catalysts

Supplementary Material: Co-Aromatization of n-Butane and Methanol over PtSnK-Mo/ZSM-5 Zeolite Catalysts: The Promotion Effect of Ball-Milling

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1. Figures

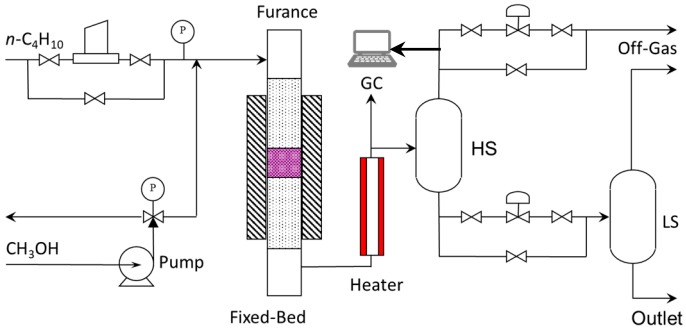


Figure S1. Schematic diagram of the co-aromatization apparatus and online analysis with two gas chromatographs used in this work.

The catalytic dehydrogenation reaction was performed in the fixed bed micro-catalytic reactor shown in Figure S1. The gaseous fraction of H_2, CO and CO_2 were analyzed by a haixing GC 2060 gas chromatograph equipped with a TCD detector, while that of C_1-C_4 alkanes and alkenes was analyzed by a GC 2060 gas chromatograph equipped with a FID detector and a KB-PLOTQ capillary column. Aqueous fraction was analyzed by a Wuhao GC 9560 gas chromatograph equipped with a FID detector and a PONA capillary column.

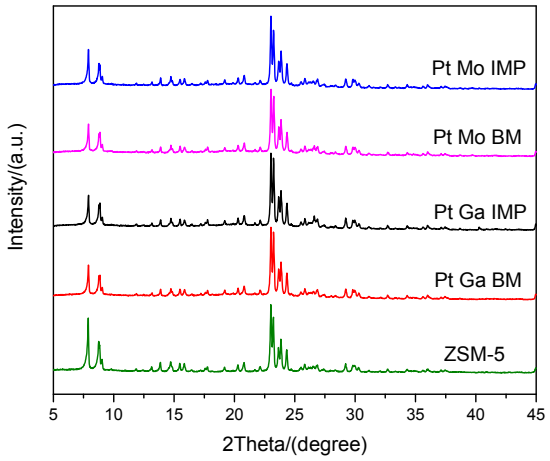


Figure S2. XRD patterns of Pt Mo, Pt Ga and ZSM-5 samples.

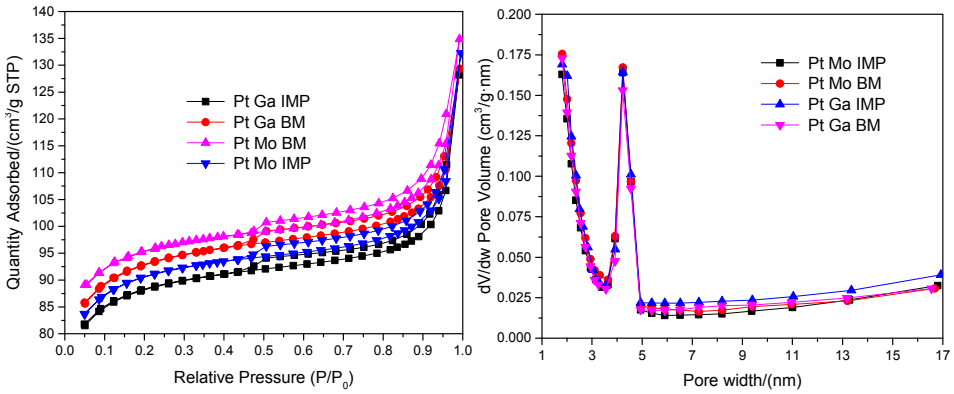


Figure S3. N_2 adsorption-desorption isotherms (**A**) and pore size distribution (**B**) for Pt Mo BM, Pt Mo IMP, Pt Ga BM and Pt Ga IMP samples.

