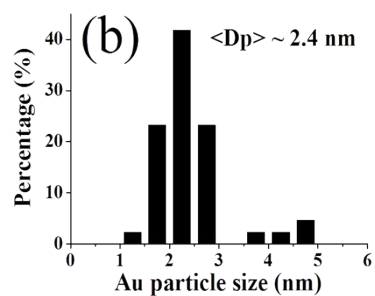
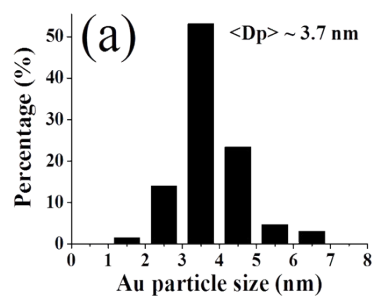
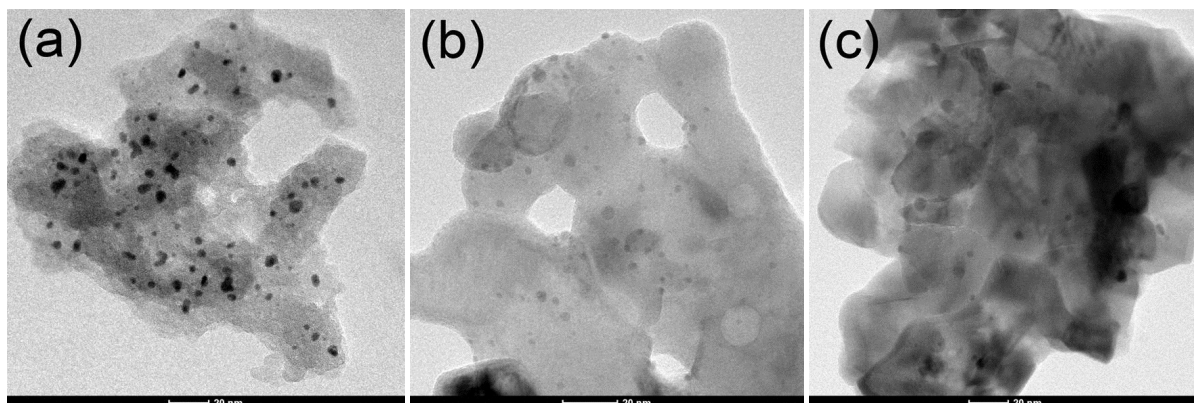


Fig. S1 In situ XRD patterns of the Al₂O₃ obtained by different calcination temperatures.

