Electronic Supplementary Material (ESI) for Green Chemistry.

Low content Au-based catalyst for hydrochlorination of C_2H_2 and its industial scale-up for future PVC process

Kai Zhou,[a] Jinchao Jia,[a] Chunhua Li,[b] Hao Xu,[a] Jun Zhou,[b] Guohua Luo,[a,*] and Fei Wei,[a,*]

Supplementary Information

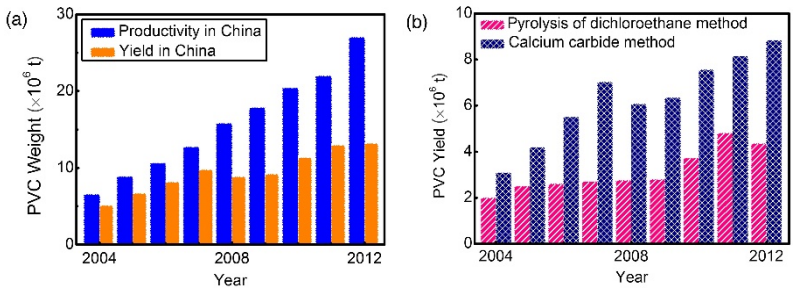

Figure S1. (a) The capacity and production of PVC in China in recent years; **(b)** The PVC yield derived from pyrolysis of dichloroethane method (ethylene method) and calcium carbide method in China in recent years.

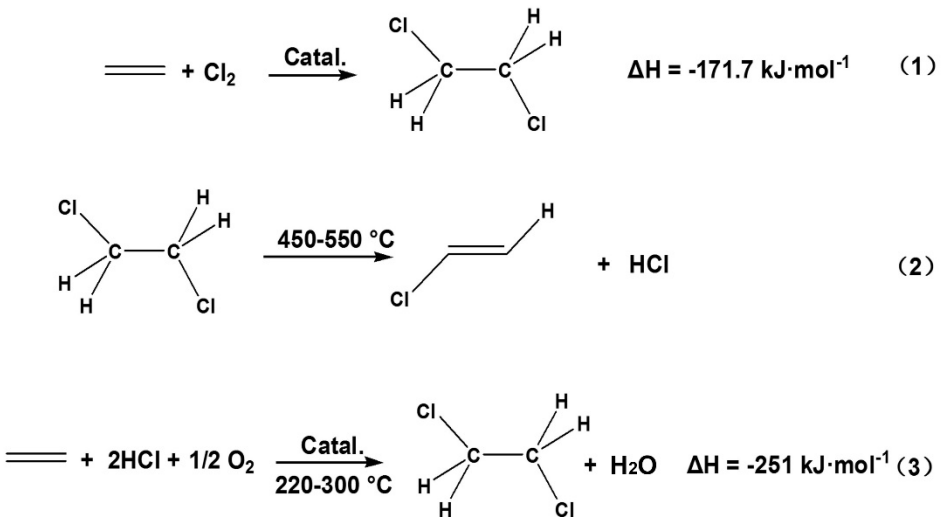

Figure S2. The main reactions of ethylene method in synthesis of VCM (addition reaction of ethylene and chlorine and pyrolysis of dichloroethane).

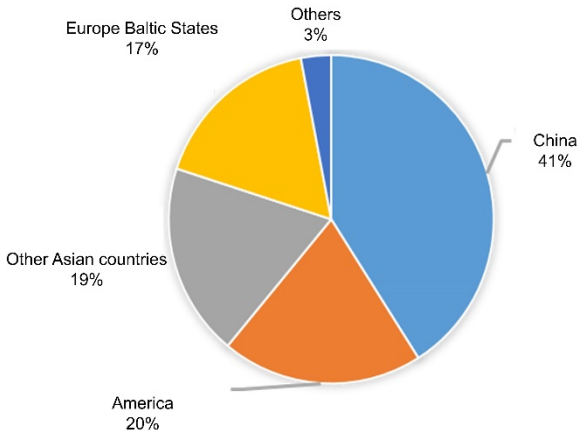

Figure S3. The distribution of global PVC production capacity in 2012.

