

Supporting Information

The application of FTIR *in situ* spectroscopy combined with methanol adsorption to the study of mesoporous sieve SBA-15 with cerium-zirconium oxides modified with gold and copper species

Piotr Kaminski*

*Adam Mickiewicz University in Poznań, Faculty of Chemistry,
Department of Heterogeneous Catalysis, ul. Umultowska 89b, 61-614 Poznań, Poland
Wroclaw Research Centre EIT+, Polymer Materials Laboratory,
ul. Stabłowicka 147, 54-066 Wrocław, Poland*

*e-mail: piotr.kaminski2905@gmail.com

The FTIR *in situ* study combined with the adsorption of methanol

The FITR spectra were recorded after:

- a) activation at 573 K for 1 h,
- b) the adsorption the first dose of methanol (~0.33 mbar) at RT,
- c) 5 min after the first dose of methanol,
- d) the adsorption of the second dose of methanol (~0.33 mbar, 10 min after the first dose),
- e) 5 min after the second dose of methanol (15 min after the first dose),
- f) The adsorption of the third dose of methanol (~0.33 mbar, 20 min after the first dose),
- g) 5 min after the adsorption of the third dose of methanol,
- h) out gassing at RT for 5 min,
- i) out gassing at RT for 10 min,
- j) out gassing at 323 K for 5 min,
- k) out gassing at 323 K for 10 min,
- l) out gassing at 373 K for 5 min,

- m) out gassing at 373 K for 10 min,
- n) out gassing at 423 K for 5 min,
- o) out gassing at 423 K for 10 min,
- p) out gassing at 573 K for 1 h.

The FTIR *in situ* study combined with the oxidation of methanol

The FTIR spectra were performed according to the program:

- a) after methanol (~1 mbar) adsorption at RT,
- b) 5 min after methanol (~1 mbar) adsorption at RT,
- c) after the adsorption of oxygen (~10 mbar) at RT,
- d) 5 min after the adsorption of oxygen (~10 mbar) at RT,
- e) 10 min after the adsorption of oxygen (~10 mbar) at RT,
- f) after heating of methanol and oxygen at 323 K for 10 min,
- g) after heating of methanol and oxygen at 373 K for 10 min,
- h) after heating of methanol and oxygen at 423 K for 10 min,
- i) after heating of methanol and oxygen at 473 K for 10 min,
- j) after heating of methanol and oxygen at 523 K for 10 min,
- k) after heating of methanol and oxygen at 573 K for 10 min,
- l) out gassing at 623 K for 10 min.

