

Supporting Information Materials

Table S1 Total pore volume and BET surface of MoO₃-SnO₂ with different calcination temperature

Calcination temperature (K)	S _{BET} (m ² /g)	V (cm ³ /g)
473	9.3	0.0127
573	3.6	0.0089
673	10.3	0.0356
773	10	0.0363
873	4.2	0.0175
973	5.5	0.0168
1073	6.7	0.0244

Table S2 Total pore volume and BET surface of MoO₃-SnO₂ with different SnO₂ contents

Sn/(Mo+Sn)	S _{BET} (m ² /g)	V (cm ³ /g)
0.00	1.097	0.000037
0.25	9.960	0.000792
0.33	19.600	0.000852
0.50	21.700	0.003720
0.67	123.850	0.018200
0.75	153.825	0.013000
1.00	50.960	0.001860

Fig S1 In situ IR pulsed reaction of dimethyl ether to methyl ether over Mo1Sn2 at 343 K

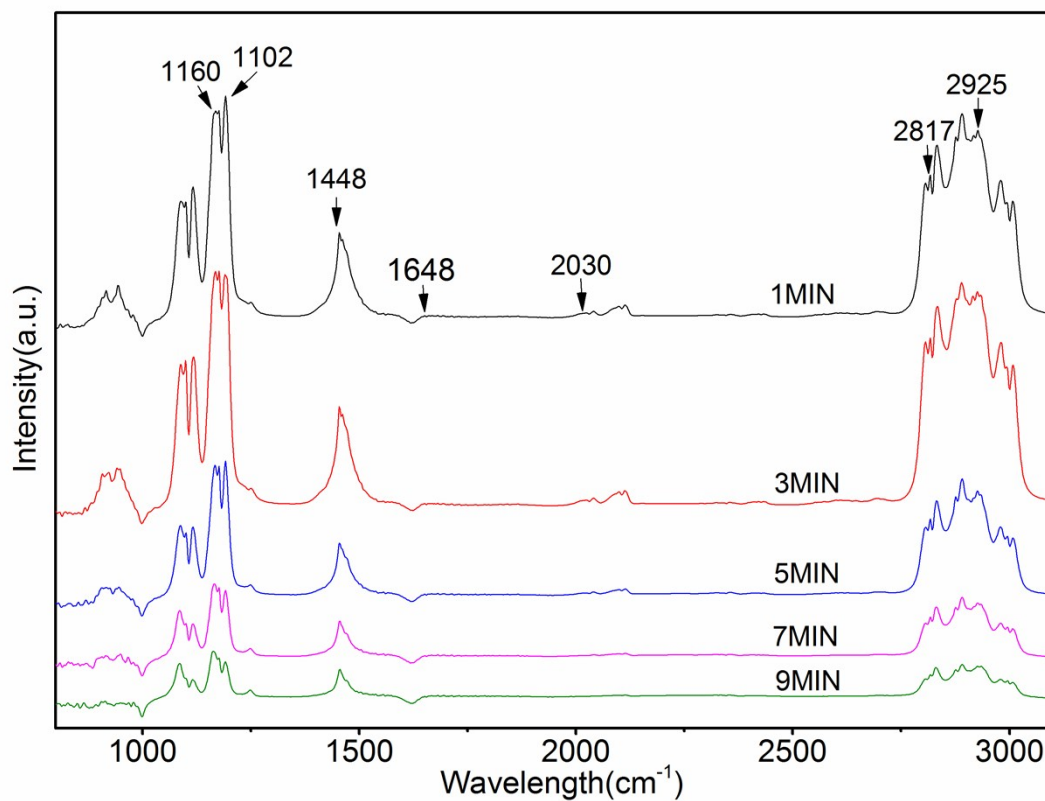


Fig S2 In situ IR pulsed reaction of dimethyl ether to methyl ether over Mo₁Sn₂ at 433 K

