Supporting Information

$NiAl_2O_4$ Spinel Supported Pt Catalyst: High Performance and Origin in Aqueous-phase Reforming of Methanol

Didi Li,[†,‖] Yi Li,[‡,‖] Xiaohui Liu,[†] Yong Guo,*[†] Chih-Wen Pao,[§] Jeng-Lung Chen,[§] Yongfeng Hu[⊥] and Yanqin Wang*[†]

[†]Shanghai Key Laboratory of Functional Materials Chemistry and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, P. R. China

[‡]School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, P. R. China.

[§] National Synchrotron Radiation Research Centre, Hsinchu, 30076, Taiwan.

[⊥] Canadian Light Source Inc., 44 Innovation Boulevard, Saskatoon, SK S7N 2V3, Canada

[‖] These two authors contribute equally to this work.

*guoyong@ecust.edu.cn

*wangyanqin@ecust.edu.cn

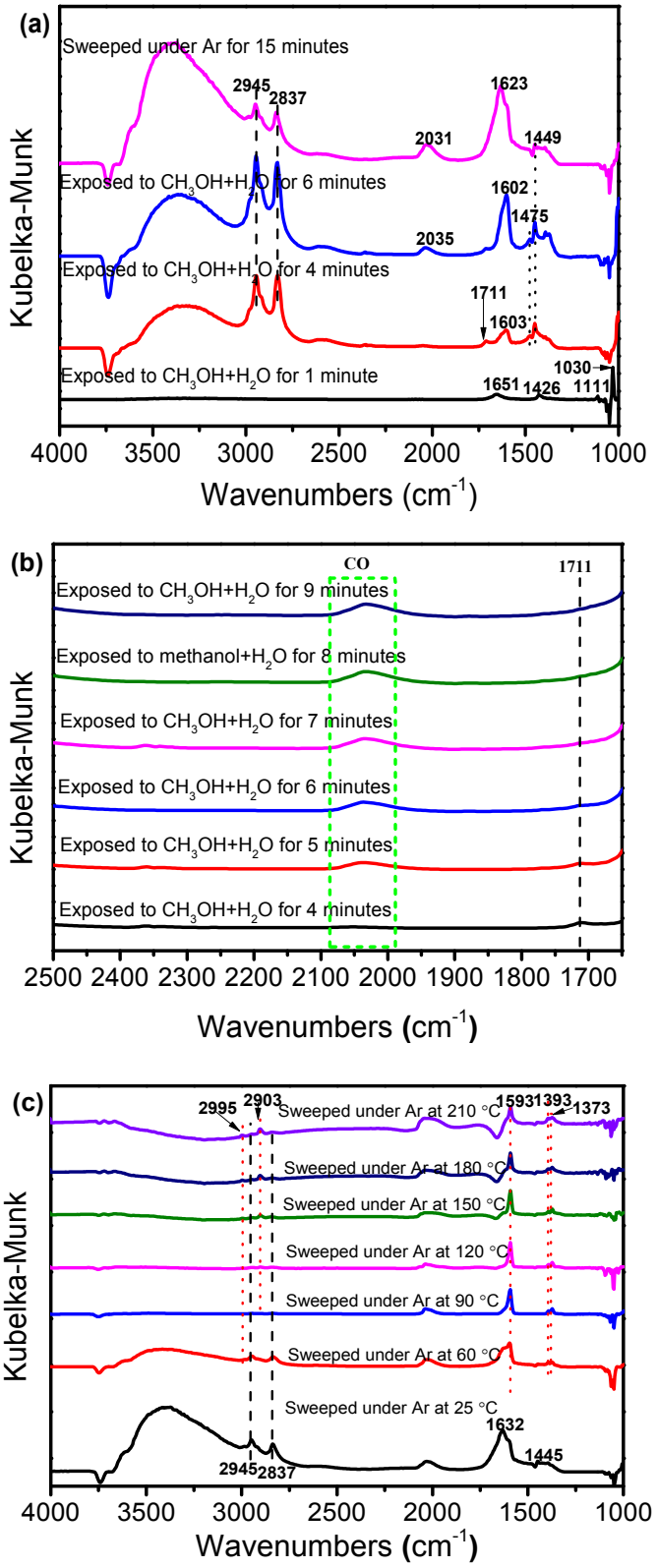

Figure. S1. *In-situ* DRIFTS of APR over Pt/γ-Al_2O_3 catalyst: (a) and (b) exposed to the mixture of CH_3OH/H_2O for 15 min followed by Ar flushing at 25

ºC and (c) increasing reaction temperature.