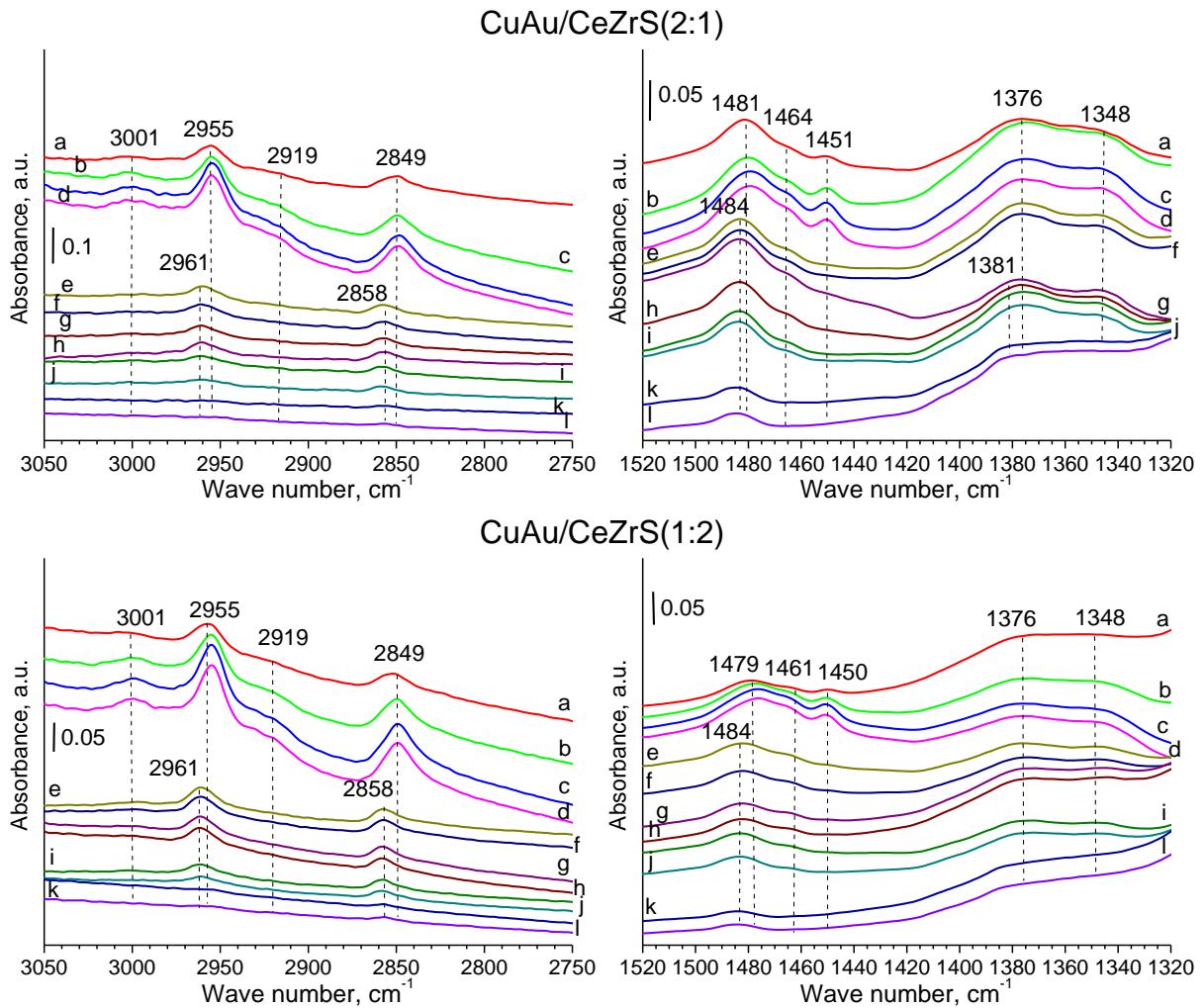


Fig. 1S. FTIR spectra recorded for SBA-15 with ceria and zirconia modified with gold and copper for regions of $3050\text{-}2750\text{ cm}^{-1}$ (left side) and $1520\text{-}1320\text{ cm}^{-1}$ (right side) after: a-c) the adsorption of methanol at RT: a) the 1st dose of $\sim 0.33\text{ mbar}$; b) the 2nd dose of $\sim 0.33\text{ mbar}$, 5 min after the 1st dose; c) the 3rd dose of $\sim 0.33\text{ mbar}$, 5 min after the 2nd dose; d) 5 min after the adsorption of last dose of methanol (total $\sim 1\text{ mbar}$) at RT; e-l) after out gassing at: e) room temperature for 10 min; f) room temperature for 20 min; g) after out gassing for 30 min; h) 323 K for 10 min; i) 373 K for 10 min; j) 423 K for 10 min; k) 623 K for 1 h; l) 623 K for 2 h.