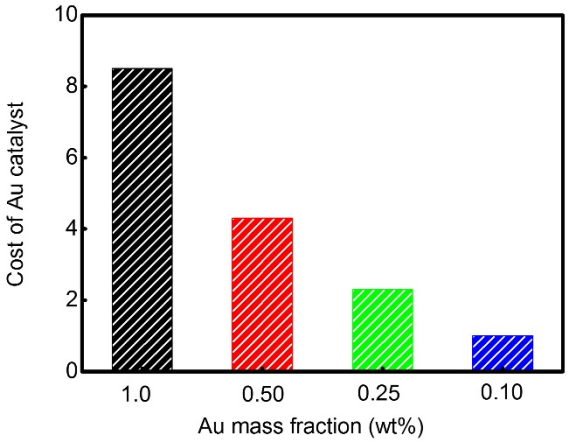

Figure S4. The cost of diffrent Au catalysts. (The cost of 0.1 wt% gold catalyst is set to be 1 as the benchmark for comparision).

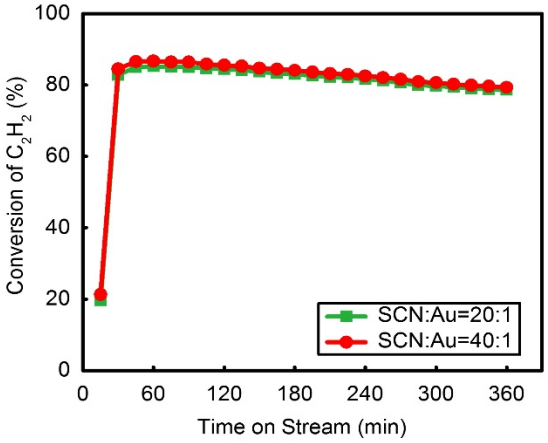

Figure S5. The reactivity evaluation of *Catal. ACS* (0.5 wt% Au, $HAuCl_4$, $CuCl_2$ and KSCN as precursors, n(Cu):n(Au)=5:1) with various mole ratio of SCN:Au=20:1 and 40:1 (T=180 °C, GHSV=1200 h^{-1}).

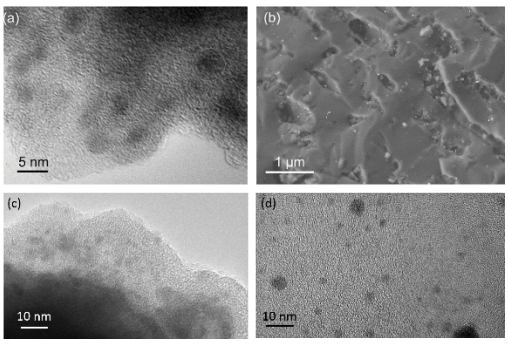

Figure S6. **(a)**, **(b)** TEM and SEM images of *Catal. ACS* respectively; **(c)** Morphology of *Catal. AC* and **(d)** *Catal. ACK*.

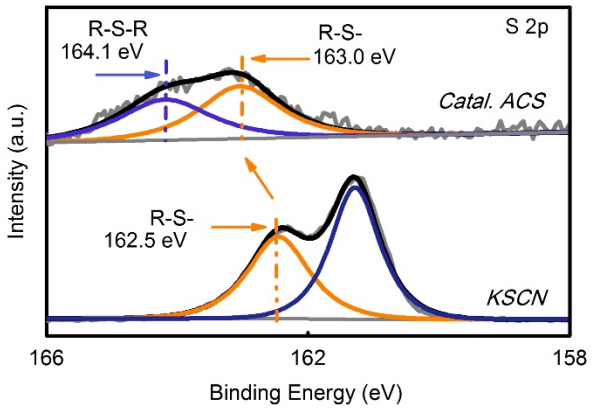

Figure S7. XPS spectrum of S 2p in KSCN and Catal. ACS.