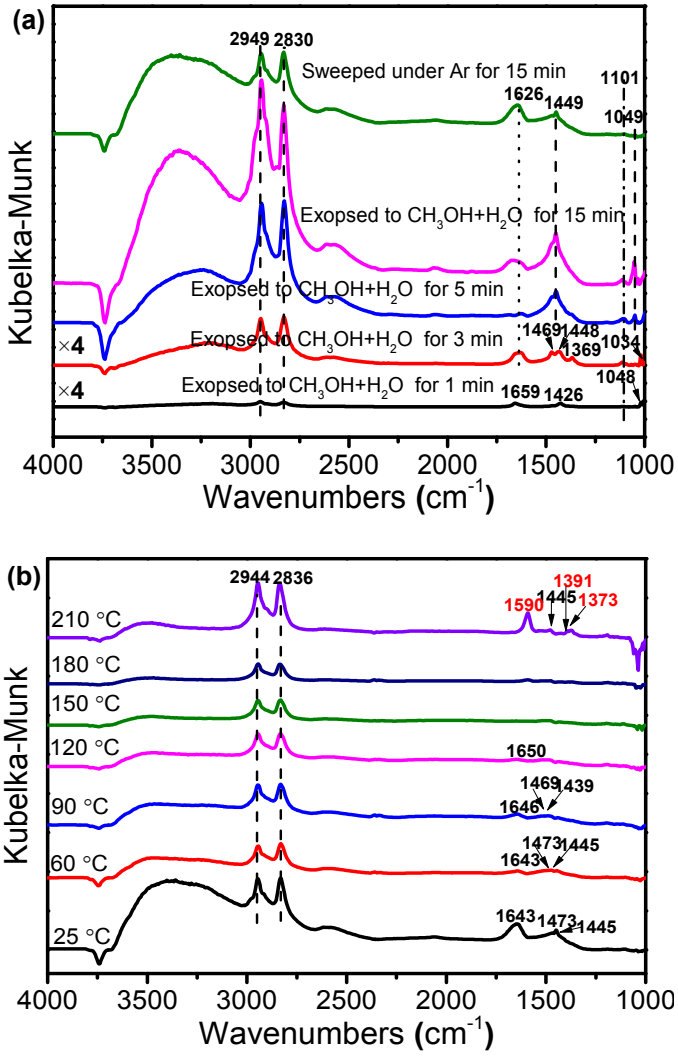

Figure. S2. *In-situ* DRIFTS of APR over $NiAl_2O_4$: (a) exposed to the mixture of CH_3OH/H_2O for 15 min followed by Ar flushing at 25 ºC and (b) increasing reaction temperature.

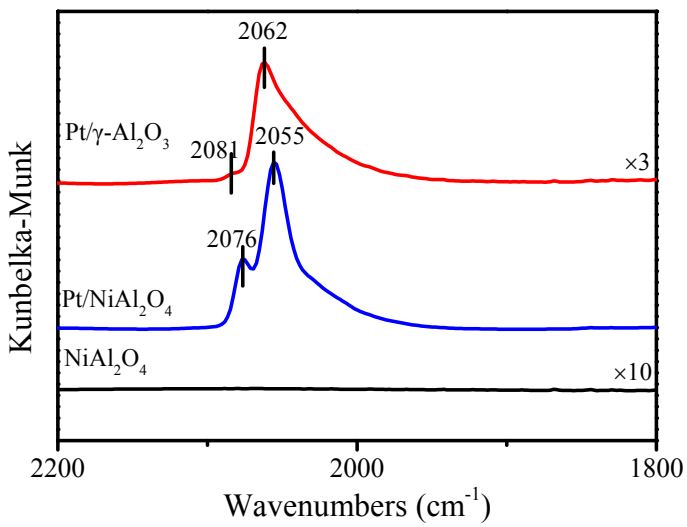

Figure S3. DRIFTS of CO-adsorption on Pt/γ-Al_2O_3, Pt/$NiAl_2O_4$, and $NiAl_2O_4$.

