

Supporting Information

Correlating the surface chemical states of molybdenum to butene selectivity in the hydrogenation of 1,3-butadiene over Mo₂C-based catalysts

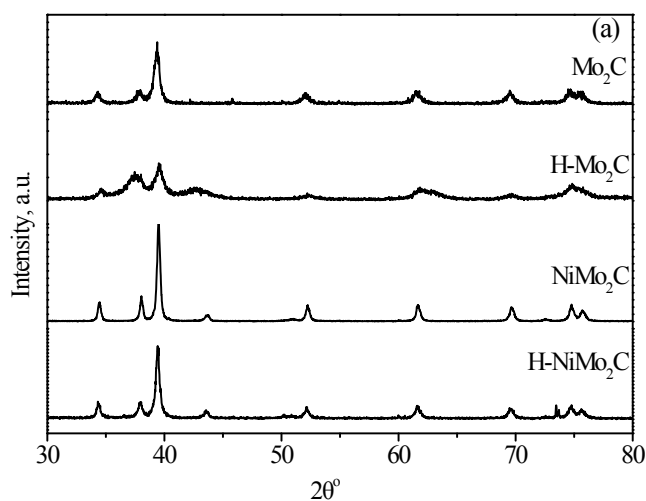
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1. Figures



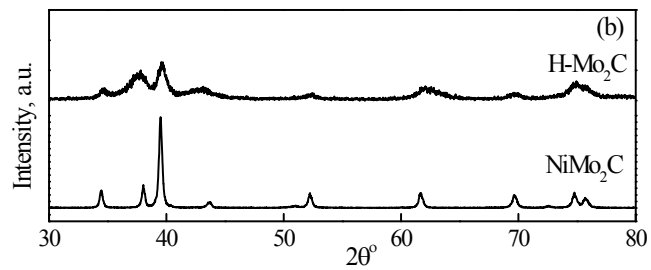


Figure S1. XRD pattern of the (a) regenerated catalysts (b) spent catalysts.

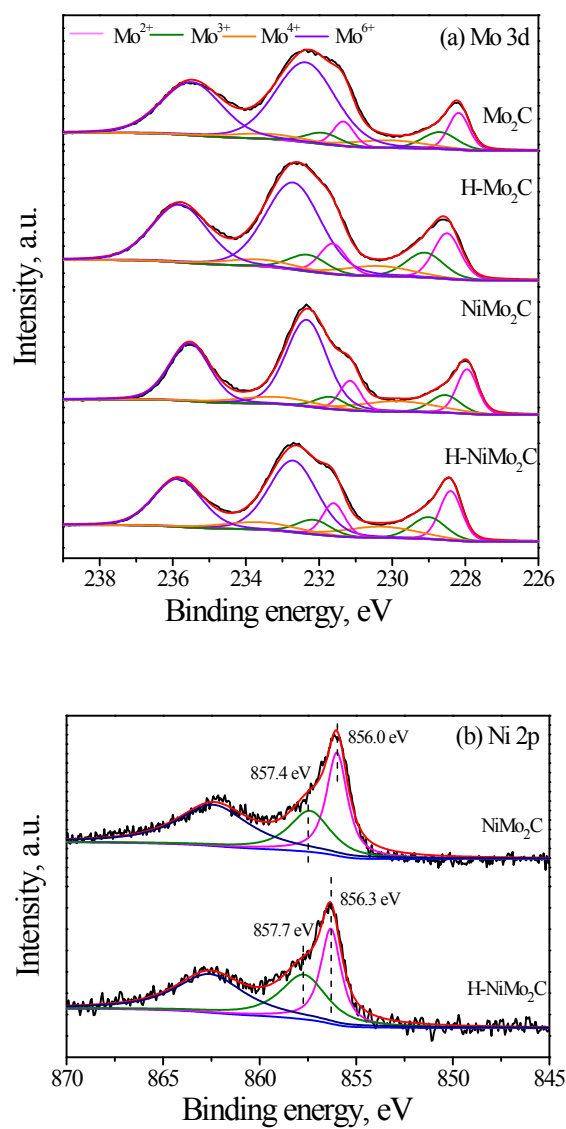


Figure S2. The XPS spectra of (a) Mo 3d and (b) Ni 2p for the as-synthesized catalysts.

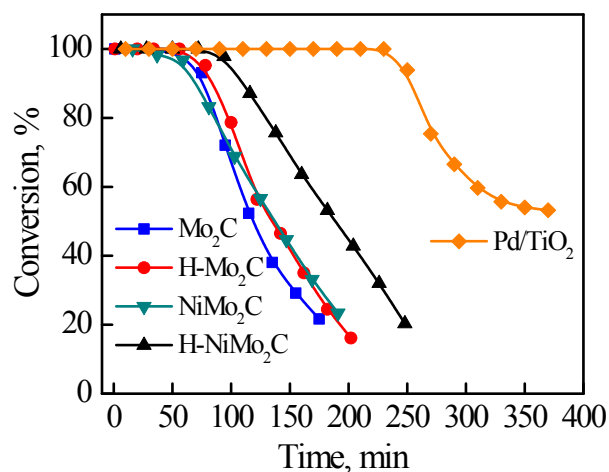


Figure S3. The comparison of TOS-Conversion curve between the Mo₂C-based catalysts and a benchmark catalyst (0.91 wt%Pd/TiO₂) at 308 K.