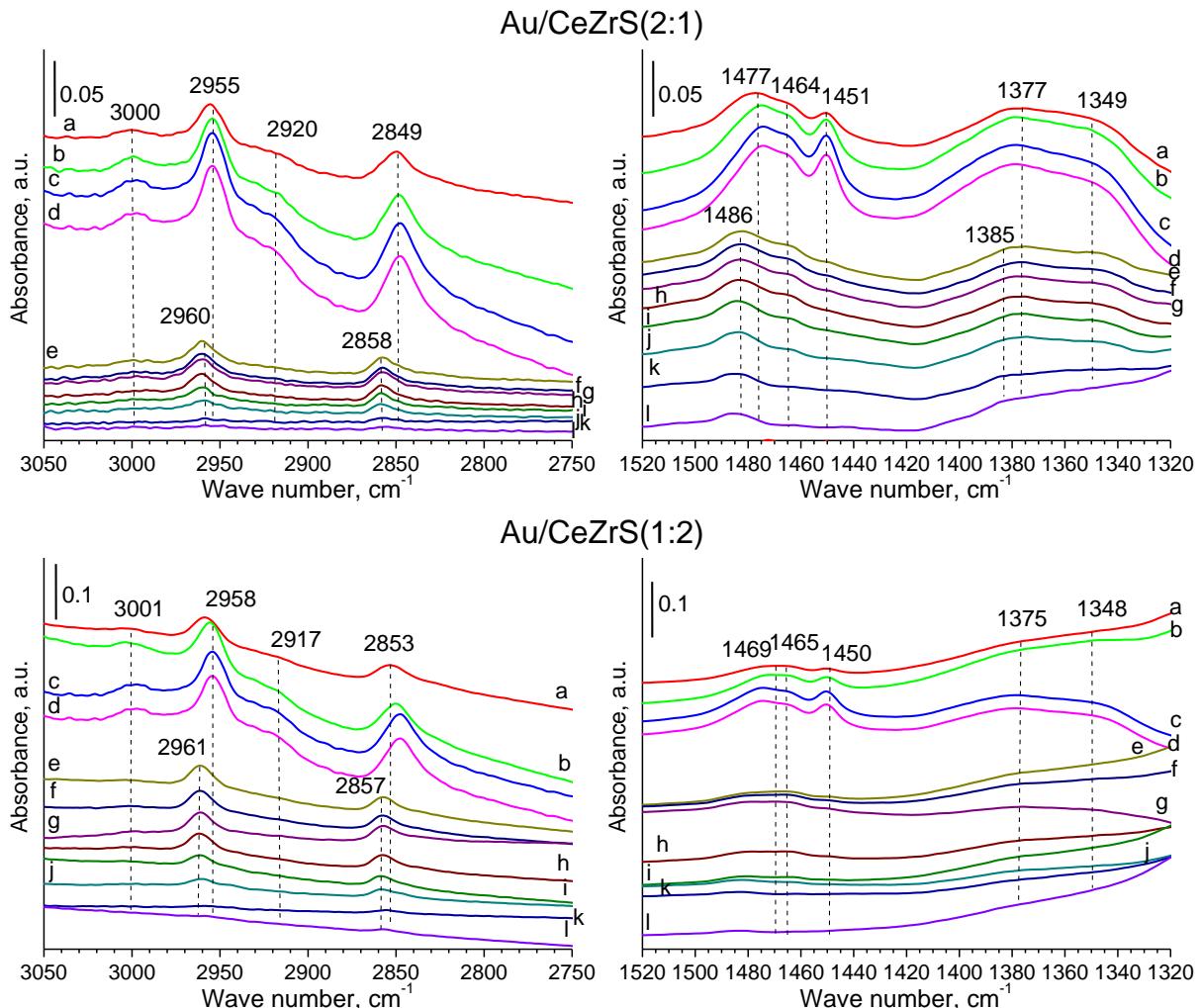


Fig. 2S. FTIR spectra were recorded for SBA-15 with ceria and zirconia modified with gold for regions of $3050\text{-}2750\text{cm}^{-1}$ (left side) and $1520\text{-}1320\text{ cm}^{-1}$ (right side) after: a-c) the adsorption of methanol at RT: a) the 1st dose of ~ 0.33 mbar; b) the 2nd dose of ~ 0.33 mbar, 5 min after the 1st dose; c) the 3rd dose of ~ 0.33 mbar, 5 min after the 2nd dose; d) 5 min after the adsorption of last dose of methanol (total ~ 1 mbar) at RT; e-l) after out gassing at: e) room temperature for 10 min; f) room temperature for 20 min; g) after out gassing for 30 min; h) 323 K for 10 min; i) 373 K for 10 min; j) 423 K for 10 min; k) 623 K for 1 h; l) 623 K for 2 h.