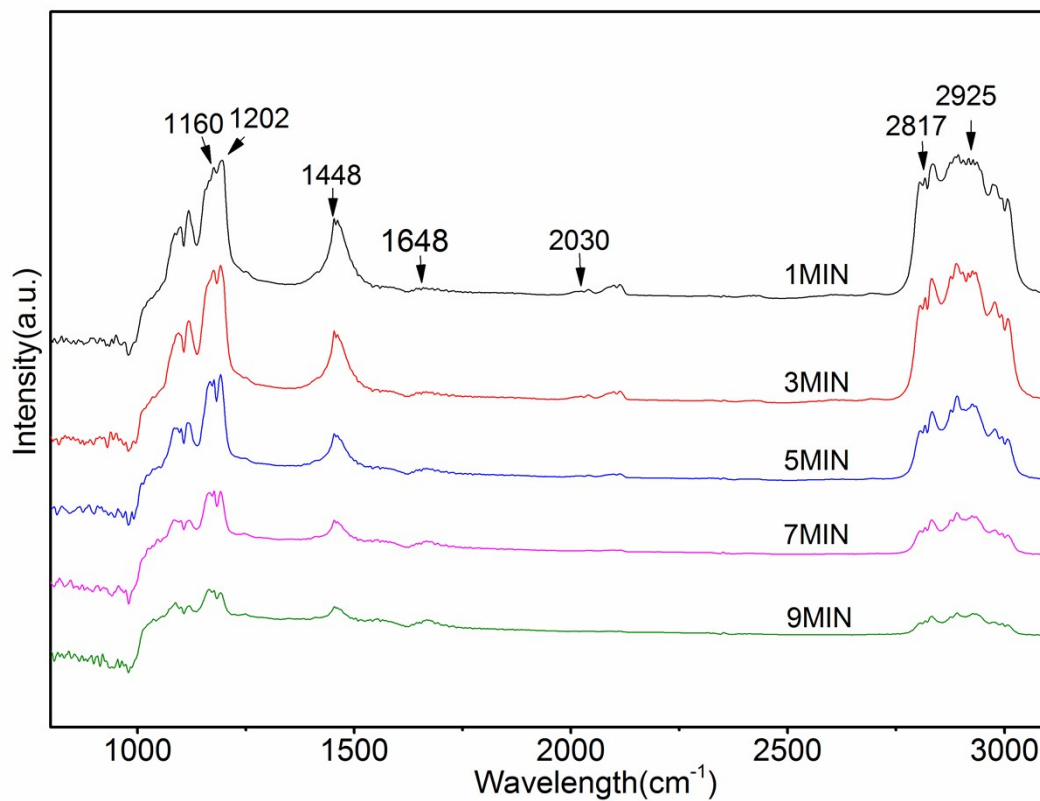


Fig S3 In situ IR pulsed reaction of dimethyl ether to methyl ether over Mo₁Sn₂ at 473 K