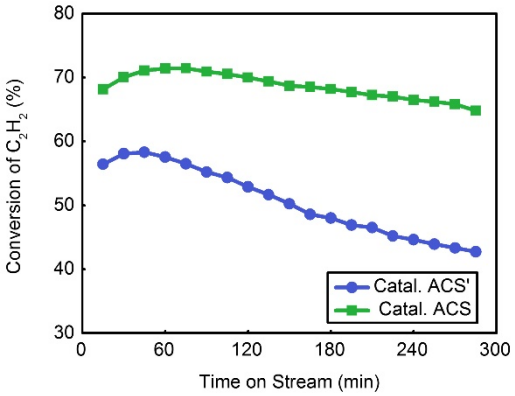

Figure S8. The reactivity evaluation of the gold catalysts with KSCN and K_2S as complexing precursors (T=180 °C, GHSV=1200 h^{-1}).

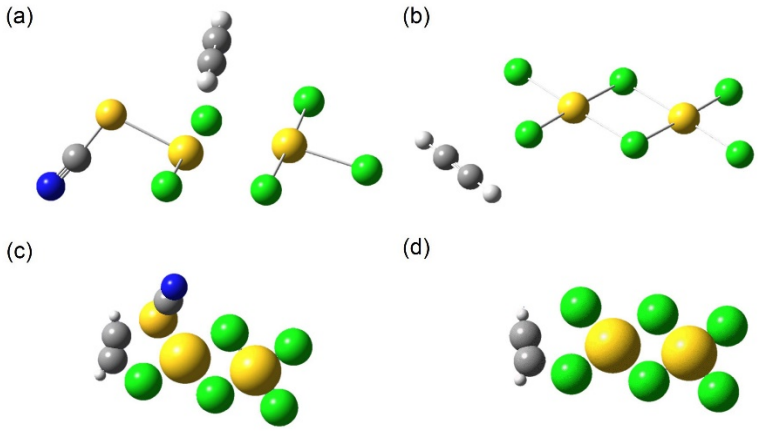

Figure S9. The optimized structure of reactant of **(a)** Au_2Cl_5-SCN and C_2H_2, **(b)** Au_2Cl_6 and C_2H_2; (c) The optimized structure of transition state of **(c)** Au_2Cl_5-SCN and C_2H_2, **(d)** Au_2Cl_6 and C_2H_2 (The yellow ball is Au, green ball is Cl, grey ball is C, blue ball is S and white ball is H).