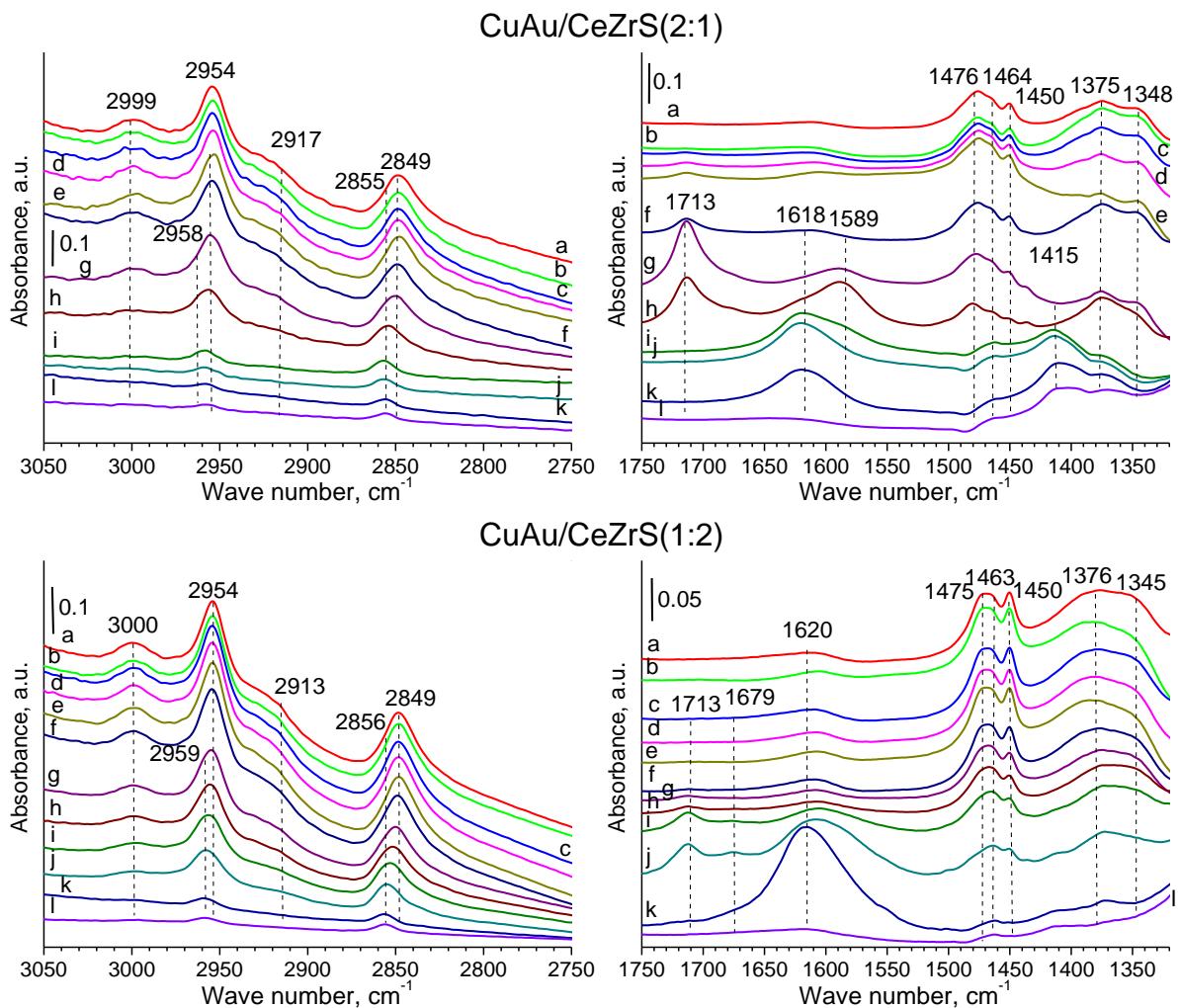


Fig. 3S. FTIR spectra were recorded for SBA-15 with ceria and zirconia modified with gold and copper for the regions of 3050-2750 cm⁻¹ (left side) and 1750-1320 cm⁻¹ (right side) after:
a) the adsorption of methanol (~ 1 mbar) at RT; b) 5 min later; c) after the adsorption of oxygen (~ 10 mbar) at RT; d) 5 min later; e) 10 min later; heating for 10 min at f) 323; g) 373; h) 423; i) 473; j) 523; k) 573; l) out gassing at 623 K for 10 min.