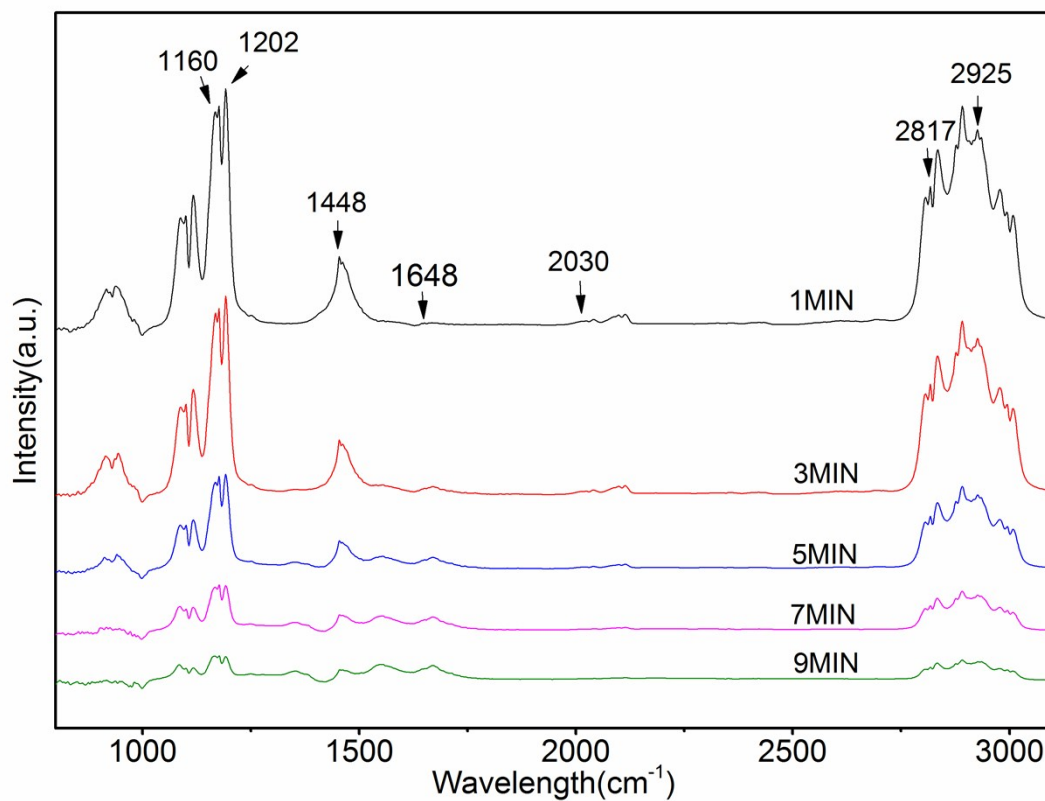


Fig S4 In situ IR pulsed reaction of dimethyl ether to methyl ether over Mo₁Sn₂ at 573K

