

Article

Synthesis of Vinyl Chloride Monomer over Carbon-Supported Tris-(Triphenylphosphine) Ruthenium Dichloride Catalysts

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Table S1. Ru content in the fresh and used Ru-based catalysts, based on the ICP analysis.

Catalysts	Nominal Loading (wt%)	Results of ICP (wt%)		Loss Ratio of Ru (%)
		Fresh	Spent	
Ru/AC	1.00	0.94	0.83	11.7
Φ -P-Ru/AC	1.00	0.96	0.91	5.2
Φ -P-Ru/AC-HCl	1.00	0.92	0.88	4.3
Φ -P-Ru/AC-HNO ₃	1.00	0.95	0.91	4.2

Table S2. The Ru species accounted for the percentage of total Ru loading in each fresh catalyst, determined by TPR profiles.

Catalyst	Ru species (%)			Reduction Temperature Center (°C)		
	RuO _x ^a	RuO ₂	RuCl ₃	RuO _x	RuO ₂	RuCl ₃
Ru/AC	4.5	6.3	6.9	150.3	257.0	324.8
Φ -P-Ru/AC	8.8	11.2	18.8	192.6	221.4	291.7
Φ -P-Ru/AC-HCl	13.0	16.9	34.5	155.2	224.3	311.0
Φ -P-Ru/AC-HNO ₃	18.0	26.4	45.2	210.6	253.9	388.4

^a RuO_x is approximately calculated as RuO₃.

Table S3. Comparative study for the catalytic efficiency of this catalytic system over the literature reported ruthenium-based catalysts.

Ref.	Catalyst	Reaction Conditions	^a Catalytic Activity
[1]	Ru1Co3/SAC (1.0 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A ≥ 95.0% (48h)
[2]	Ru/SAC-C300 (1.0 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A = 96.5% (48h)
[3]	Ru1Co(III)3Cu(II)1/SAC (0.1 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A = 99.0% (48h)
[4]	Ru-in-CNT (1.0 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 90 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A ≥ 95.0% (10h)
[5]	Ru@TPPB/AC (1.0 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 360 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.15	X _A = 99.7% (48h)
[6]	Ru-O/AC-O (1.0 wt% Ru)	180 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.15	X _A ≥ 93.0% (24h)
[7]	Ru/AC-NHN (1.0 wt% Ru)	180 °C, GHSV(C ₂ H ₂) = 360 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.15	X _A ≥ 91.8% (48h)
[8]	Ru1K1/SAC (1.0 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A ≥ 86.5% (48h)
[9]	Ru5Cl7/AC (1.0 wt% Ru)	180 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.15	X _A ≥ 80.0% (48h)
[10]	Ru[BMIM]BF ₄ /AC (10 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A = 98.9% (24h)
[11]	Ru/SAC-N700 (1.0 wt% Ru)	170 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.1	X _A = 99.8% (30h)
[12]	TPAP/AC-HCl (1.0 wt% Ru)	180 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.15	X _A = 91.0% (48h)
This work	Φ-P-Ru/AC-HNO ₃ (0.1 wt% Ru)	180 °C, GHSV(C ₂ H ₂) = 180 h ⁻¹ , V(HCl)/V(C ₂ H ₂) = 1.15	X _A = 99.2% (48h)

^a X_A represents the conversion of acetylene.

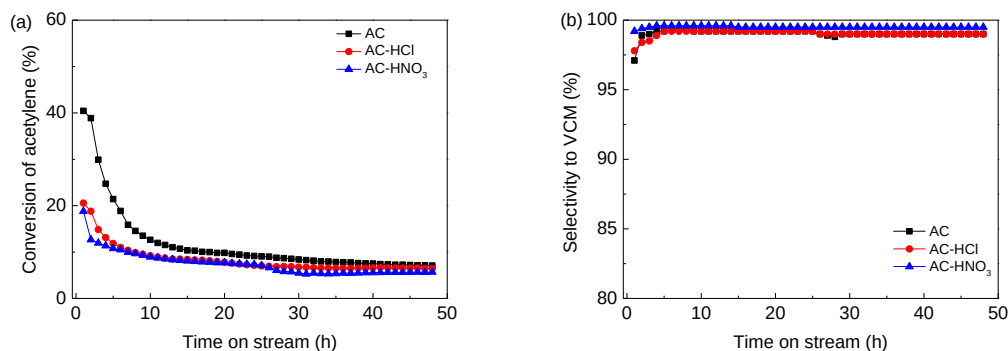


Figure S1. The acetylene conversion (a) and selectivity to VCM (b) over the supports.