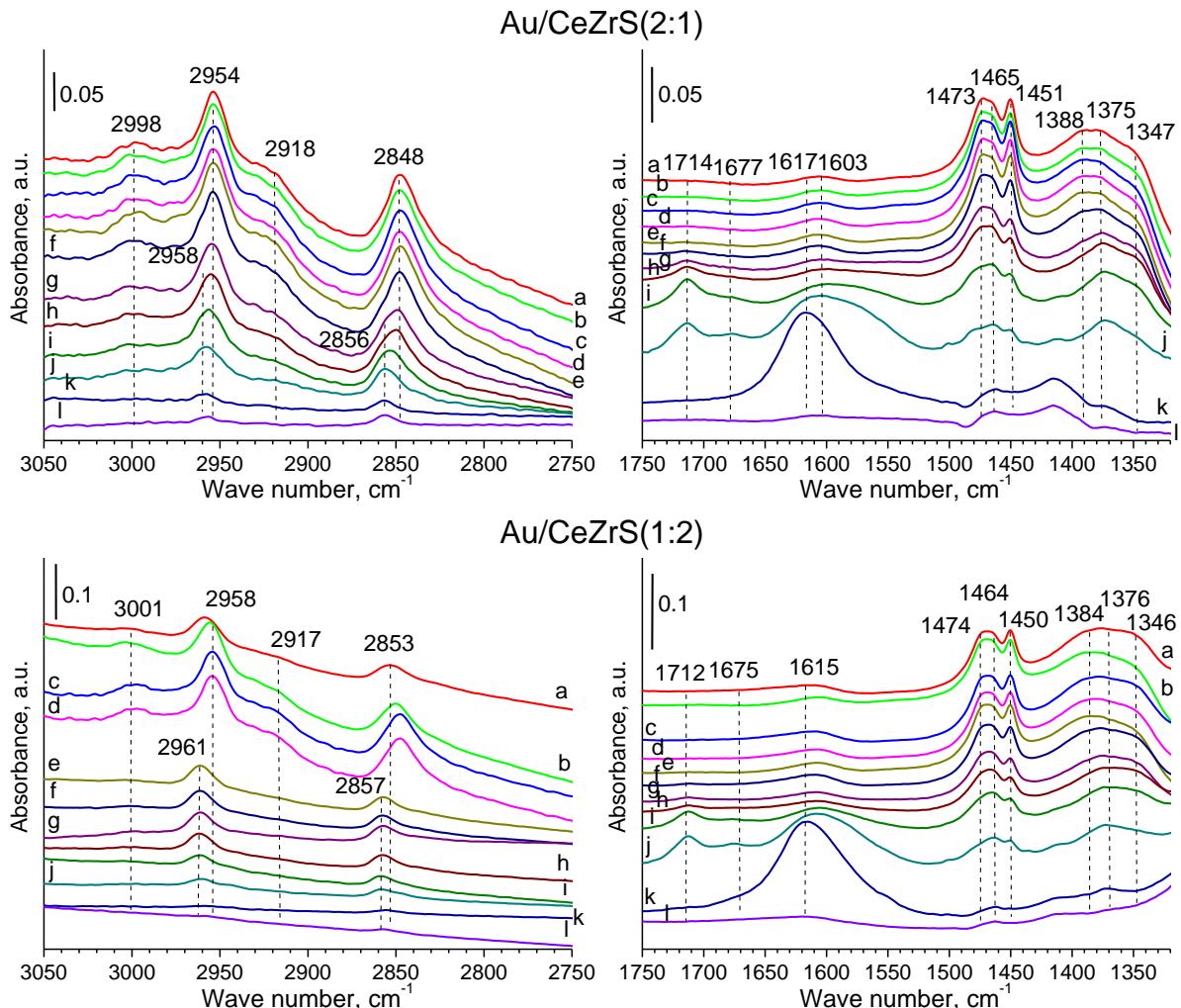


Fig. 4S. FTIR spectra were recorded for SBA-15 with ceria and zirconia modified with gold for the regions of 3050-2750 cm⁻¹ (left side) and 1750-1320 cm⁻¹ (right side) after: a) the adsorption of methanol (~ 1 mbar) at RT; b) 5 min later; c) after the adsorption of oxygen (~ 10 mbar) at RT; d) 5 min later; e) 10 min later; heating for 10 min at f) 323; g) 373; h) 423; i) 473; j) 523; k) 573; l) out gassing at 623 K for 10 min.