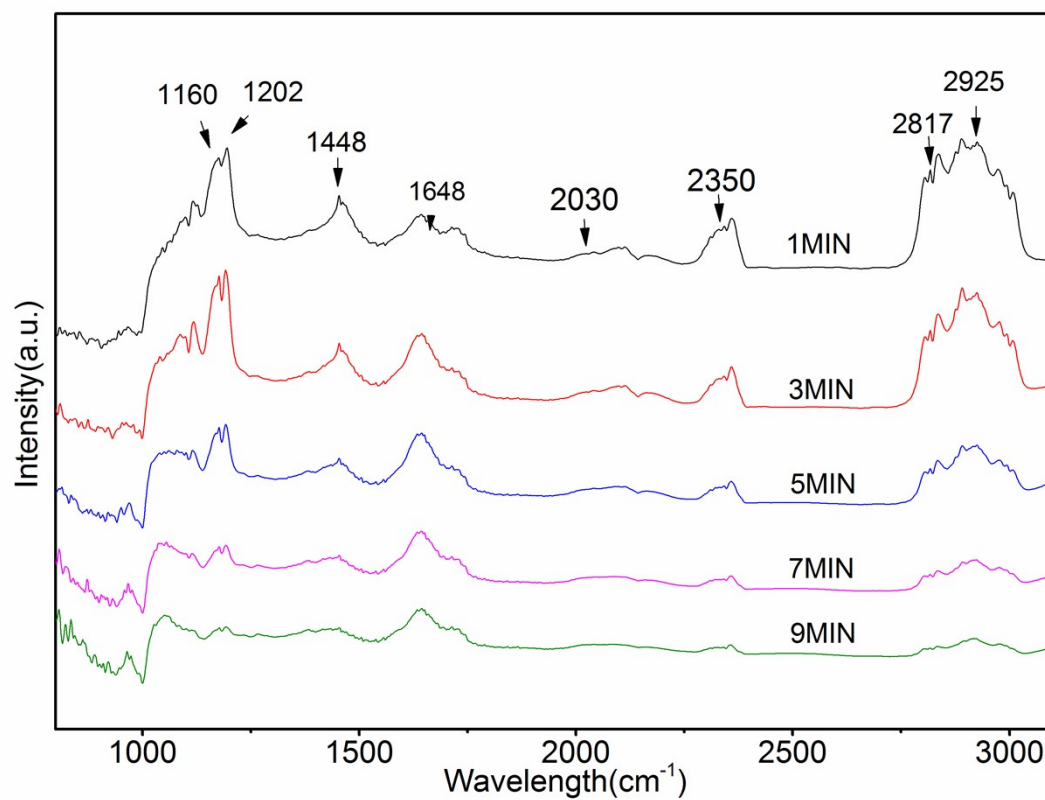


Fig S5 H₂-TPR profiles of MoO₃-SnO₂ with different SnO₂ contents

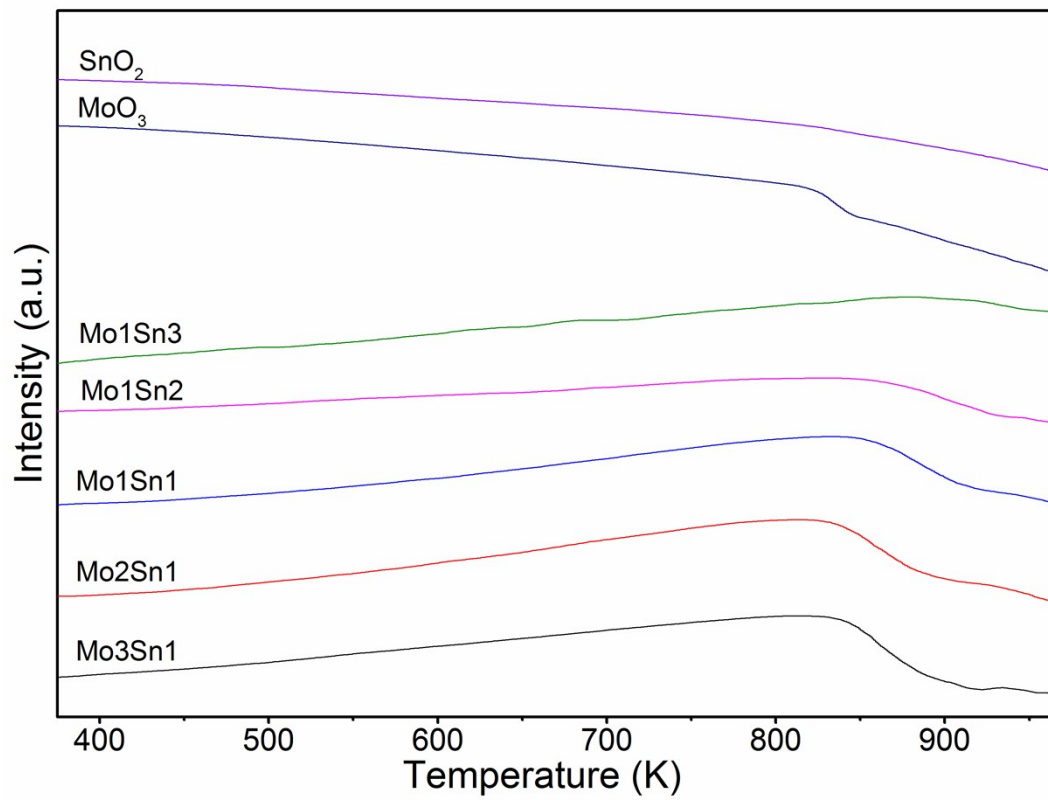