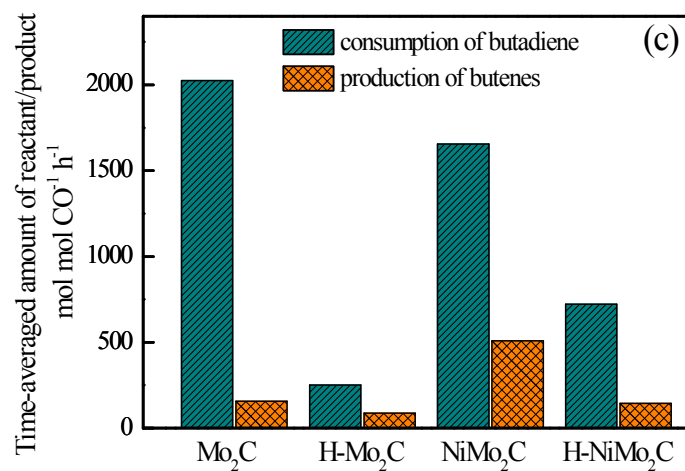


Figure S4. Time-averaged consumption of 1,3-butadiene and time-averaged production of butenes over Mo₂C, NiMo₂C, H-NiMo₂C normalized by CO uptake.

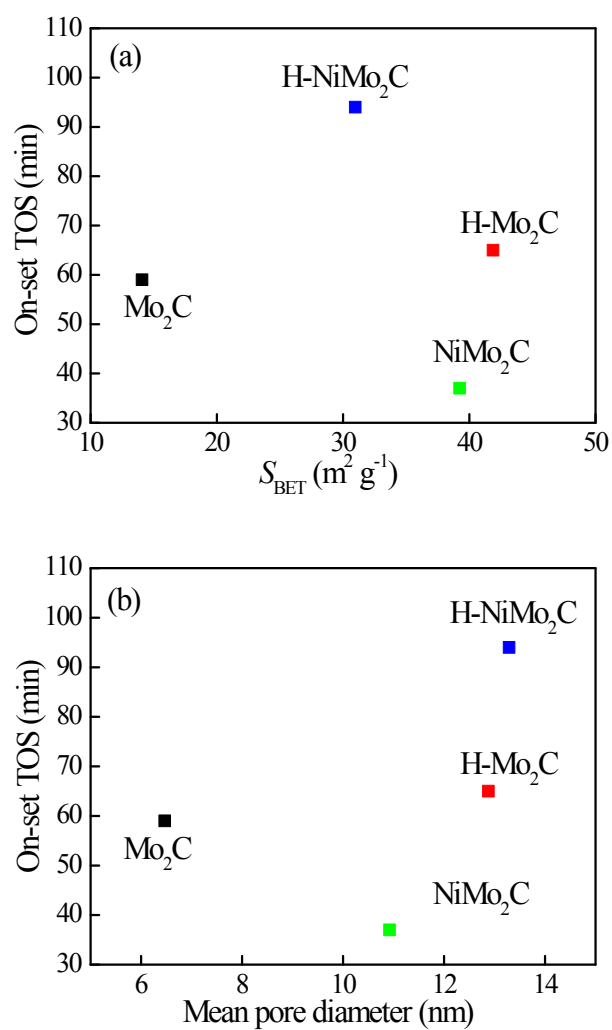


Figure S5. The correlation between the on-set TOS and (a) surface area; (b) mean pore diameter of the catalysts.

2. Tables

Table S1. The lattice parameters obtained from XRD data.

□ Sample	a (Å)	b (Å)	c (Å)	Volume (Å ³)
Mo ₂ C	3.0078	3.0078	4.7378	37.120
NiMo ₂ C	3.0096	3.0096	4.7363	37.151
H-NiMo ₂ C	3.0094	3.0094	4.7389	37.168

Table S2. The results of XP spectra for Mo 3d over the as-synthesized catalysts

Sample	Mo d _{5/2} Binding Energy (eV)				Mo ²⁺ /Mo _{total}	Mo ³⁺ /Mo _{total}	Mo ⁴⁺ /Mo _{total}	Mo ⁶⁺ /Mo _{total}
	Mo ²⁺	Mo ³⁺	Mo ⁴⁺	Mo ⁶⁺	(%)	(%)	(%)	(%)
Mo ₂ C	228.2	228.7	230.1	232.4	11.5	8.8	8.5	71.3
H-Mo ₂ C	228.4	229.0	230.4	232.7	12.0	16.1	9.5	62.3
NiMo ₂ C	228.0	228.6	229.9	232.3	16.0	9.1	14.5	60.5
H-NiMo ₂ C	228.4	229.0	230.3	232.7	17.9	12.2	13.8	56.0

Table S3. Surface atomic content of the regenerated catalysts from XP spectra analysis

Sample(G2)	Atomic Composition (%)			
	Mo	C	O	Ni
Mo ₂ C	19.03	36.11	44.86	
H-Mo ₂ C	20.26	34.76	42.99	
NiMo ₂ C	14.74	31.66	47.76	5.85
H-NiMo ₂ C	11.88	40.73	45.32	2.06

Table S4. Surface atomic content of the as-synthesized catalysts from XP spectra analysis.