2. TEM micrographs and corresponding Au particle size distributions for Au catalysts loaded on various supports



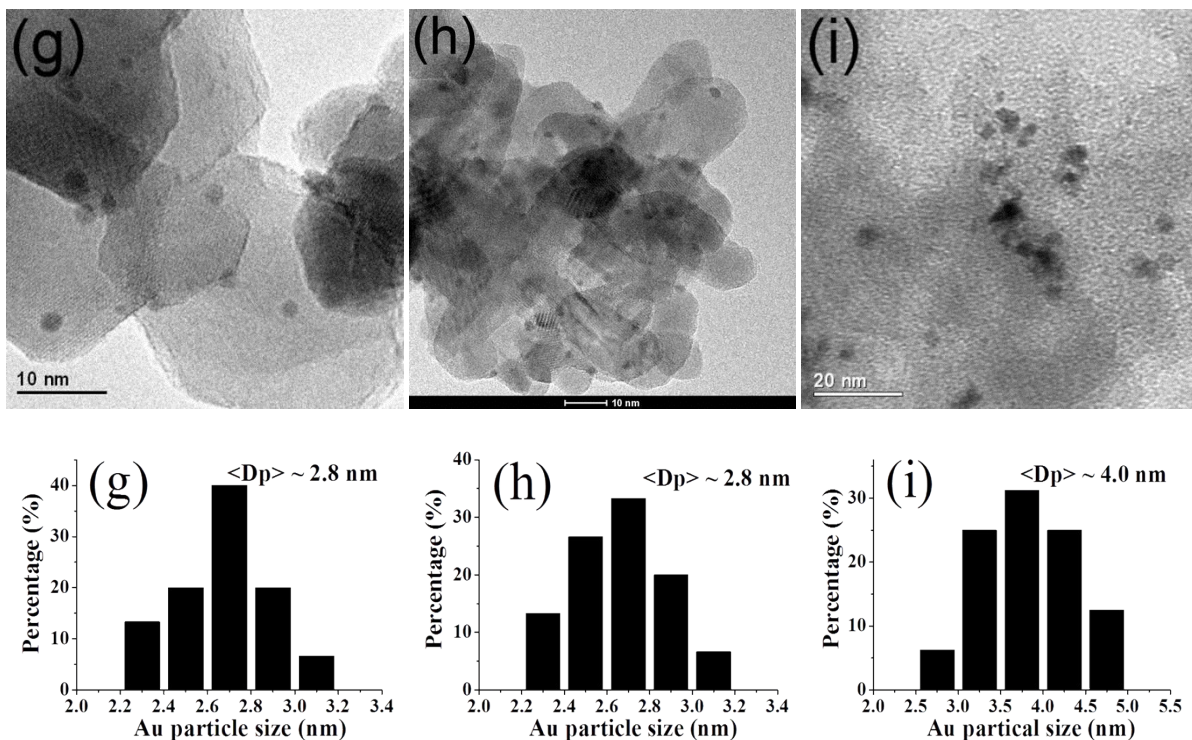


Fig. S2 TEM micrographs and corresponding Au particle size distributions for Au catalysts loaded on various supports: (a) Au/SiO₂, (b) Au/Mn₂O₃, (c) Au/Co₃O₄, (d) Au/MgO, (e) Au/Al₂O₃, (f) Au/CeO₂, (g) Au/TiO₂, (h) Au/ZnO, and (i) Au/C.

3. Effects of pressure on catalytic performances of Au/Al₂O₃ catalyst for direct methylation of N-methylaniline with CO₂/H₂

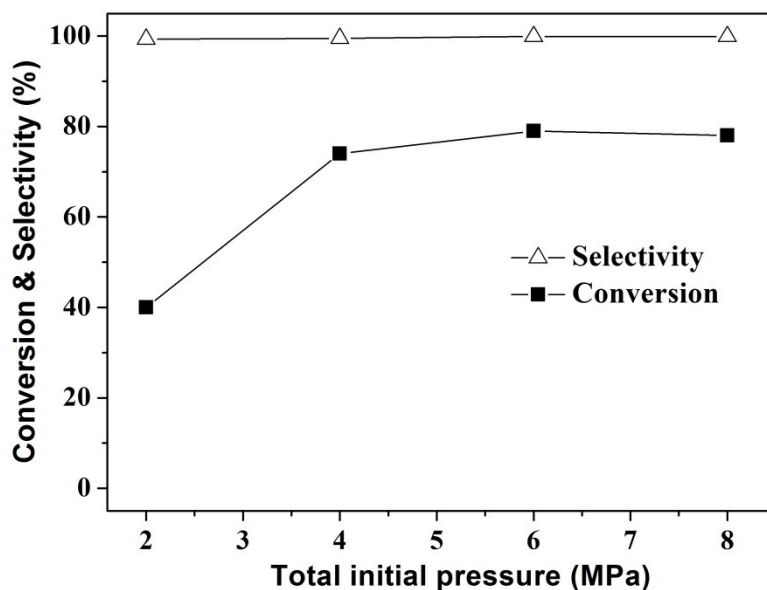


Fig. S3 Effects of pressure on catalytic performances of Au/Al₂O₃ catalyst for direct methylation of N-methylaniline with CO₂/H₂. Reaction condition: 0.5 mol% Au, 1.0 mmol N-methylaniline, cyclohexane 10 mL, CO₂ (1 MPa), H₂ (3 MPa), T = 140 °C, t = 5 h.

4. Effects of temperature on the catalytic performances of Au/Al₂O₃ catalyst for direct methylation of N-methylaniline with CO₂/H₂