Fig S6 HRTEM images of Mo1Sn3

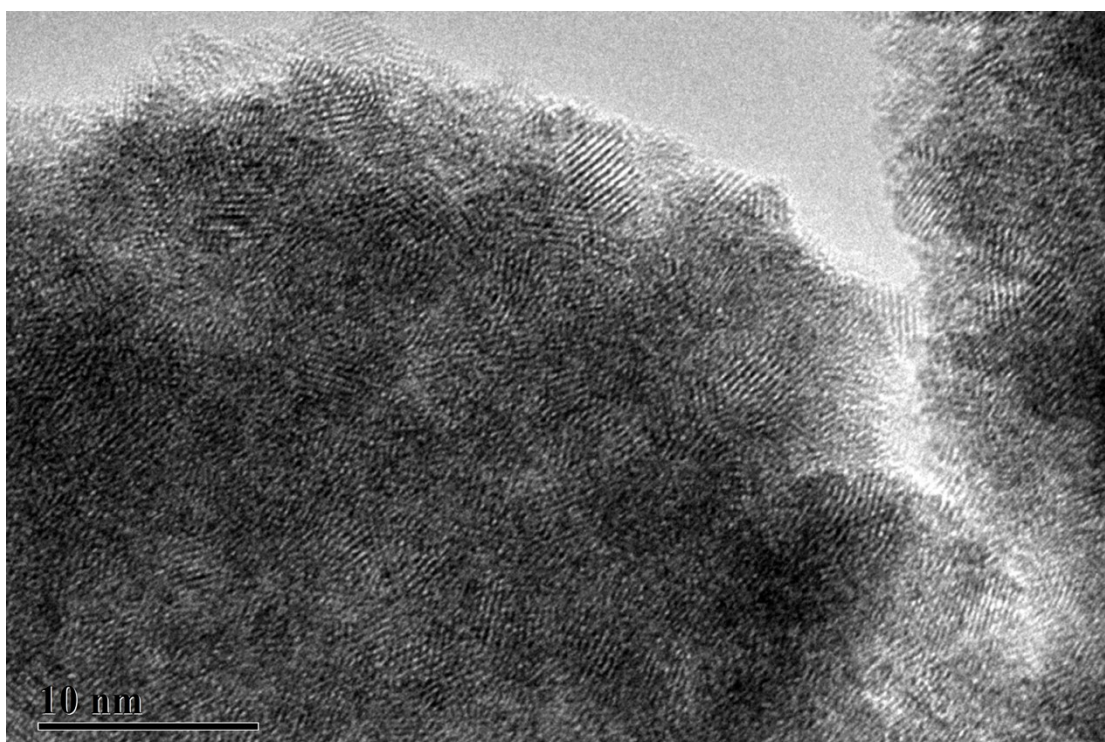
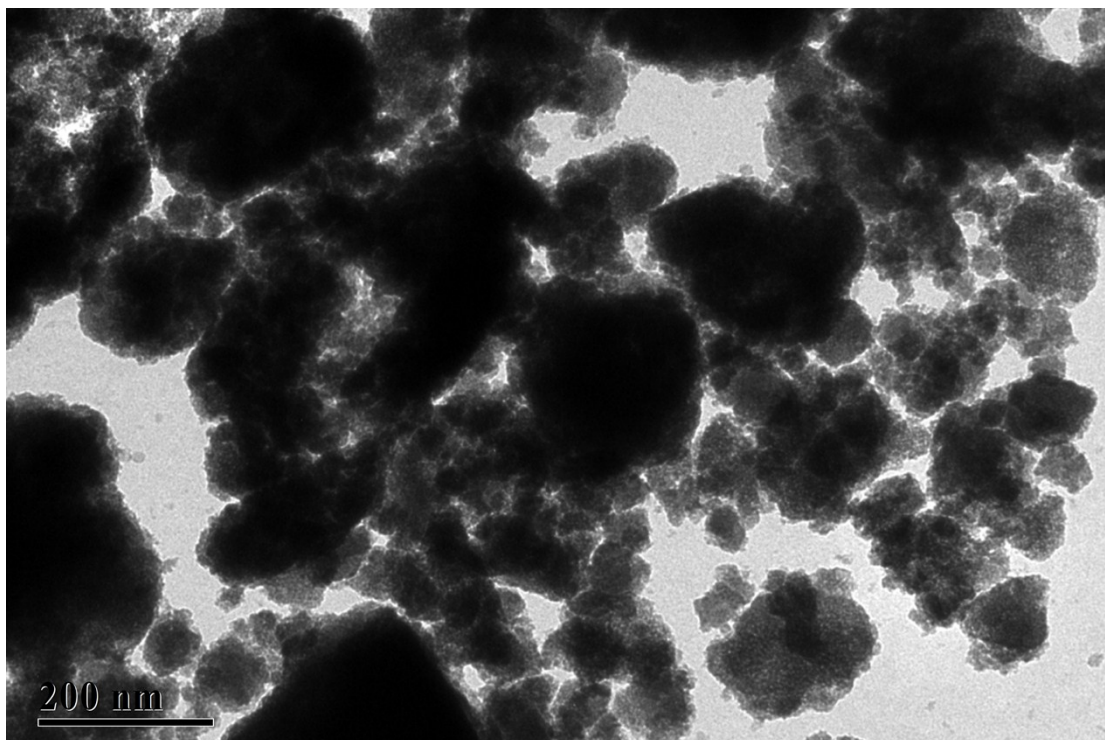


