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ARTICLE TYPE

The Conversion of CO_2 and CH_4 to Acetic Acid over the Au-exchanged ZSM-5 catalyst: A Density Functional Theory Study

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Supporting Information

Tabel SI1. The electron configurations of Au and charge in various steps along with the methane activation.

Reaction Step	Electron Configuration of Au	NBO Charge of Au
Au-ZSM-5	[core]6S(0.26)5d(9.93)6p(0.07)6d(0.01)7p(0.01)	0.723
	Homolytic mechanism	
CH_4_Ads.	[core]6S(0.50)5d(9.78)6p(0.09)7p(0.01)	0.626
TS_1.1	[core]6S(0.66)5d(9.54)6p(0.11)7p(0.01)	0.679
INT_1.1	[core]6S(0.76)5d(9.41)6p(0.14)6d(0.01)7p(0.01)	0.690
TS_1.2	[core]6S(0.79)5d(9.45)6p(0.11)6d(0.01)	0.652
INT_1.2	[core]6S(1.05)5d(9.66)6p(0.08)7p(0.01)	0.213
	Heterolytic mechanism	
CH_4_Ads.	[core]6S(0.50)5d(9.78)6p(0.09)7p(0.01)	0.626
TS_1	[core]6S(0.66)5d(9.75)6p(0.09)7p(0.01)	0.496
INT_1.2	[core]6S(1.05)5d(9.66)6p(0.08)7p(0.01)	0.213

Tabel SI2. The electron configurations of Au and charge in various steps along with the acetic formation.

Reaction Step	Electron Configuration of Au	NBO Charge of Au
	The mono-functional gold catalyst	
Au-ended_Co-Ads.	[core]6S(1.04)5d(9.68)6p(0.08)7p(0.01)	0.201
TS_CO_2-insertion	[core]6S(0.76)5d(9.79)6p(0.10)7p(0.01)	0.335
INT_2	[core]6S(0.85)5d(9.61)6p(0.10)7p(0.02)	0.432
TS_H-transfer	[core]6S(0.66)5d(9.46)6p(0.11)7p(0.01)	0.766
CH_3COOH_Ads.	[core]6S(0.58)5d(9.73)6p(0.09)7p(0.01)	0.583
	The concerted bi-functional mechanism	
H-ended_Co-Ads.	[core]6S(1.07)5d(9.68)6p(0.11)7p(0.01)	0.138
TS_Concerted	[core]6S(0.68)5d(9.82)6p(0.07)7p(0.01)	0.428
CH_3COOH_Ads.	[core]6S(0.58)5d(9.73)6p(0.09)7p(0.01)	0.583

Table SI3. The main geometry parameters of the optimized structures of the methane activation step. Bond distances are in Å and bond angles are in degrees.

Parameters	CO_2_Ads.	Reaction Step					
		CH_4_Ads.	TS_1	TS_1.1	INT_1.1	TS_1.2	INT_1.2
Bond distances							
Au-O1	2.16	2.16	2.47	2.33	2.30	2.22	2.45
Au-O2	2.59	2.60	3.10	2.27	2.25	2.96	3.05
Al-O1	1.76	1.76	1.70	1.73	1.74	1.75	1.71
Al-O2	1.70	1.70	1.76	1.74	1.74	1.71	1.81
C1-H′		1.11	1.50	1.64	2.29	2.46	3.33
Au-C1		2.43	2.12	2.12	2.05	2.04	2.03
Au-H′		2.20	1.92	1.57	1.54	1.54	2.13
O2-H′		3.49	1.45	3.37	3.01	2.00	1.01
Au-O3	2.28						
Au-C2	3.10						
C2-O3	1.18						
C2-O4	1.16						
Bond angles							
O1-Au-O2		62.7	51.7	65.1	66.4	56.3	53.4
O1-Al-O2		92.8	92.1	90.9	91.3	94.1	91.9
C1-Au-H′		27.1	43.3	50.1	77.9	85.2	106.6
Au-O3-C2	124.0						
O3-C2-O4	179.2						

The C-H bond distances of isolated methane are 1.09 Å.
The C=O bond distances of isolated CO_2 are 1.17 Å.