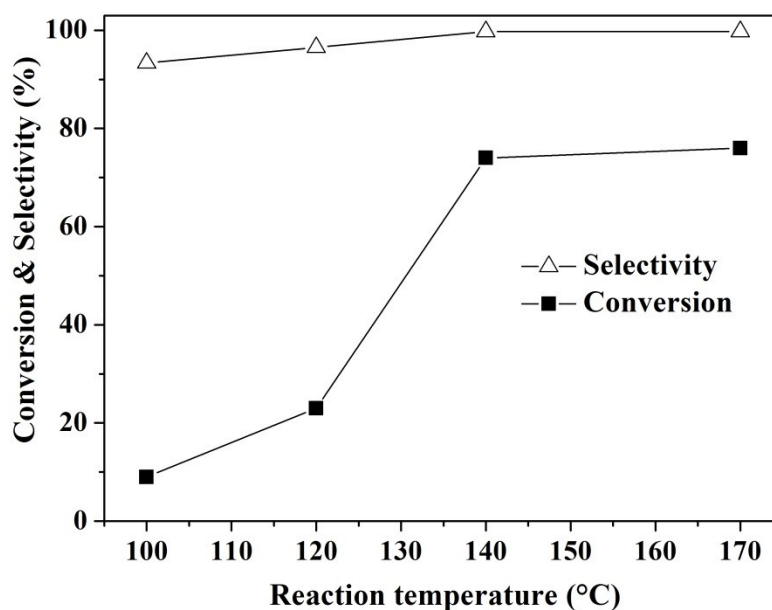


Fig. S4 Effects of temperature on the catalytic performances of Au/Al₂O₃ catalyst for direct methylation of N-methylaniline with CO₂/H₂. Reaction condition: 0.5 mol% Au, 1.0 mmol N-methylaniline, cyclohexane 10mL, CO₂ (1 MPa), H₂ (3 MPa), T = 140 °C, t = 5 h.

5. Time courses for the conversions of N-methylaniline with CO₂/H₂ during the initial stage using Au/Al₂O₃ catalysts with different Au NP sizes from 1.8 to 8.3 nm and Al₂O₃

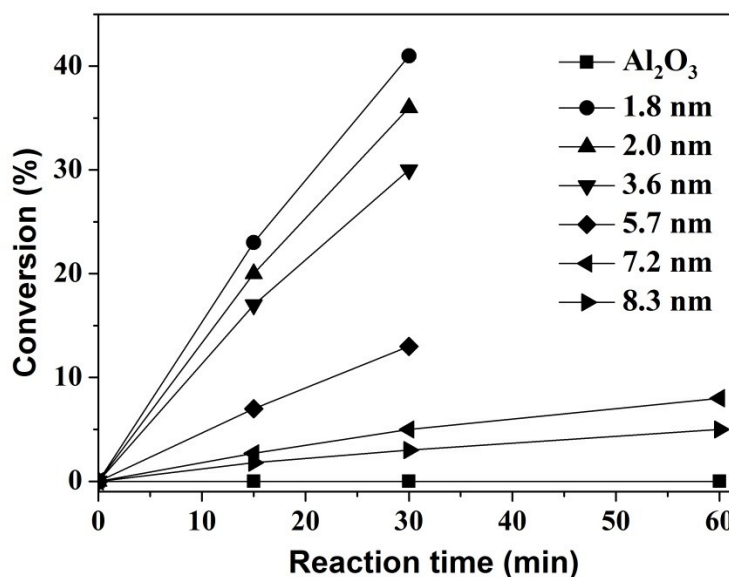


Fig. S5 Time courses for the conversions of N-methylaniline with CO₂/H₂ during the initial stage using Au/Al₂O₃ catalysts with different Au NPs sizes from 1.8 to 8.3 nm and Al₂O₃. Reaction conditions: catalyst 0.14 g (Au 2.7-5 μmol), 1.0 mmol N-methylaniline, cyclohexane 10 mL, CO₂ (1 MPa), H₂ (3 MPa), T = 140 °C.

Table S1 Initial reaction rates of the Au/Al₂O₃ catalysts with various mean Au NPs sizes and Al₂O₃ for direct methylation of N-methylaniline with CO₂/H₂^a

Catalyst	Au loading (wt %)	Mean size (nm)	Initial reaction rate ^b (mmol h ⁻¹ g ⁻¹ (cat.))
Al ₂ O ₃	0	-	0
Au/Al ₂ O ₃	0.40	1.8	5.86
Au/Al ₂ O ₃	0.73	2.0	5.14
Au/Al ₂ O ₃	0.70	3.6	4.00
Au/Al ₂ O ₃	0.70	5.7	1.86
Au/Al ₂ O ₃	0.46	7.2	0.61
Au/Al ₂ O ₃	0.47	8.3	0.36

^a Reaction conditions: catalyst 0.14 g (Au 3-5 μmol), 1.0 mmol N-methylaniline, cyclohexane 10mL, CO₂ (1 MPa), H₂ (3 MPa), T = 140 °C. ^b Measured from Figure S5.