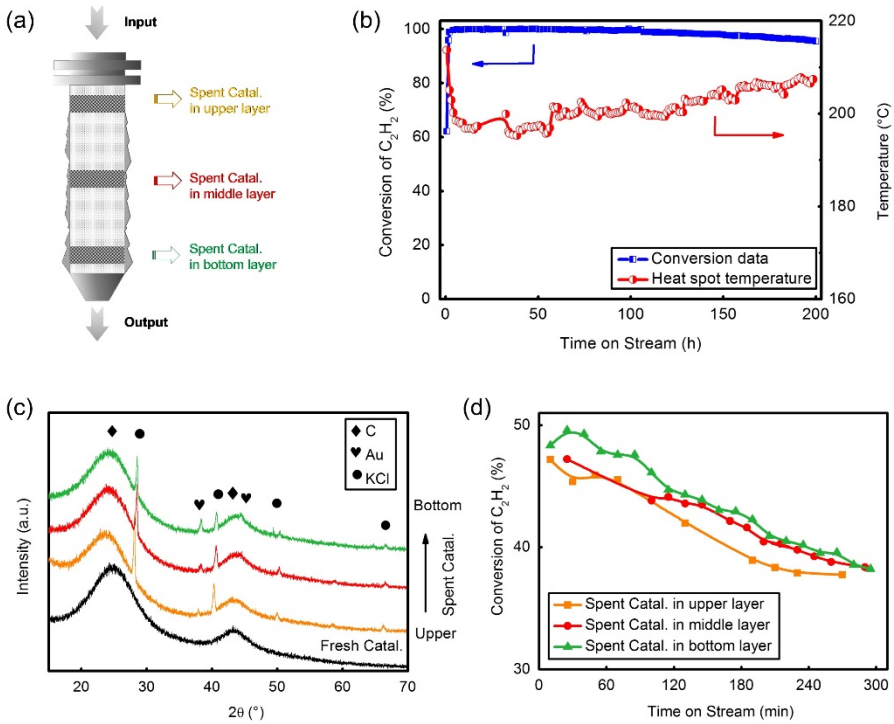

Figure S10. (a) The schematic diagram of the reactor and selected spent catalyst; **(b)** 200 hrs' reactivity evaluation of 96 kg·a^{-1} scale test in fixed bed reactor; **(c)** XRD patterns of the fresh catalyst and the spent catalyst selected from different layers of the reactor (♦: C, ●: KCl, ♥:Au); **(d)** The reactivity evaluation of the spent catalyst selected from the different layers of the reactors (T=180 °C and GHSV=360 h^{-1}).

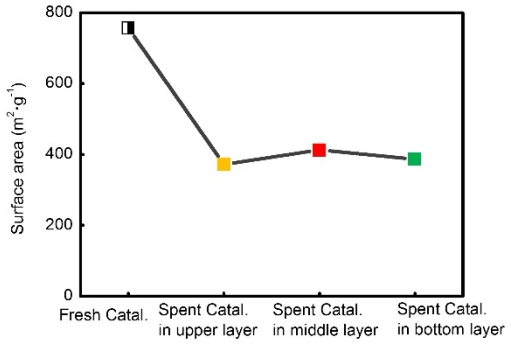

Figure S11. Surface area of fresh catalyst and spent catalysts in the upper, middle and bottom layer in the 96 kg·a^{-1} scale fixed bed reactor.

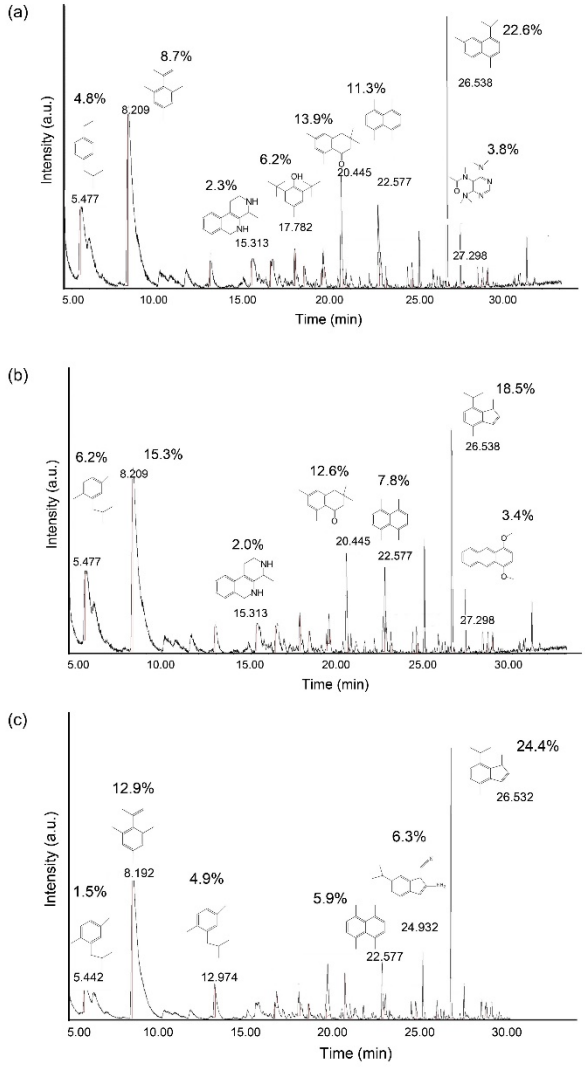

Figure S12. GC-MS spectrums of the coke species in **(a)** upper layer, **(b)** middle layer and **(c)** bottom layer of the spent catalysts.