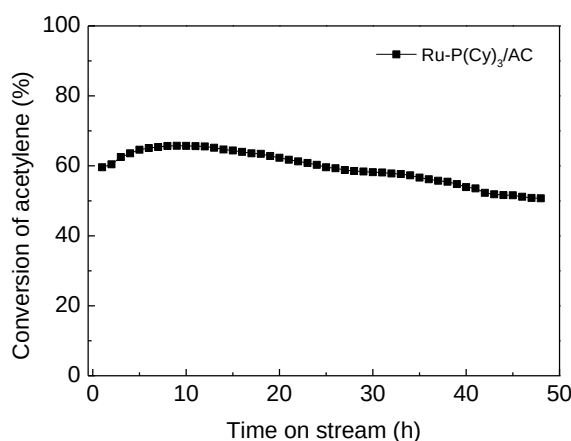


Figure S2 The acetylene conversion of the Ru-P(Cy)₃/AC catalyst. Reaction conditions: temperature (T) = 180 °C, GHSV (C₂H₂) = 180 h⁻¹ and V_{HCl}/V_{C₂H₂} = 1.15.

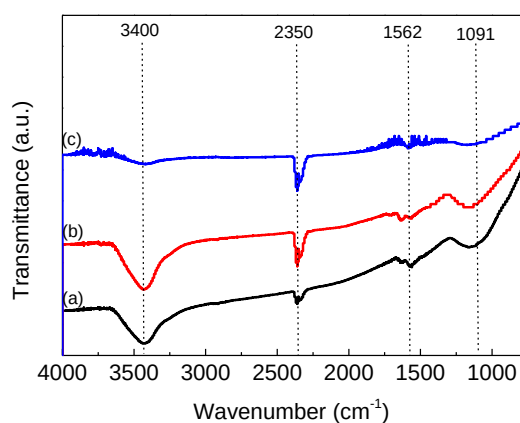


Figure S3. FT-IR spectra of catalyst support: (a) AC, (b) AC-HNO₃, (c) AC-HCl. The characteristic peaks are centered at: 1091 cm⁻¹: C-OH; 1562 cm⁻¹: COOH; 2350 cm⁻¹: C≡N; 3400 cm⁻¹: phenolic hydroxyl.

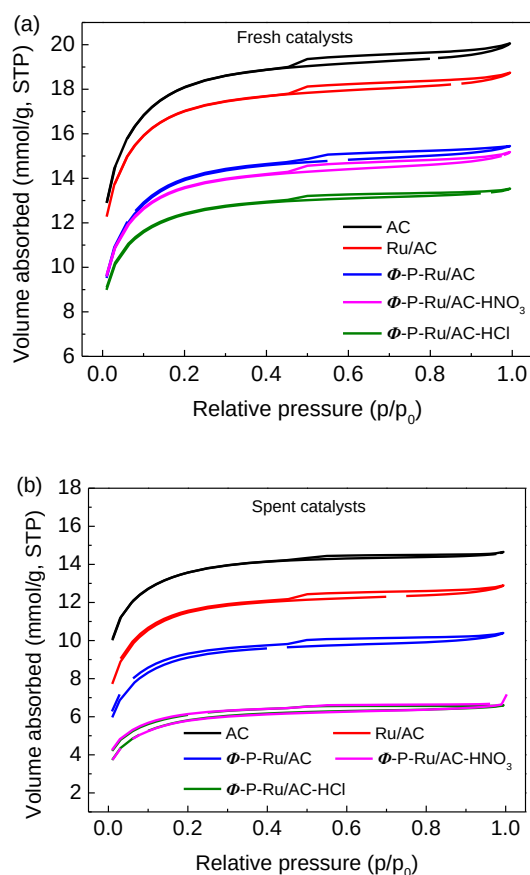


Figure S4. Nitrogen adsorption-desorption isotherms of the fresh (a) catalysts and spent (b) catalysts.