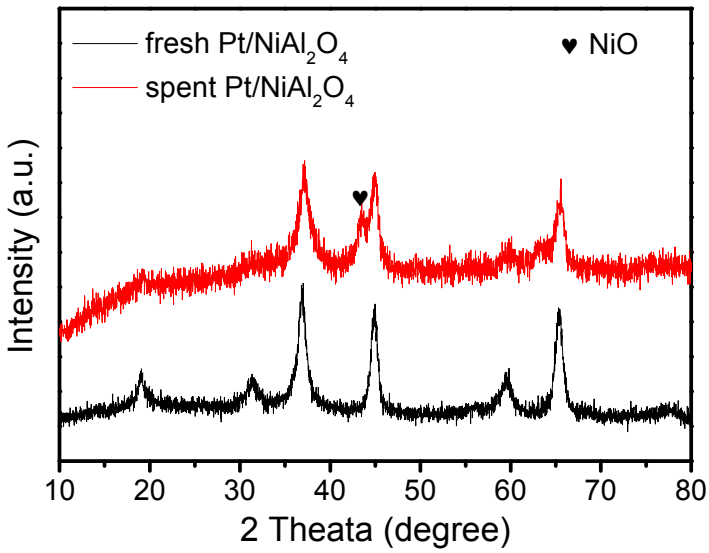

Figure S4. XRD patterns of the fresh Pt/$NiAl_2O_4$ and spent Pt/$NiAl_2O_4$.

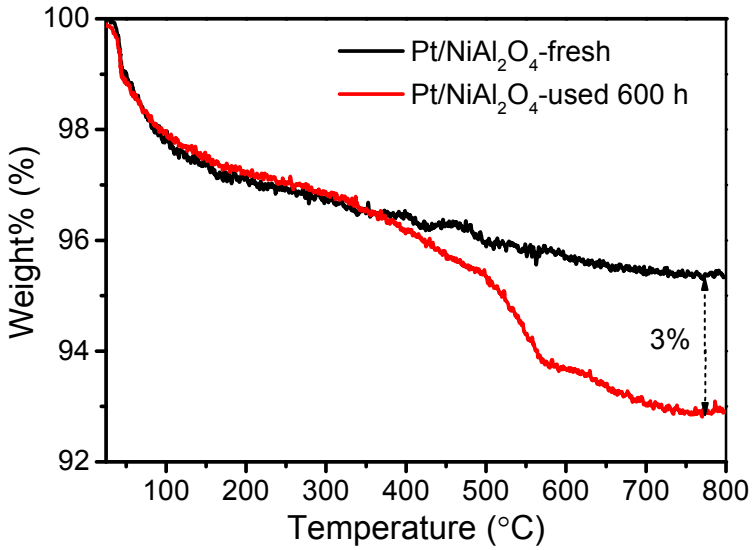

Figure S5. TGA analysis for fresh $Pt/NiAl_2O_4$ and used $Pt/NiAl_2O_4$.

Table S1. Catalytic performance for APR of methanol.[a]

Samples	Conv. of C to gas /%	Mass time yield /μmol·min^{-1}·g^{-1}cat			Selectivity /%		Yield /%
		H_2	CO	CH_4	CO_2	H_2	H_2
$Pt/\gamma\text{-}Al_2O_3$	26.5	107.3	0.02	0.97	99.01	88.66	23.3
$Pt/NiAl_2O_4$	>99.9	439.2	0.05	0.23	99.72	96.05	95.7
$NiAl_2O_4$	0.2	1.7	0	0	100	100	0.3

[a]Reaction conditions: 1 g catalyst, 10wt% methanol/water, WHSV=2.94 h^{-1}, 2.9 MPa, 210 °C.