Sample	Atomic Composition (%)			
	Mo	C	O	Ni
Mo ₂ C	13.56	39.78	46.67	--
H-Mo ₂ C	14.73	39.73	45.54	--
NiMo ₂ C	7.87	53.05	35.76	3.32
H-NiMo ₂ C	12.77	38.24	45.67	3.32

Table S5. The mole ratios of Ni/Mo from SEM-EDX and XPS.

Sample	as-synthesized		regenerated	
	NiMo ₂ C	H-NiMo ₂ C	NiMo ₂ C	H-NiMo ₂ C
EDX	0.23	0.20	0.19	0.17
XPS	0.42	0.26	0.40	0.17

3. Details on Data Processing

3.1 Calculation of strain and crystallite size from XRD

The crystallite size and strain were estimated from XRD data by Jade software. The details of the calculation follow the steps of

(i) The width of diffraction peak of half height ($FW(S)$) was measured.

(ii) The $\frac{\sin(\theta)}{\lambda}$ values were collected as X, and the $\frac{FW(S) \cdot \cos(\theta)}{\lambda}$ values were collected as Y.

(iii) Least square method was used to fit the plot ($Y = aX + b$), obtaining a straight line with the slope of “a” and the intercept of “b”.

(iv) The crystallite size and the strain were calculated according to Equations (S1) and (S2):

$$\text{Strain (\%)} = 2a \times 100\% \quad (\text{S1})$$

$$\text{Crystallite size} = 1/b \quad (\text{S2})$$

3.2 Calculation of time-averaged consumption of 1,3-butadiene and time-averaged production of butenes

The time-averaged consumption of 1,3-butadiene was calculated according to Equation (S3) based on the curve of “conversion–TOS”:

$$X_R = \frac{F \cdot \int_{t_1}^{t_2} x \cdot dt}{m \cdot (t_2 - t_1)} \quad (\text{S3}),$$

where X_R is the time-averaged consumption of 1,3-butadiene; F is the molar flow rate of 1,3-butadiene; x is the conversion of 1,3-butadiene; m is the mass of catalyst; t is the time on stream. The initial reaction time of 0 min was selected as t_1 , and the time corresponding to the conversion of 22% was selected as t_2 . It is noted that when there was no data corresponding to the conversion of 22% directly, interpolation of adjacent values for 22% would be obtained as t_2 .

Similarly, the time-averaged production of butenes was calculated according to Equation (S4) based on the curve of “yield–TOS”:

$$X_p = \frac{F \cdot \int_{t_1}^{t_2} y \cdot dt}{m \cdot (t_2 - t_1)} \quad (\text{S4})$$

where X_p is the time-averaged amount of products of butenes; y is the butene yield.

3.3 Kinetic analysis of deactivation

In order to understand the deactivation patterns of the catalysts. Simplified kinetic model has been used for Figure 4(c). The reaction rate with deactivation can be written as

$$-r = a(t)(-r_{fresh}) \quad (\text{S5})$$

where $-r$ is the reaction rate, $-r_{fresh}$ is the reaction rate of the fresh catalyst, $a(t)$ is the active factor as a function of time. The reaction rate under steady state without deactivation ($-r_{fresh}$) does not change with time; therefore, the deactivation of conversion in Figure 4(c) corresponds to the active factor (a). The active factor can be expressed by a differential equation for the interpretation of deactivation rate:

$$r_d = k_d a^n = -\frac{da}{dt} \quad (\text{S6})$$

where r_d is the deactivation rate, k_d is the deactivation rate constant, n is the deactivation order. The equation could be integrated to $a(t) = 1 - k_d t$ when $n=0$, and to $a(t) = e^{-k_d t}$ when $n=1$, corresponding to a linear deactivation pattern and an exponential deactivation pattern. The 0 order deactivation could be applied to the Ni-modified catalysts, and the 1st order deactivation could be applied to the non-modified catalysts. The regressed deactivation rate constants (k_d) are summarized in Table S6.

Table S6. Regressed deactivation rate constants (k_d)

	Deactivation model	TPC	HA-TPC
	1 st order,		
Non-modified Mo ₂ C	$-r = e^{-k_d t} a(t)(-r_{fresh})$	0.01442	0.01191
	0 order		
Ni-modified Mo ₂ C	$-r = (1 - k_d t)(-r_{fresh})$	0.00559	0.00502