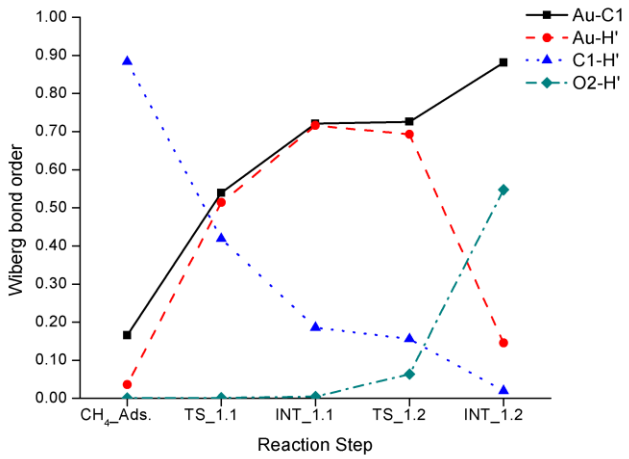
Table SI4. The main geometry parameters of the optimized structures of the acetic formation step via the mono-functional gold catalysis. Bond distances are in Å and bond angles are in degrees.

Parameters	Reaction Step				
	Au-ended_ Co-Ads.	TS_ CO_2-insertion	INT_2	TS_ H-transfer	CH_3COOH_Ads.
Bond distances					
Au-O1	3.13	2.37	2.25	2.14	2.15
Au-O2	3.25	3.17	3.05	2.82	2.65
Al-O1	1.66	1.71	1.72	1.78	1.77
Al-O2	1.57	1.82	1.81	1.70	1.70
Au-C1	2.02	2.47	3.12	3.23	3.28
Au-H′	2.27	2.33	2.20	1.59	2.75
O2-H′	1.00	0.99	1.00	2.42	4.07
C2-O3	1.17	1.24	1.34	1.38	1.42
C2-O4	1.16	1.23	1.22	1.21	1.20
C1-C2	5.44	1.63	1.51	1.50	1.49
O3-H′	3.25	5.17	3.50	1.71	0.97
Au-O3	2.43	2.98	2.01	2.08	2.17
Bond angles					
O1-Au-O2	38.6	51.6	54.6	59.8	62.5
O1-Al-O2	98.6	90.7	91.3	94.0	93.5
O3-C2-O4	178.6	138.7	119.4	115.3	118.9

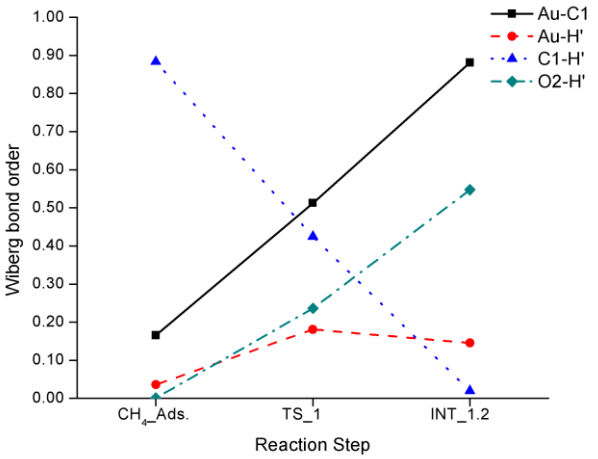
The C=O bond distances of isolated CO_2 are 1.17 Å.
The C-O, C=O, C-C, O-H bond distances of isolated acetic acid are 1.36, 1.21, 1.50, 0.97 Å, respectively.

Table SI5. The main geometry parameters of the optimized structure of the acetic formation step, the concerted bi-functional mechanism. Bond distances are in Å and bond angles are in degrees.

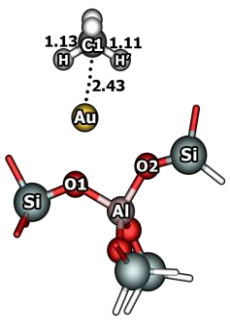
Parameters	Reaction Step		
	H-ended_Co-Ads.	TS_Concerted	CH_3COOH_Ads.
Bond distances			
Au-O1	2.43	2.82	2.15
Au-O2	3.08	3.92	2.65
Al-O1	1.71	1.70	1.77
Al-O2	1.81	1.78	1.70
Au-C1	2.03	2.19	3.28
Au-H′	2.41	3.81	2.75
O2-H′	0.99	1.17	4.07
C2-O3	1.17	1.24	1.42
C2-O4	1.17	1.19	1.20
C1-C2	3.58	1.89	1.49
O3-H′	2.10	1.25	0.97
Au-O3	3.38	4.25	2.17
Bond angles			
O1-Au-O2	54.2	42.2	62.5
O1-Al-O2	94.0	98.6	93.5
O3-C2-O4	178.9	140.0	118.9
H′-O3-C2	121.8	124.1	108.5



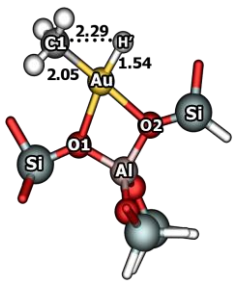
(a) Homolytic mechanism



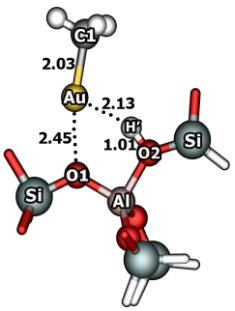
(b) Heterolytic mechanism



CH_4_Ads.