It is observed that all samples exhibit very similar adsorption/desorption behavior and the adsorption-desorption curve for IMP is a little lower than for the BM samples. High values of sorption for all isotherms reflects a micro porosity in the samples. The sudden rise in the adsorption capacity at high relative pressures ($P/P_0 > 0.8$) along with the hysteresis loops suggests the existence of mesopores in the samples. These mesopores were created by intercrystallite spaces and are commonly observed in zeolites with nanosized crystals.

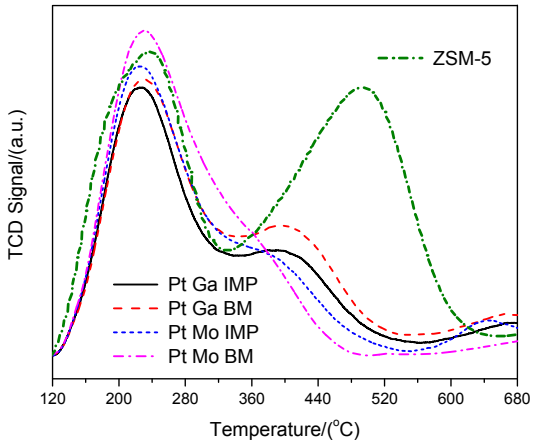


Figure S4. NH_3-TPD profiles of Pt Mo BM, Pt Mo IMP, Pt Ga BM, Pt Ga IMP and ZSM-5.

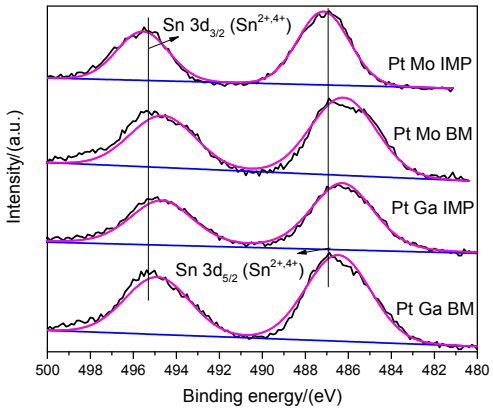


Figure S5. XPS spectra of Sn $3d_{5/2}$ and Sn $3d_{3/2}$ regions for Pt Mo/Ga samples. All samples are reduced at 500℃.

The Sn $3d_{5/2}$ peaks can be decomposed into four components: ca. 483.0 eV attributed to Sn^0, ca. 485.5 eV was assigned to Sn in the Pt-Sn alloy, ca. 486.5 eV was attributed to oxidized Sn (II, IV) and

ca. 488.6 eV was known as $SnCl_x$ species bound to the support. On Pt Mo/Ga samples, only oxidized Sn component was observed in our catalyst system.