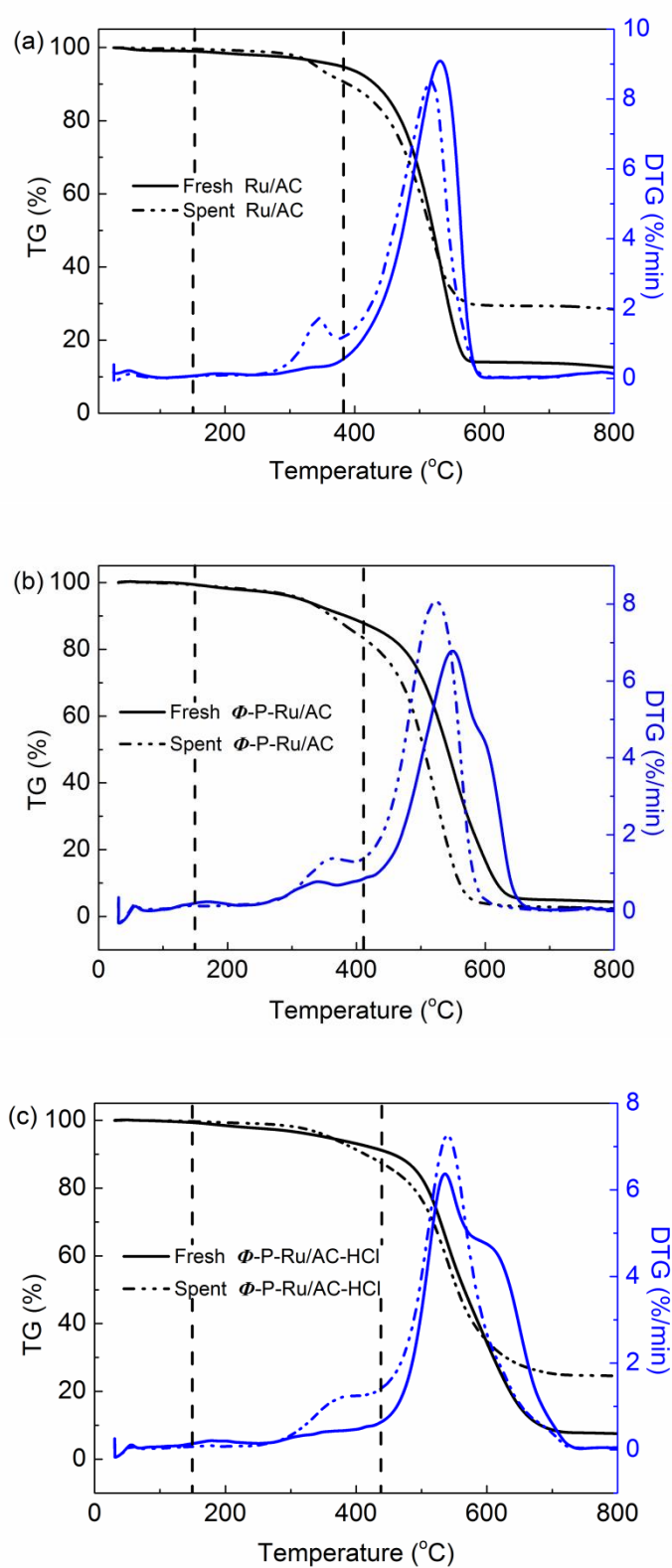


Figure S5. Thermogravimetric analysis (TGA) curves of fresh and spent catalysts recorded in air atmosphere. (a) Ru/AC, (b) ϕ -P-Ru/AC, (c) ϕ -P-Ru/AC-HCl.