6. TEM micrographs and corresponding Au particle size distributions for the Au/Al₂O₃ catalysts reduced at different temperatures

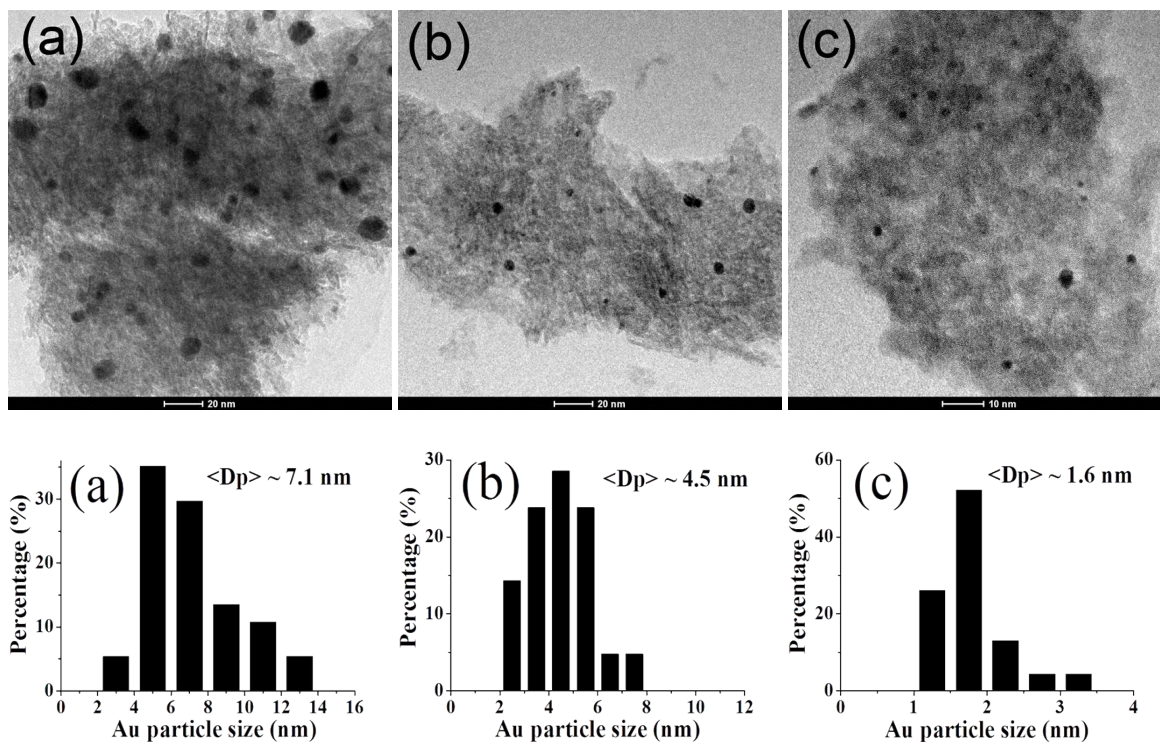


Fig. S6 TEM micrographs and corresponding Au particle size distributions for the Au/Al₂O₃ catalysts reduced at different temperatures: (a) 150, (b) 250 and (c) 450 °C.

7. Influence of mean Au NPs size on conversion and selectivity of direct methylation of N-methylaniline with CO₂/H₂.

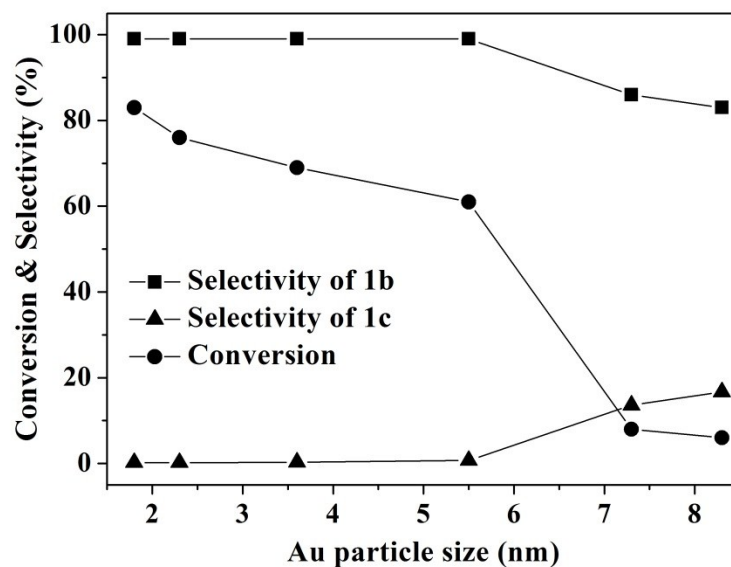


Fig. S7 Influence of mean Au particle size on conversion and selectivity of direct methylation of N-methylaniline with CO₂/H₂. Reaction condition: 1.0 mmol N-methylaniline, 3-5 μ mol Au, cyclohexane 10 mL, CO₂ (1 MPa), H₂ (3 MPa), T = 140 $^{\circ}$ C, t = 5 h. Note: N-methylformanilide (**1c**), N, N-dimethylaniline (**1b**).