Table S2. Comparison of the performance of $Pt/NiAl_2O_4$ catalyst with other catalysts reported.

T /°C/ P /MPa	Catalysts	Methanol concentration	WHSV /h^{-1}	Conv.[a] /%	Mass time H_2 yield /μmol·min^{-1}·g^{-1}cat	S_{H2} /%	Ref.
225/2.86	$3Pt/Al_2O_3$	1wt%	0.8	94	11.7	99	1
265/5.53							
225/2.81	0.5Pt/NaY	1wt%	0.8	81	9.7	97.6	2
265/5.51				98.8	12.3	96.9	
230/3.2	13Ni1.3Ce /$\gamma\text{-}Al_2O_3$	5wt%	2	7.0	84.7	-	3
275/20	1.15Pt0.35Ni/γ-Al_2O_3	1wt%	1.2	~60	-	-	4
190/2	2Pt/α-MoC	$n(CH_3OH)/n(H_2O)=1/3$	50 mL 0.1g cat	-	7776	-	5
190/2	$2Pt/Al_2O_3$			-	294	-	
190/2	$2Pt/TiO_2$			-	252	-	
210/2.9	$1Pt/Al_2O_3$	10wt%	2.94	26.5	107.3	88.7	This

210/2.9	1Pt/$NiAl_2O_4$	10wt%	2.94	>99.9	439.2	96.1	work

[a]Conv.= Conversion of C to gas.

Table S3. Influence of temperature for APR of methanol.[a]

Pressure /MPa	T. /ºC	Conv. of C to gas /%	Mass time yield /μmol·min^{-1}·g^{-1}cat	Selectivity /%		
			H_2	CO	CH_4	CO_2
2.9	190	5.8	46.1	0.02	0.69	99.29
	200	23.6	197.7	0.14	0.92	98.94
	210	40.3	360.5	0.04	0.15	99.81
	215	42.07	352.63	0.07	0.47	99.46

[a]Reaction conditions: W_{cat}=1 g, 10 wt% methanol/water, WHSV=5.88 h^{-1}.

Table S4. Influence of pressure for APR of methanol.[a]

T. /ºC	Pressure /MPa	Conv. of C to gas /%	Mass time yield /μmol·min^{-1}·g^{-1}cat	Selectivity /%		
			H_2	CO	CH_4	CO_2
210	2.9	40.3	360.5	0.04	0.15	99.81
	2.95	45.6	364.1	0.04	0.63	99.33
	3.0	43.4	326.0	0.05	0.91	99.04
	3.1	44.7	344.7	0.06	0.94	99.00

3.2	46.0	358.9	0.02	0.46	99.52
3.5	50.4	391.2	0.06	0.67	99.27

[a]Reaction conditions: W_{cat}=1 g, 10 wt% methanol/water, WHSV=5.88 h^{-1}.

Table S5. Influence of WHSV for APR of methanol.[a]

WHSV /h^{-1}	Conv. of C to gas /%	Mass time yield /μmol·min^{-1}·g^{-1}cat	Selectivity /%		
		H_2	CO	CH_4	CO_2
1.97	> 99.9	194.8	0.04	0.65	99.31
2.94	>99.9	400.6	0.04	0.35	99.61
5.88	40.3	360.5	0.04	0.15	99.81
8.82	29.7	371.2	0.07	0.67	99.26
11.76	20.7	373.3	0.07	0.52	99.41

[a]Reaction conditions: W_{cat}=1 g, 10 wt% methanol/water, 2.9 MPa, 210 °C.

Table S6. BET specific surface area (S_{BET}), and Pt content for fresh Pt/$NiAl_2O_4$ and spent Pt/$NiAl_2O_4$.

Samples	S_{BET} /m^2·g^{-1}	Pt content /wt%[a]
Fresh-Pt/$NiAl_2O_4$	147	0.97
Spent-Pt/$NiAl_2O_4$	140	0.93

[a]Measured by ICP-AES.

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