Fig S7 STEM-EDX images of Mo₁Sn₃

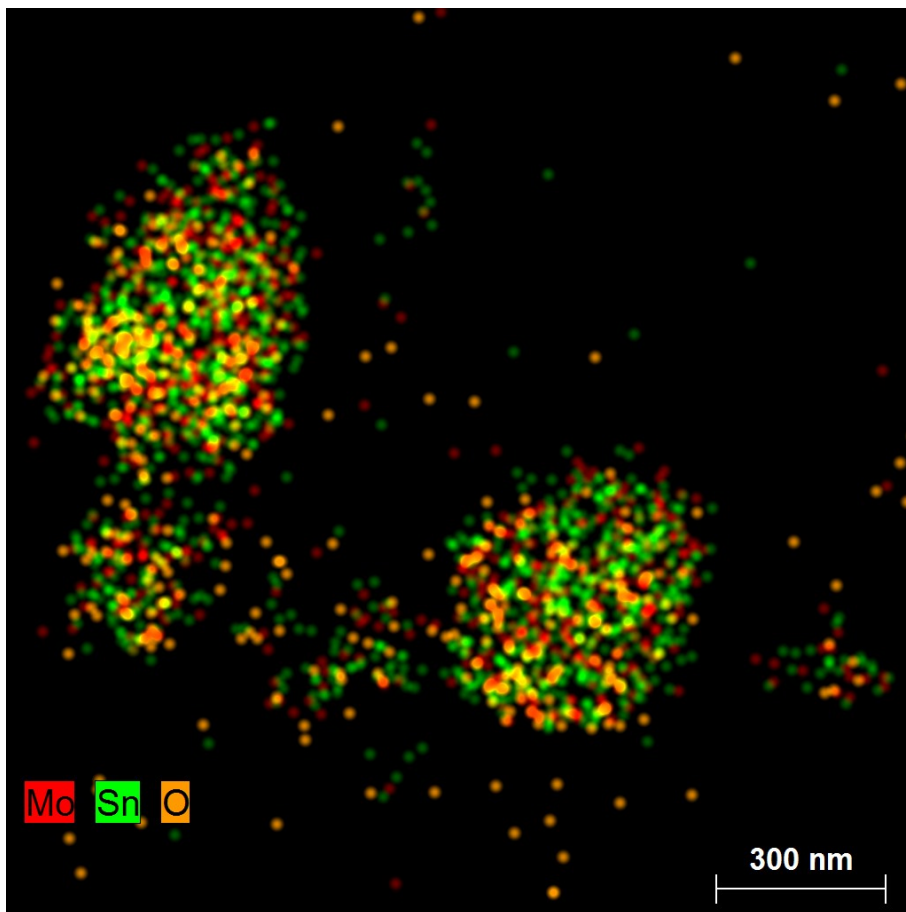
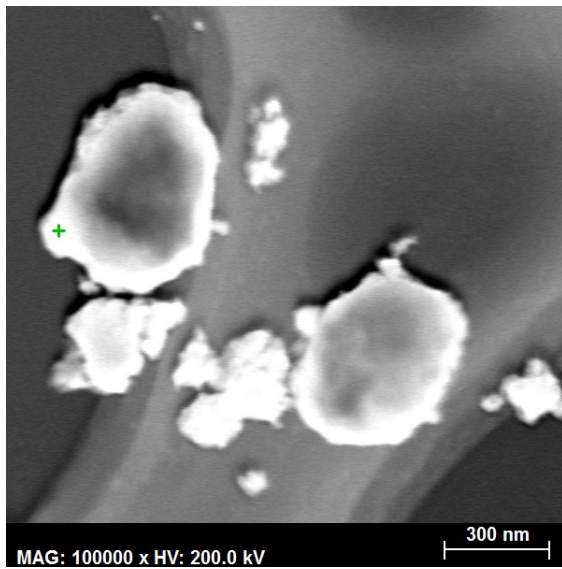


Table S3 The ratio of Mo to Sn of Mo₁Sn₃

Method	Mo/Sn atomic ratio
Theory value	0.33
EDX	0.34
XPS	0.38

Simplified kinetics analysis of the selective oxidation of dimethyl ether to methyl formate

over MoO₃-SnO₂

1. Elimination of mass transfer resistances.

Table S4 Gas-Solid Internal Diffusion Effects

Feed rate (mL/min)	16	24	32
conversion	17.4	17.0	18.3

Reaction conditions: DME/O₂=1:1, MoO₃/SnO₂=1:2, T_R=403 K, W/V=0.0625 g·min/mL, C₀=0.0223 mol/L.

Table S5 Gas-Solid External Diffusion Effects

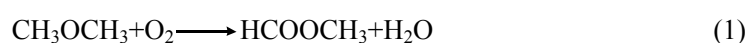
D _p (mm)	0.90-0.45	0.45-0.36	<0.36
conversion	17.4	17.6	18.5

Reaction conditions: DME/O₂=1:1, MoO₃/SnO₂=1:2, T_R=403 K, W=2 g, V=16 mL/min.