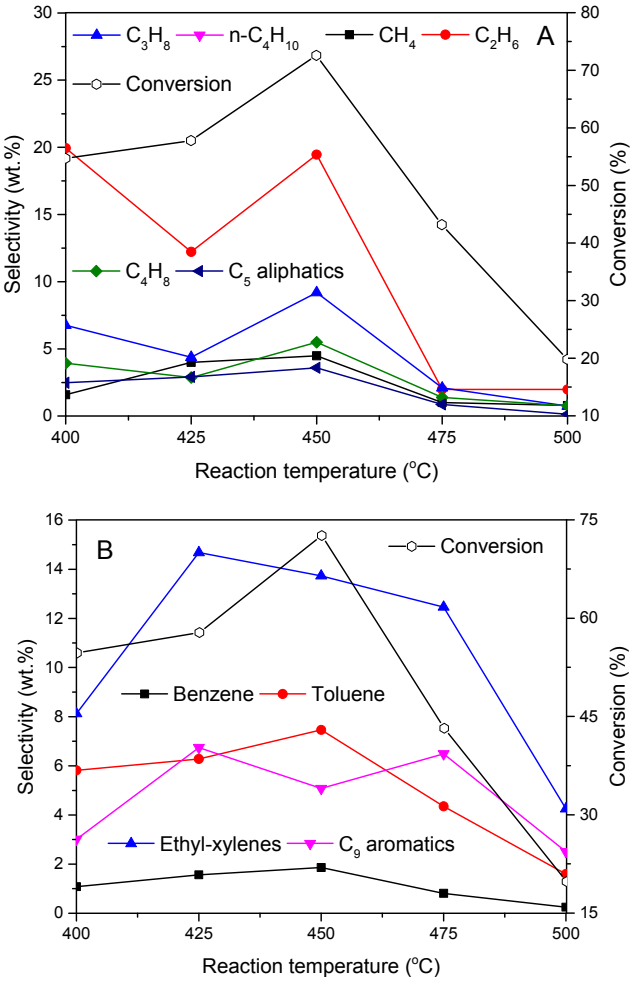
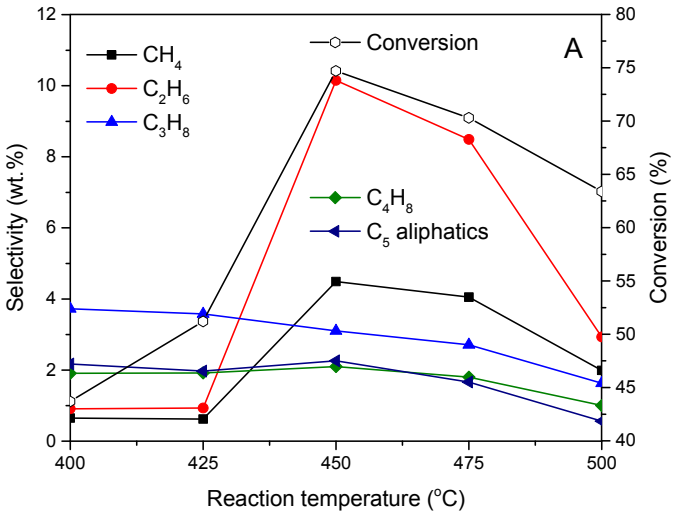


Figure S6. Effect of reaction temperature on n-butane conversion, selectivity to aliphatics (**A**) and selectivity to aromatics (**B**) over Pt Ga IMP. C_5H_{10} in aliphatics was used to simplify molar calculations for C_5 aliphatics.



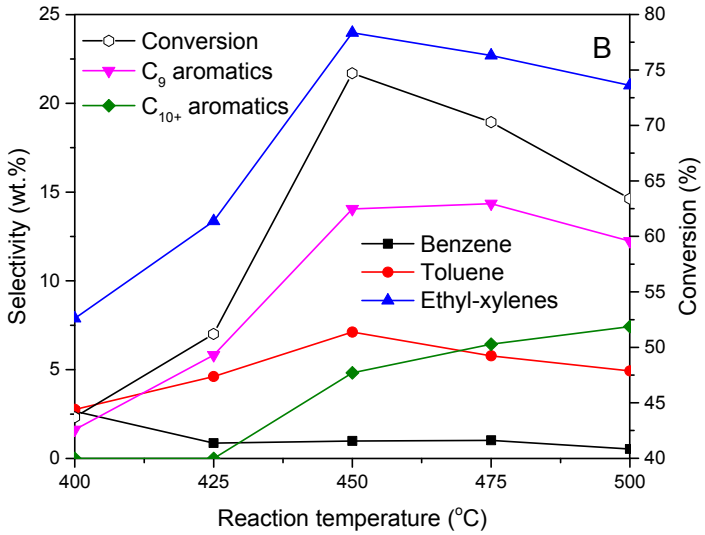


Figure S7. Effect of reaction temperature on n-butane conversion, selectivity to aliphatics (**A**) and selectivity to aromatics (**B**) over Pt Ga BM. C_5H_{10} in aliphatics and $C_{10}H_{14}$ in aromatics were used to simplify molar calculations for C_5 aliphatics and C_{10+} aromatics.