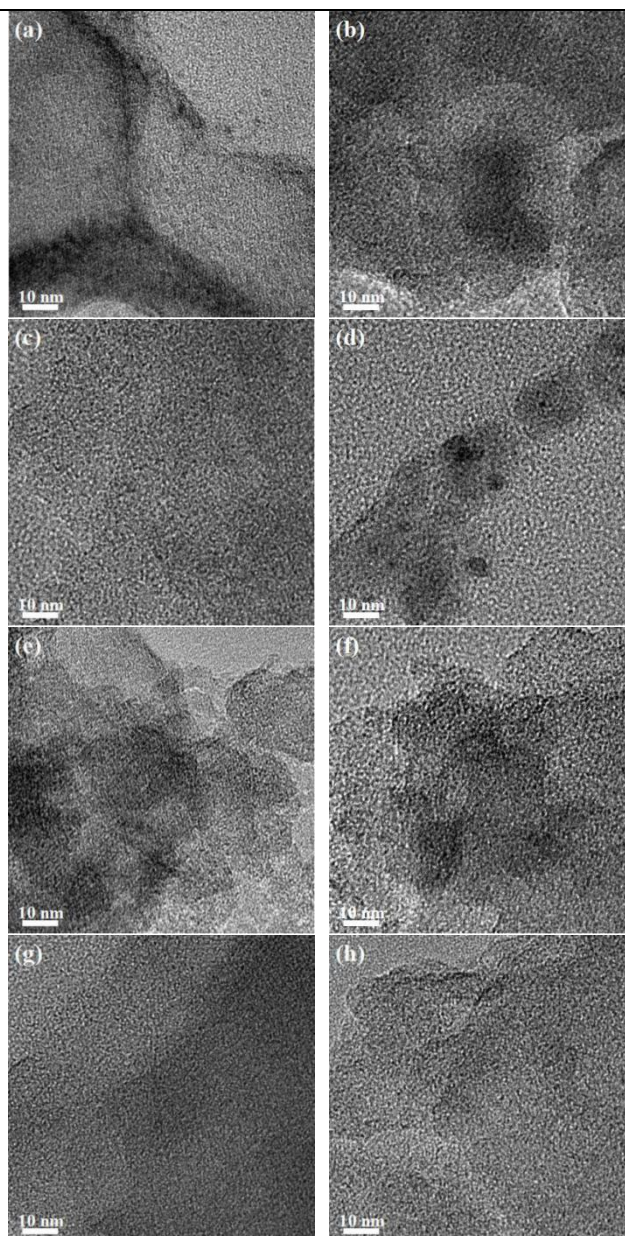


Figure S6. Particle size distribution of Ru-based catalysts: (a) Fresh Ru/AC, (b) Spent Ru/AC, (c) Fresh Φ -P-Ru/AC, (d) Spent Φ -P-Ru/AC, (e) Fresh Φ -P-Ru/AC-HCl, (f) Spent Φ -P-Ru/AC-HCl, (g) Fresh Φ -P-Ru/AC-HNO₃, (h) Spent Φ -P-Ru/AC-HNO₃.

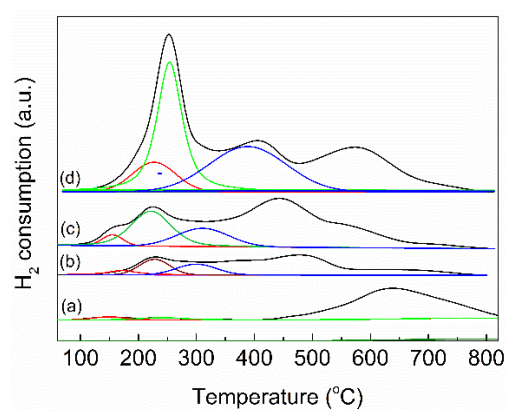


Figure S7. The deconvoluted H₂-TPR profiles of the fresh catalysts: (a) Ru/AC, (b) Φ -P-Ru/AC, (c) Φ -P-Ru/AC-HCl, (d) Φ -P-Ru/AC-HNO₃.

