# **Electronic Supplementary Information**

#### 1. Experimental details

**1.1 Materials Preparation.** α-MoO<sub>3</sub> nanobelts 8 nm thick, 60 nm wide, and 0.7-7.5 µm long were hydrothermally synthesized, as we previously reported.<sup>1</sup> Molybdenum carbide nanobelts were prepared by reducing and carburizing the α-MoO<sub>3</sub> precursor with gas mixtures of CH<sub>4</sub> or n-C<sub>4</sub>H<sub>10</sub> and hydrogen at 700-850 °C in a quartz tubular reactor. In a typical procedure, 100 mg α-MoO<sub>3</sub> nanobelts were heated from room temperature to 200 °C at a rate of 5 °C/min under N<sub>2</sub> flow (30 mL/min) and maintained at this temperature for 1 h. Then, the sample was heated to 850 °C at a rate of 1 °C/min under the flow of a 20% CH<sub>4</sub>/H<sub>2</sub> mixture (50 ml/min) and maintained at this temperature for 2 nanobelts. Synthesis of α-MoC<sub>1-x</sub> nanobelts was conducted with the same procedure, but a 5% n-C<sub>4</sub>H<sub>10</sub>/H<sub>2</sub> gas mixture was used as the reducing and carburizing agent and the temperature was kept at 700 °C for 4 h. After being cooled down to room temperature, the samples were passivated in a flow of 1% O<sub>2</sub>/N<sub>2</sub> (30 ml/min) for 4 h prior to exposure to air.

**1.2 Characterization.** The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max2500V/PC powder diffractometer with a CuK $\alpha$  radiation source operated at 40 kV and 100 mA. The N<sub>2</sub> adsorption-desorption isotherms were measured on a Nova 4200e instrument at -196 °C. Before the measurement, the sample was degassed at 300°C for 6 h under vacuum. The specific surface area was calculated by a multipoint Braunauer-Emmett-Teller method.

The transmission electron microscopy (TEM) images were taken on a Philips Tecnai G<sup>2</sup> Spirit microscope (120 kV). The high-resolution TEM (HRTEM) images were recorded on a FEI TecnaiG<sup>2</sup> F30 Spirit microscope (300 kV). The specimen was prepared by ultrasonically dispersing the sample into ethanol, depositing droplets of the suspensions onto a carbon-enhanced copper grid, and drying them in air. The field-emission scanning electron microscopy (FESEM) images were taken on a Philips Fei Quanta 200F instrument operated at 20 kV. The sample was placed on a conductive carbon tape adhered to an aluminum sample holder.

The X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB MK2 spectrometer using an Al K $\alpha$  ( $\lambda$ =1486.6 eV) radiation source operated with an accelerating voltage of 12.5 kV. The passivated samples were pressed into thin discs and mounted on a sample rod

placed in the analysis chamber. Before the test, the samples were pretreated with hydrogen at 400 °C for 2 h to regenerate the molybdenum carbides. The spectra of Mo 3d, C 1s, and O 1s were recorded. The charging effect was corrected by adjusting the binding energy of C 1s to 284.5 eV. To determine the distribution of molybdenum species at different oxidation states, the spectra of Mo 3d were deconvoluted using a XPSPEAK program with a combined Gaussian– Lorentzian function. The bind energies of Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  were separated by 3.2 eV with a peak area ratio of 3/2. The binding energies of Mo  $3d_{5/2}$  were set as follows: Mo<sup>0</sup> (227.6 eV), Mo<sup>2+</sup> (228.3 eV), Mo<sup>4+</sup> (229.6 eV), Mo<sup>5+</sup> (231.4 eV) and Mo<sup>6+</sup> (232.7 eV).<sup>2</sup>

**1.3 Catalytic test.** Dehydrogenation of benzyl alcohol was conducted in a 10 ml two-neck flask that was connected with a reflux condenser under nitrogen atmosphere. The fresh molybdenum carbides (60 mg) were liquid-sealed by dimethyl sulfoxide under nitrogen flow and quickly transferred into the flask. 2 mmol benzyl alcohol ( $C_6H_5CH_2OH$ ) was then added to the flask containing 4 ml dimethyl sulfoxide and the catalyst. The reaction system was heated to 120 °C and maintained at this temperature for 8 h under stirring. After reaction, the product was collected by centrifugation and analyzed by an off-line Agilent GC-7890 gas chromatography equipped with a HP-5 capillary column (30 m× 0.32 mm × 0.25 µm). A blank test without the use of catalyst did not produce any benzaldehyde, confirming the heterogeneous catalysis nature of the reaction.





Fig. S1 XRD patterns (a) and SEM images (b-d) of the samples obtained at 1 h (b), 4 h (c), and 6 h (d) during the reduction and carburization of the belt-shaped  $\alpha$ -MoO<sub>3</sub> precursor with a 20% CH<sub>4</sub>/H<sub>2</sub> mixture at 850 °C.