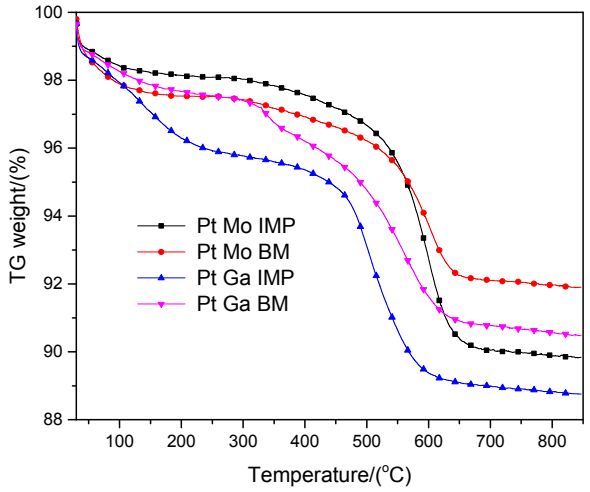
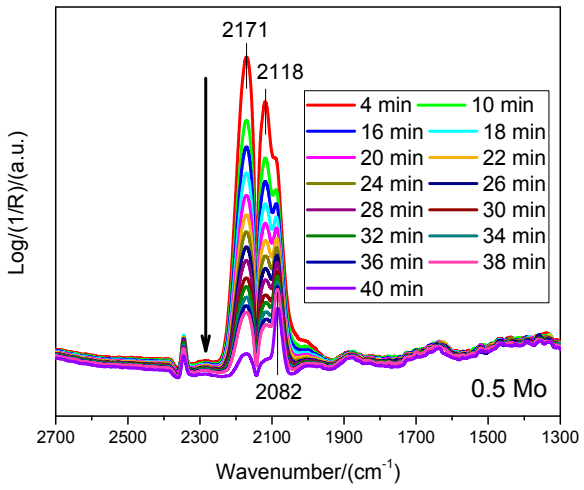
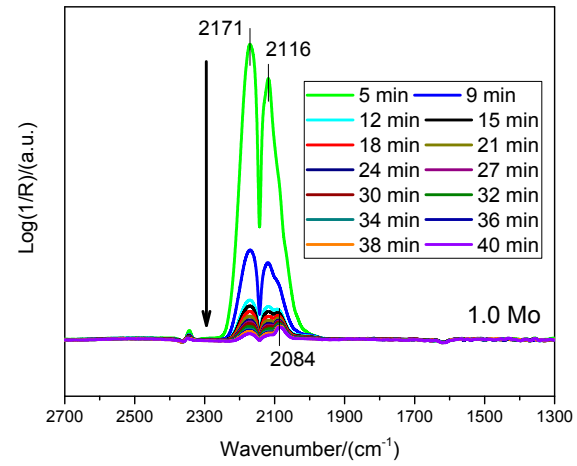


Figure S8. TG profiles of used Pt Mo BM, Pt Mo IMP, Pt Ga BM and Pt Ga IMP samples under air.