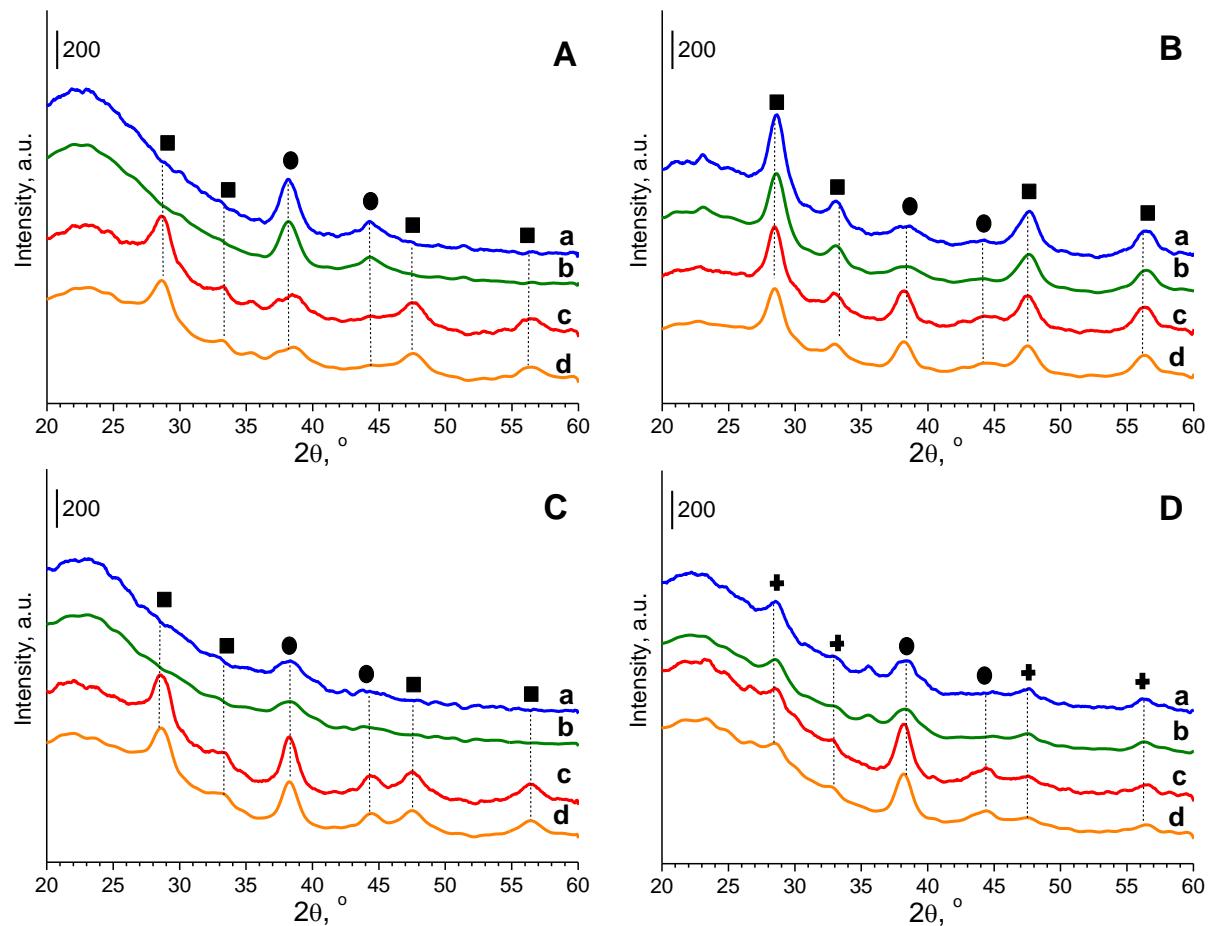


Fig. 5S. XRD patterns recorded for the samples based on: [A] CeS; [B] CeZr(2:1); [C] CeZrS(1:2); [D] ZrS, before (**a** and **c** patterns) and after (**b** and **d** patterns) the FTIR *in situ* measurements of methanol oxidation over the bimetallic copper-gold catalysts (**a** and **b** patterns) and the monometallic gold catalysts (**c** and **d** patterns), where ● means the reflection of the crystal phase of metallic gold particles (Au^0); ■ is due to the reflection of the crystal phase of ceria (CeO_2) and + is attributed to the reflection of the crystal phase of zirconia (ZrO_2).