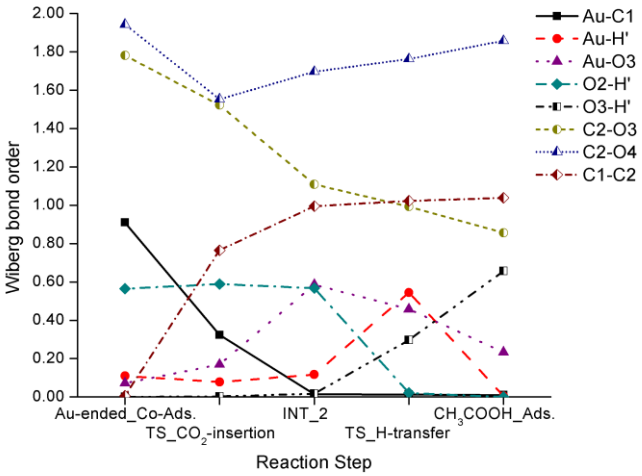


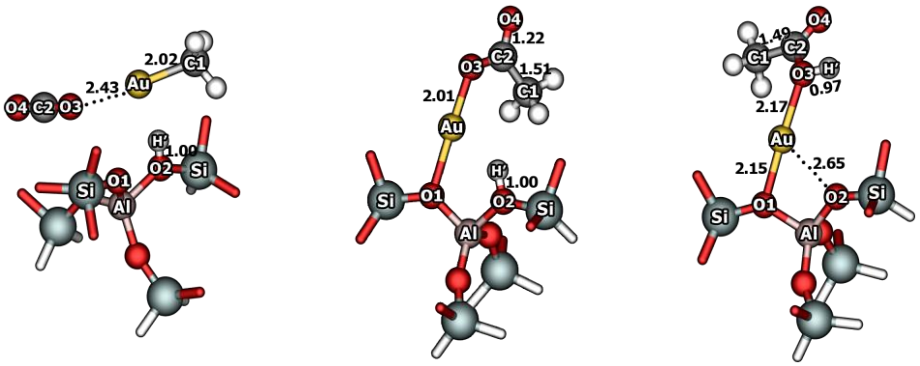
INT_1.1



INT_1.2

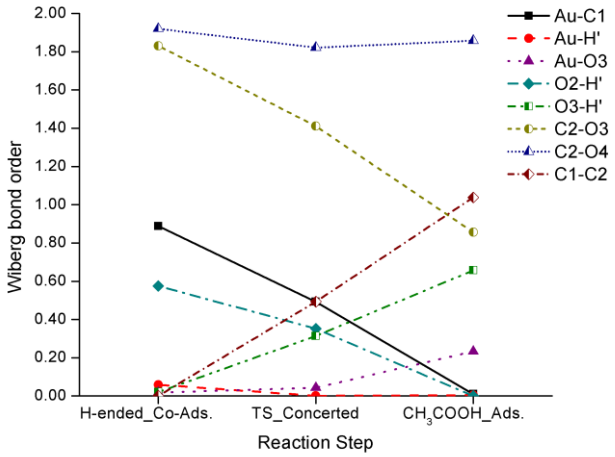
Fig. SI1 Shows the Wiberg bond order of the important bonds along with the methane activation reaction: (a) via the homolytic mechanism, (b) via the heterolytic mechanism.

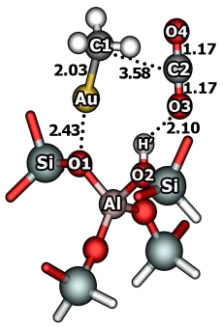




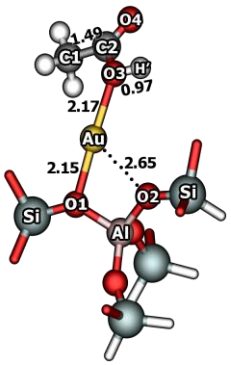
Au-ended_Co-Ads. INT_2 CH_3COOH_Ads.

Fig. SI2 Shows the Wiberg bond order of the important bonds along with the acetic formation via the mono-functional gold catalysis.





H-ended_Co-Ads.



CH_3COOH_Ads.

Fig. SI3 Shows the Wiberg bond order of the important bonds along with the acetic formation via the concerted bi-functional mechanism.