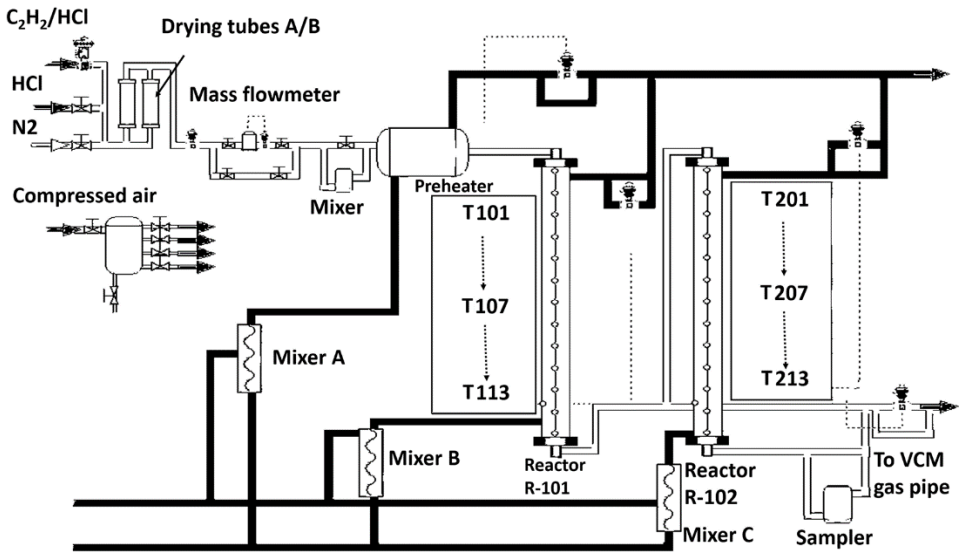

Figure S13. Flow chart of 4 $t \cdot a^{-1}$ pilot-trial analysis.

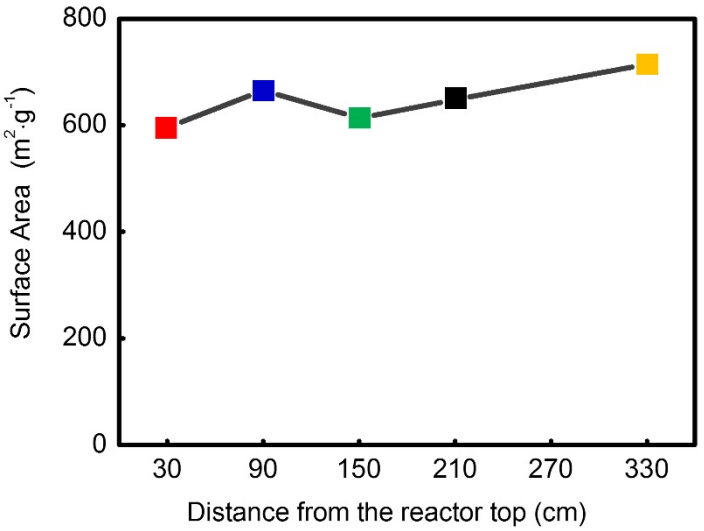

Figure S14. Surface area of spent catalysts in five different layers in the pilot-trial test.

Table S1. Quantification and identification of fresh and spent Au species over *Catal. ACS* from XPS data.

Catalyst type	Au species (%)			Binding energies (eV)		
	Au^{3+}	Au^{0}	Au^{0}-s	Au^{3+}	Au^{0}	Au^{0} -s
Fresh Catalyst	68.0	29.1	2.9	86.4	84.0	84.9
Spent Catalyst	20.1	75.3	4.6	86.3	84.1	85.0

Table S2. Textural properties of *Catal. ACK*, *Catal. ACS* and Catal. *AC*.