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2116
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12 min
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18 min
21 min
24 min
27 min
30 min
32 min
34 min
36 min
38 min
40 min
1.0 Mo
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Log(1/R)/(a.u.)
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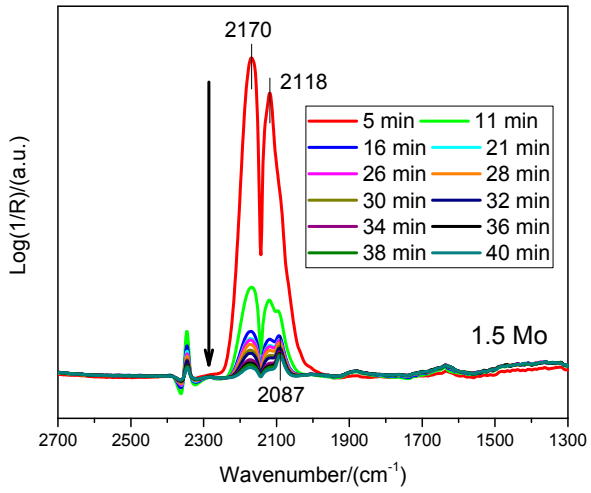
2500
2300
2100
1900
1700
1500
1300
Wavenumber/(cm-1)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1.5 Mo
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Log(1/R)/(a.u.)
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1700
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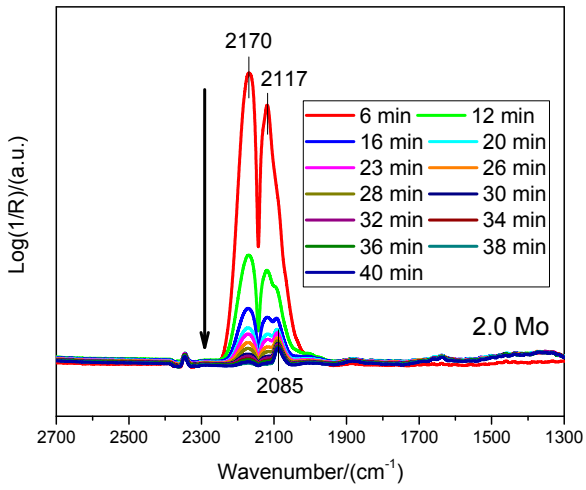
1300
Wavenumber/(cm-1)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Wavenumber/(cm-1)

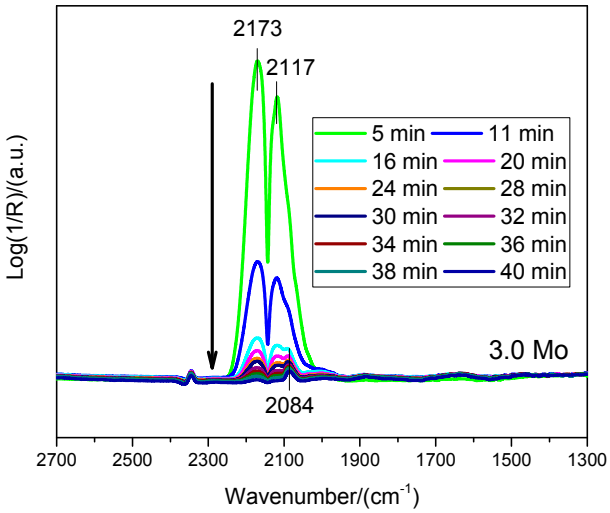

Figure S9. Effect of Mo content on evolution of the *in situ* CO-FTIR spectra of Pt Mo BM catalysts under N_2 during 40 min. All samples are *in situ* reduced at 500°C.

2. Tables

Table S1. Textural properties of Pt Mo BM, Pt Mo IMP, Pt Ga BM, Pt Ga IMP and ZSM-5.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	t-plot		
		S_{micro} ($m^2 \cdot g^{-1}$)	V_{micro} ($cm^3 \cdot g^{-1}$)	D (nm)
ZSM-5	331	246	0.112	3.1
Pt Mo IMP	333	246	0.093	2.7
Pt Ga IMP	324	242	0.092	2.8
Pt Mo BM	348	261	0.100	2.6
Pt Ga BM	341	252	0.095	2.7

S_{BET}, surface area derived from BET-method; S_{micro}, micropore surface area; V_{micro}, micropore volume; D, average pore diameter.