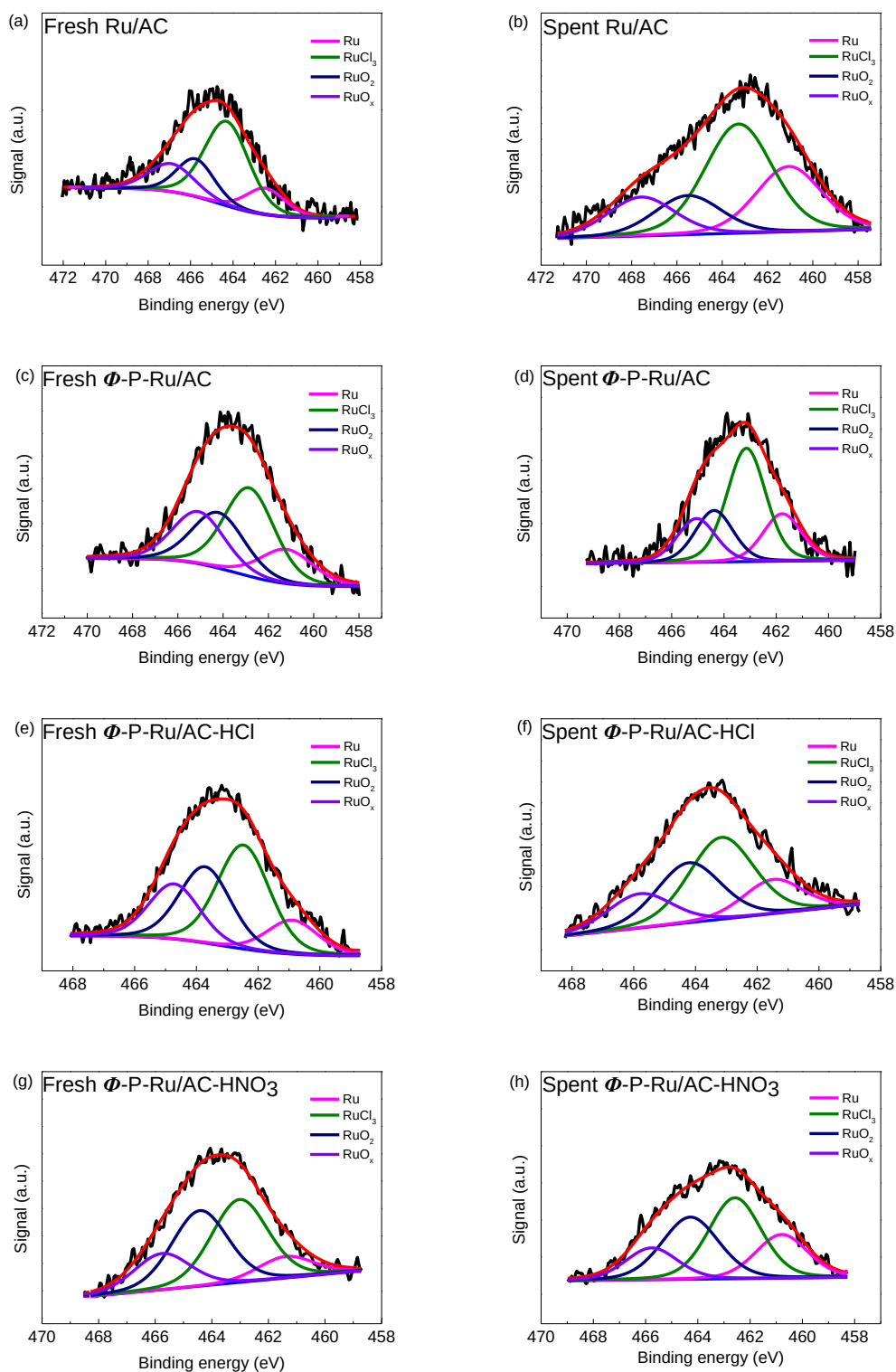


Figure S8. High-resolution XPS spectra of Ru 3p for the fresh and spent catalysts: (a) Fresh Ru/AC, (b) Spent Ru/AC, (c) Fresh Φ -P-Ru/AC, (d) Spent Φ -P-Ru/AC, (e) Fresh Φ -P-Ru/AC-HCl, (f) Spent Φ -P-Ru/AC-HCl, (g) Fresh Φ -P-Ru/AC-HNO₃, (h) Spent Φ -P-Ru/AC-HNO₃.

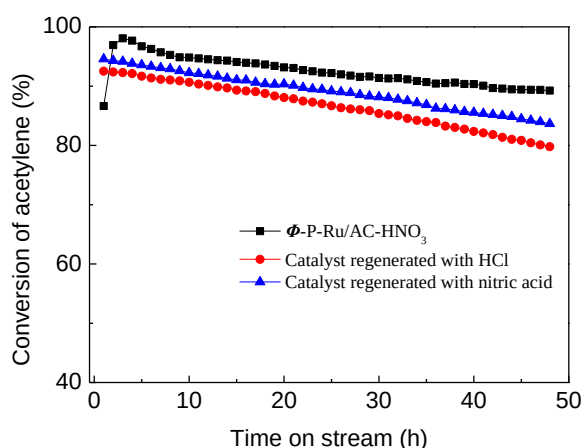


Figure S9. The activity of the catalyst regenerated by HCl and nitric acid. Reaction conditions: temperature (T) = 180 °C, GHSV (C_2H_2) = 180 h^{-1} and $V_{HCl}/V_{C_2H_2}$ = 1.15.

The regeneration was mainly aimed at the reversible deactivation caused by the coke deposition and the reduction of active components. The offline regeneration by HNO_3 solution and the online regeneration by HCl gas were conducted, and the results are shown in Figure S9.

The offline regeneration by HNO_3 solution refers to that the spent catalyst is soaked with 10 mL nitric acid (5 mol·L⁻¹), and the mixture was placed at room temperature for 6 h under stirring, then it was filtered and washed to pH = 7 with distilled water, followed by desiccation at 140 °C for 24 h. The online regeneration by HCl refers to that a HCl flow of 20 mL·min⁻¹ is passed through the catalyst bed at 180 °C for 12 h to reactivate the spent catalyst. The conversions of acetylene increase from 89.25% to 94.58% and 92.52%, respectively, over the catalysts regenerated by HNO_3 solution and HCl gas. The possible reason is that HNO_3 solution and HCl gas partially oxidize the reduced Ru species to high-valent active species, and the HNO_3 solution can also remove the coke deposition to some extent.

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