Sample	Status	S_{BET} ($m^2 \cdot g^{-1}$)	S_{micro} ($m^2 \cdot g^{-1}$)	S_{ext} ($m^2 \cdot g^{-1}$)	V_{tot} ($cm^3 \cdot g^{-1}$)	V_{mic} ($cm^3 \cdot g^{-1}$)	D (nm)
Catal. ACK	Fresh	719.7	626.3	93.4	0.3213	0.2743	2.7
	Spent	571.3	489.6	81.7	0.2588	0.2260	2.5
Catal. ACS	Fresh	756.4	663.8	92.6	0.3454	0.3061	2.4
	Spent	674.9	600.3	74.6	0.3068	0.2769	2.3
Catal. AC	Fresh	874.8	768.9	105.9	0.4143	0.3563	3.2
	Spent	669.9	596.4	73.5	0.3053	0.2756	2.2

Table S3. Energy changes in DFT study of Au_2Cl_6 and C_2H_2

	Au_2Cl_6	C_2H_2	**Initial State** $Au_2Cl_6+C_2H_2$	**R**	**TS**	**P**	**CHClCHCl**	Au_2Cl_4	**Final State** $ClC_2H_2Cl + Au_2Cl_4$
$E_{453.15K}$ **(Kcal/mol)**	-	-	0	-0.096	22.081	-45.585	-	-	-39.474
$H_{453.15K}$ **(Kcal/mol)**	-	-	0	-0.996	21.181	-46.485	-	-	-39.474
$G_{453.15K}$ **(Kcal/mol)**	-	-	0	6.519	33.025	-35.748	-	-	-41.613

Table S4. Energy changes in DFT study of Au_2Cl_5–SCN and C_2H_2

	Au_2Cl_5-SCN	**C_2H_2**	**Initial State** Au_2Cl_5-SCN +C_2H_2	**R**	**TS**	**P**	**C_2H_2Cl-SCN**	**Au_2Cl_4**	**Final State** C_2H_2Cl-SCN + Au_2Cl_4
$E_{453.15K}$ (Kcal/mol)	-	-	0	-7.597	20.700	-54.159	-	-	-41.059
$H_{453.15K}$ (Kcal/mol)	-	-	0	-2.849	25.447	-49.412	-	-	-35.412
$G_{453.15K}$ (Kcal/mol)	-	-	0	8.014	37.215	-32.306	-	-	-37.483

Table S5. Test of by-products in outlet by GC analysis during the evaluation.

Test Time (h)	**1.1-dichloroethane (µL/L)**	**Trans-1,2-dichloroethylene (µL/L)**
120	299.41	101.58
1000	90.36	54.49
1460	22.86	-
1800	122.24	-
2390	101.43	-
2920	19.68	10.92

Table S6. Quantification of Au content in *Catal. ACS* by ICP analysis.

Sample		Au
expected Set	*ω_0 (%)*	*0.25*
Test 1 (m_0=0.5072 g)	ICP (mg/L)	24.6
	ω_1 (%)	0.24
	Δ (%)	-3.2
Test 2 (m_0=0.5069 g)	ICP (mg/L)	26.3
	ω_2 (%)	0.26
	Δ (%)	+4.0

Table S7. The correlation of Au^{3+} content and conversion of C_2H_2.

Sample weight (g)	*n*(Au) (mol)	*n* (Au^{3+}) (mol)	mol C_2H_2 converted (mol·s^{-1})	mol C_2H_2 converted /mol Au (s^{-1})	mol C_2H_2 converted/mol Au^{3+} (s^{-1})
0.506	4.36E-06	3.74E-08	2.49E-07	0.057	6.67
0.502	3.08E-06	3.32E-08	2.70E-07	0.088	8.12
0.504	3.47E-06	2.98E-07	1.04E-06	0.300	3.48
0.502	3.70E-06	3.45E-07	1.12E-06	0.303	3.26
0.501	4.03E-06	5.08E-07	1.78E-06	0.443	3.51