Table S2. ZSM-5 catalyst performance in the aromatization of cofeeding n-butane with methanol.

Reaction temperature (°C)	450	475
n-Butane conversion (%)	33	39
Hydrocarbons distribution of reactor effluent (wt.%)		
CH_4	0.8	0.5
$C_2H_6 + C_3H_8 + i\text{-}C_4H_{10}$	13	17
$C_2H_4 + C_3H_6 + C_4H_8$	3.6	3.6
$n\text{-}C_4H_{10}$	67	61
$CO + CO_2 + H_2 + C_2H_6O$	2.0	2.0
C_5 + aliphatics	1.8	1.2
Aromatics	11.8	14
Aromatics selectivity in the liquid product (wt.%)		
Benzene	7	5
Toluene	32	27
Xylenes + ethylbenzene	48	47
$C_{n\geq 9}$ aromatics	13	21
Coke (mg/g.cat.)	--	10

Table S3. Effect of Mo content on the catalytical performance of Pt Mo BM catalysts in the aromatization of cofeeding n-butane with methanol.

Mo content (wt.%)	0.5	1.0	1.5	2.0	3.0
n-Butane conversion (%)	85	89	86	83	68
Hydrocarbons distribution of reactor effluent (wt.%)					
CH_4	2.4	3.8	1.3	3.5	3.7

$C_2H_6 + C_3H_8 + i\text{-}C_4H_{10}$	20	23	16.5	20	29
$C_2H_4 + C_3H_6 + C_4H_8$	3.5	7	3.5	6.6	4.9
$n\text{-}C_4H_{10}$	15	11	14	17	32
$CO + CO_2 + H_2 + C_2H_6O$	0.8	1.2	1	2.7	1.6
C_5 + aliphatics	0.3	2	0.7	3.4	1
Aromatics	53	47	59	41	22
Aromatics selectivity (wt.%)					
Benzene	9.5	6.5	5.3	6.6	11
Toluene	50.4	43	15.7	35.2	41
Xylenes + ethylbenzene	33.8	45.4	60	46.9	34.5
$C_{n\geq 9}$ aromatics	6.3	5.1	19	11.3	13.5
Coke (mg/g.cat.)	73	75	80	80	84

Reaction conditions: 475ºC, 0.6 h^{-1}, 0.2 MPa, TOS = 4 h, n-butane/methanol = 60/40.

Table S4. Effect of cofeeding composition on the catalytical performance of Pt Mo (1.5 wt.%) BM catalyst in the aromatization of cofeeding n-butane with methanol.

n-Butane/methanol	100/0	80/20	60/40	40/60	20/80	0/100
n-Butane conversion (%)	54	65	86	90	96	--
Hydrocarbons distribution of reactor effluent (wt.%)						
CH_4	3.5	2.3	1.3	1	1.2	7
$C_2H_6 + C_3H_8 + i\text{-}C_4H_{10}$	21	17.6	16.5	15.5	9	13
$C_2H_4 + C_3H_6 + C_4H_8$	1.2	2	3.5	4.6	2	6
$n\text{-}C_4H_{10}$	46	35	14	10	4	12
$CO + CO_2 + H_2 + C_2H_6O$	1	1.6	1	1.4	1	2
C_5 + aliphatics	1.1	1.3	0.7	1.3	1.2	3
Aromatics	21	35	59	60	75	50
Aromatics selectivity (wt.%)						
Benzene	8.5	7.5	5.3	3.8	2.3	0.7
Toluene	33.8	26.4	15.7	18.8	13.9	7.3
Xylenes + ethylbenzene	35.2	44.9	60	55.4	57.8	50.6
$C_{n\geq 9}$ aromatics	22.5	21.2	19	22	26	41.4
Coke (mg/g.cat.)	74	75	80	90	94	100

Reaction conditions: 475ºC, 0.6 h^{-1}, 0.2 MPa and TOS = 4 h.