### 3. Temperature effect on the synthesis of the molybdenum carbide nanobelts

The temperature of carburization affected the formation of the  $\beta$ -Mo<sub>2</sub>C nanobelts. As shown in Fig. S2, when the carburization of the  $\alpha$ -MoO<sub>3</sub> nanobelts with a 20% CH<sub>4</sub>/H<sub>2</sub> gas mixture was performed at 650 °C for 4 h, the product showed diffraction lines of both MoO<sub>2</sub> (JCPDS#65-5787) and  $\beta$ -Mo<sub>2</sub>C (JCPDS#35-0787). This result implies that MoO<sub>2</sub>-like intermediate was formed during the transformation from  $\alpha$ -MoO<sub>3</sub> to  $\beta$ -Mo<sub>2</sub>C. At 750 °C for 4 h, the diffraction intensity of MoO<sub>2</sub> decreased remarkably whereas that of  $\beta$ -Mo<sub>2</sub>C enhanced significantly, suggesting the increasing carburization. As the carburization was conducted at 850 °C for 4 h, only diffraction lines of  $\beta$ -Mo<sub>2</sub>C were observed, indicating the complete conversion of  $\alpha$ -MoO<sub>3</sub> to  $\beta$ -Mo<sub>2</sub>C. SEM images of the samples obtained at different temperatures verified the nanobelt shape with the width of about 60 nm and the length of 0.5-7 µm.



Fig. S2 XRD patterns (a) and SEM/TEM images (b-e) of the samples obtained during the reduction and carburization of the belt-shaped  $\alpha$ -MoO<sub>3</sub> precursor with a 20% CH<sub>4</sub>/H<sub>2</sub> mixture at 650 °C (b), 750 °C (c), and 850 °C (d, e). The selected area electron diffraction (f) indicated the polycrystalline nature of the β-Mo<sub>2</sub>C nanobelts.

Similar to the situation of the  $\beta$ -Mo<sub>2</sub>C nanobelts, the temperature of carburization is also a crucial parameter in forming the  $\alpha$ -MoC<sub>1-x</sub> nanobelts. Reduction and carburization of the belt-shaped  $\alpha$ -MoO<sub>3</sub> precursor with the 5% n-C<sub>4</sub>H<sub>10</sub>/H<sub>2</sub> mixture at temperatures lower than 700 °C, for examples 550 or 600 °C, mainly produced MoO<sub>2</sub>-like compounds (Fig. S3).



Fig. S3 XRD patterns (a) and SEM/TEM images (b-e) of the products obtained during the reduction and carburization of the belt-shaped  $\alpha$ -MoO<sub>3</sub> precursor with a 5% n-C<sub>4</sub>H<sub>10</sub>/H<sub>2</sub> mixture at 550 °C (b), 600 °C (c), and 700 °C (d, e) for 4 h. The selected area electron diffraction (f) indicated the polycrystalline nature of the  $\alpha$ -MoC<sub>1-x</sub> nanobelts.

### 4. Synthesis of molybdenum carbide particles and catalytic tests

For comparison,  $\beta$ -Mo<sub>2</sub>C and  $\alpha$ -MoC<sub>1-x</sub> particles were synthesized by reducing and carburizing a commercial  $\alpha$ -MoO<sub>3</sub> precursor with a 20% CH<sub>4</sub>/H<sub>2</sub> mixture 850 °C for 4 h and a 5% n-C<sub>4</sub>H<sub>10</sub>/H<sub>2</sub> mixture at 700 °C for 4 h, respectively, as shown in Fig. S4. When being used to catalyze dehydrogenation of benzyl alcohol, the conversion of benzyl alcohol on the  $\beta$ -Mo<sub>2</sub>C particles was 12 % at 1 h, increased steadily with time, and approached 94 % at 8 h. On the  $\alpha$ -MoC<sub>1-x</sub> particles, the conversion of benzyl alcohol was 9% at 2 h and gradually increased to 86% at 12 h. As comparing with the reaction results on the molybdenum carbide nanobelts (Fig. 2), it is obvious that the belt-shaped molybdenum carbides are much more active for the dehydrogenation of

benzyl alcohol than the conversional molybdenum carbide particles, clearly demonstrating the size and shape effects.



Fig. S4 XRD patterns and SEM images of the  $\beta$ -Mo<sub>2</sub>C (a, b) and  $\alpha$ -MoC<sub>1-x</sub> (c, d) particles and their catalytic performance (e) in dehydrogenation of benzyl alcohol to benzaldehyde. Reaction conditions: 2 mmol benzyl alcohol, 4 ml dimethyl sulfoxide, 60 mg catalyst, 120 °C.

### 5. Distribution of molybdenum species on the carbide nanobelts

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	Distribution of Mo species (%)				
Sample	M0 <sup>6+</sup>	Mo <sup>5+</sup>	Mo <sup>4+</sup>	Mo <sup>2+</sup>	Mo <sup>0</sup>
$\Box\beta$ -Mo <sub>2</sub> C	2.4	15.92	19.18	43.72	18.78
$\Box \alpha$ -MoC <sub>1-x</sub>	0.01	11.46	14.23	39.12	35.18

Table S1 Distribution of Mo species in the molybdenum carbide nanobelts.

## References

- 1. Z. C. Li, Y. Li, E. S. Zhan, N. Ta and W. J. Shen, J. Mater. Chem. A, 2013, 1, 15370.
- (a) M. J. Ledoux, C. P. Huu, J. Guille and H. Dunlop, J. Catal., 1992, 134, 383; (b) M. Nagai, Y. Goto, A. Irisawa and S. Omi, J. Catal., 2000, 191, 128.