The effects of gas-solid external and internal diffusion are shown in Table S4 and Table S5. Under the same retention time, when the conversions of reactant did not change along with the feed rates, the gas-solid external diffusion mass transfer resistance could be neglected. Table S4 showed conversion of the same retention time with different feed rates. It was easy to come to the conclusion that the conversion of dimethyl ether did not change obviously and the gas-solid external diffusion could be neglected when the feed rate was faster than 16 mL/min. When conversions of the reactant did not change along with the diameter of the catalyst particle, the gas-solid internal diffusion mass transfer resistances could be neglected. Table S2 showed that the conversions of dimethyl ether did not change obviously when the diameter of the catalyst particle was not larger than 0.90 mm. As a result, the internal mass transfer resistances were negligible in this simplified model.

2. Intrinsic Kinetic Model.

The overall selective oxidation of dimethyl ether to methyl formate over MoO₃-SnO₂ can be represented as equation 1.



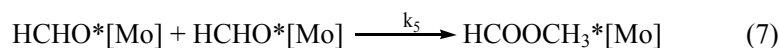
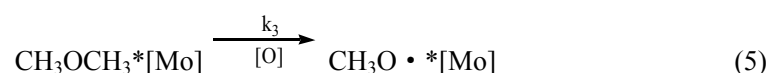
The intrinsic kinetic experiments were conducted in the absence of mass transfer resistances.

The reaction rate of selective oxidation of dimethyl ether to methyl formate is defined as

equation 2.

$$r_p = - \frac{dF_p}{dw} = - \frac{dx}{F_{p0} dW} = \text{Error!} \quad (2)$$

The possible reaction pathway in Scheme 1 was used to derive a rate equation for the selective oxidation reaction from dimethyl ether to methyl formate. According to this model, the reaction consisted of several steps: the adsorption of dimethyl ether and O₂, a series of surface reaction and desorption of methyl formate. Equation 1 describes the overall reaction of dimethyl ether and O₂ to form methyl formate. The elemental steps of the overall reaction are assumed in equations 3-8. At first, dimethyl ether was adsorbed on the surface of molybdenum oxide. O₂ was also adsorbed on the surface of the catalyst. Then dimethyl ether was dissociated and activated intermediate CH₃O • * [Mo] was formed with the assistance of the activated [O] species. Next CH₃O • * [Mo] reacted with [O] to produce HCHO* [Mo]. Finally, methyl formate was formed and desorbed from the surface of the catalyst.



It was assumed that the equation 6 was the rate-determining step, equation 3 and 8 were assumed to be fast reaction and be equilibrium states, CH₃O • * [Mo] was assumed to be activated intermediates, and the concentration of [O] was assumed to be constant, therefore, equations 9-11 were obtained.

$$r_p = k_4[\text{CH}_3\text{O} \cdot ^*[\text{Mo}]][\text{O}] \quad (9)$$

$$\frac{d[\text{CH}_3\text{O} \cdot ^*[\text{Mo}]]}{dt} = k_3[\text{CH}_3\text{OCH}_3^*[\text{Mo}]] - k_4[\text{CH}_3\text{O} \cdot ^*[\text{Mo}]][\text{O}] = 0 \quad (10)$$

$$\frac{k_1}{k_{-1}} \frac{[\text{CH}_3\text{OCH}_3^*[\text{Mo}]]}{[\text{CH}_3\text{OCH}_3]} = 1 \quad (11)$$

Finally, equation 12 was derived to be the rate equation of the overall reaction after a reasonable mathematical procedure. Combine equation 2 and equation 12, and use the initial condition (x₀=0, W₀=0), equation 13 is obtained.

$$r_p = \frac{k_1 k_3}{k_2 - 1} [\text{CH}_3\text{OCH}_3] = k C_0 [\text{CH}_3\text{OCH}_3] = k C_0 (1-x) \quad (12)$$

$$-\ln(1-x) = k C_0 \frac{W}{F P_0} \quad (13)$$

Table S6 Intrinsic Kinetic Data

W(g)	2	3	4
x	0.174	0.215	0.367
W/F _{P0} (× 10 ³ , min g mol ⁻¹)	5.6	8.4	11.2
-ln(1-x)	0.191	0.242	0.457

Reaction conditions: DME/O₂=1:1, MoO₃/SnO₂=1:2, T_R=403 K, C₀=0.0223 mol/L, V =16 mL/min.