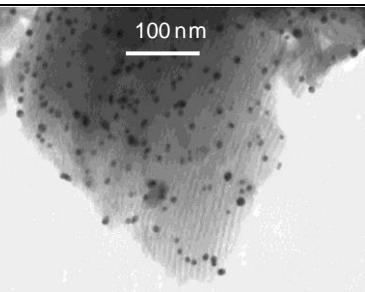
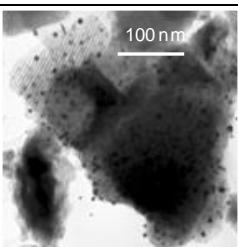
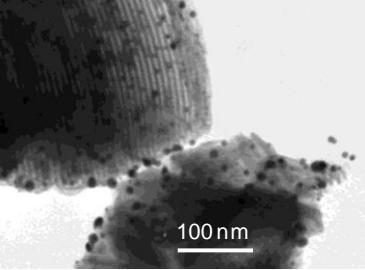
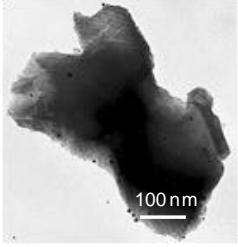
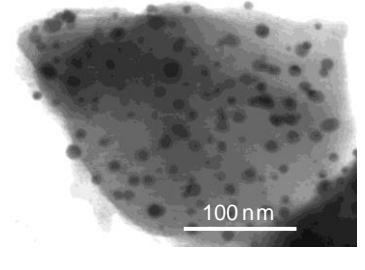
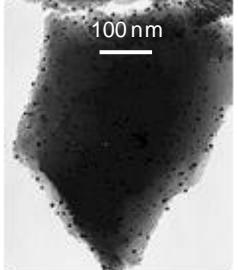
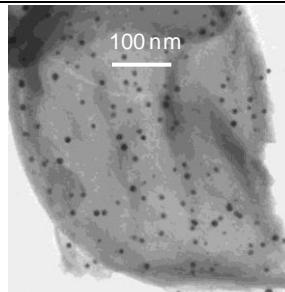
Catalyst	Before	Average size of gold particles, nm	After	Average size of gold particles, nm
Au/CeS		8.2		9.9
Au/CeZrS(2:1)		9.0		9.1
Au/CeZrS(1:2)		9.2		6.3
Au/ZrS		9.8		6.6

Fig. 6S. The TEM images of samples before and after the FTIR *in situ* spectroscopy combined with adsorption and oxidation of methanol molecules. TEM images were recorded for the monometallic gold catalysts.

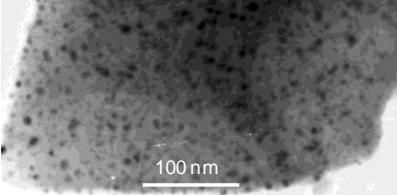
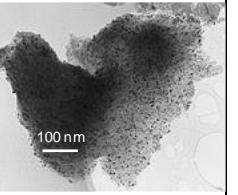
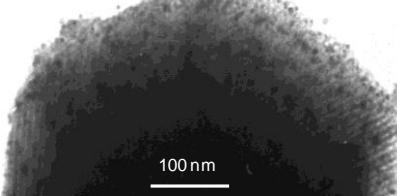
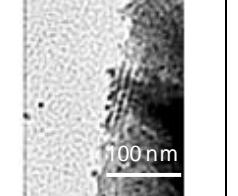
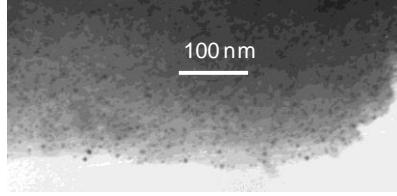
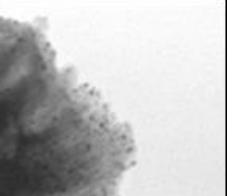
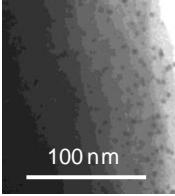
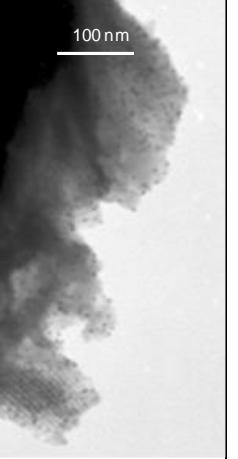
Catalyst	Before	Average size of gold particles, nm	After	Average size of gold particles, nm
CuAu/CeS		5.5		5.6
CuAu/CeZrS(2:1)		6.7		4.7
CuAu/CeZrS(1:2)		4.8		6.3
CuAu/ZrS		5.5		5.4

Fig. 7S. The TEM images of samples before and after the FTIR *in situ* spectroscopy combined with adsorption and oxidation of methanol molecules. TEM images were recorded for the bimetallic copper-gold catalysts.