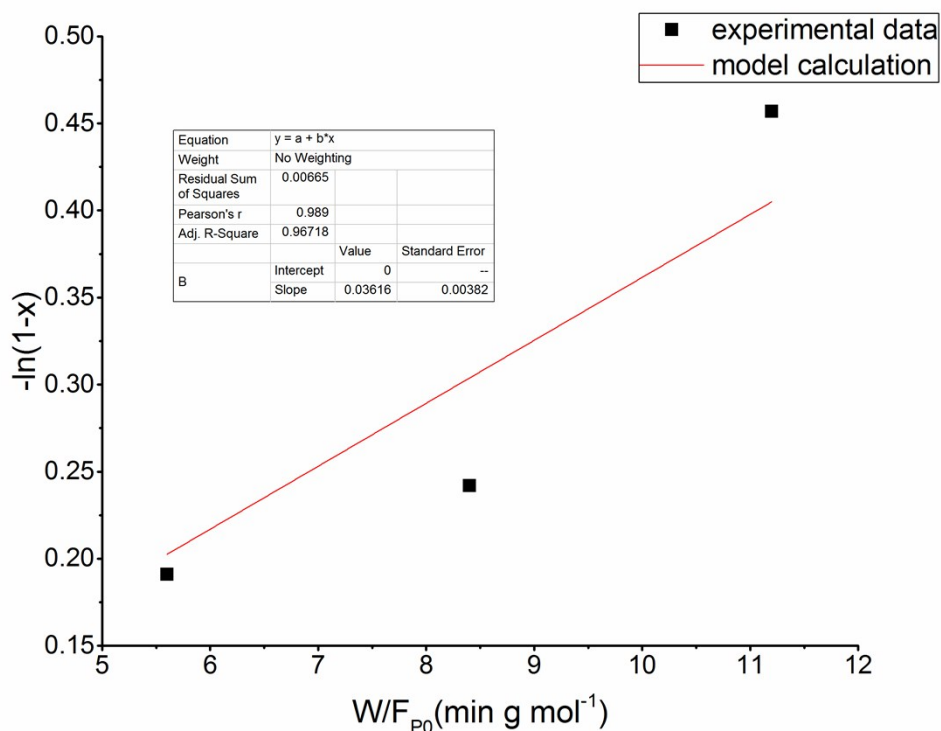


Fig. S8 Experimental data and model calculation of kinetics

(DME/O₂=1:1, MoO₃/SnO₂=1:2, T_R=403 K, C₀=0.0223 mol/L, V =16 mL/min).

Fig. S8 shows experimental data and model calculation of kinetics of Mo1Sn2 at 403 K. Model parameters of temperature of 393 K were also regressed, and both results are shown in Table S7. Similarly, model parameters of Mo1Sn1 were also regressed and the results are shown in Table S7.

Table S7 Regression of Model Parameters over Mo1Sn2 under Different Temperature.

T (K)	k (L g ⁻¹ min ⁻¹)
393	0.00023
403	0.00058

Reaction conditions: DME/O₂=1:1, MoO₃/SnO₂=1:2, C₀=0.0223 mol/L, V =16 mL/min.

Table S8 Regression of Model Parameters over Mo1Sn1 under Different Temperature.

T (K)	k (L g ⁻¹ min ⁻¹)
393	0.00007
403	0.00021

Reaction conditions: DME/O₂=1:1, MoO₃/SnO₂=1:1, C₀=0.0223 mol/L, V =16 mL/min.

The Arrhenius Law was used to analyze the kinetic data in the Table S7. The activation energy was estimated to be 120.7 kJ/mol over Mo1Sn2. Similarly, model parameters of Mo1Sn1 were regressed, and the activation energy was estimated to be 144.6 kJ/mol over Mo1Sn1.

$$k = Ae^{-E_a/RT} \quad (14)$$

$$\ln k = \ln A + \left(-\frac{E_a}{R}\right)\frac{1}{T} \quad (15)$$

Using the results of the simplified kinetics model analysis, it was easy to come to the conclusion that the formation rates of methyl formate over Mo1Sn2 was faster than that of methyl formate over Mo1Sn1, and activation energies of methyl formate over Mo1Sn2 was lower than that of methyl formate over Mo1Sn1. Based on the XRD and Raman results, the relative quantity of MoO_x domains over Mo1Sn2 was obviously more than that over Mo1Sn1, which possibly had a positive connection with the faster formation rates and lower activation energies of methyl formate over Mo1Sn2.