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### A Ni-foam-structured MoNi<sub>4</sub> $-MoO_x$ nanocomposite catalyst for hydrogenation of dimethyl oxalate to ethanol<sup>†</sup>

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We report a Ni-foam-structured  $MoNi_4-MoO_x$  nanocomposite catalyst derived from NiMoO<sub>4</sub> spinel *in situ* grown on Ni-foam, which is highly active, selective (>93%) and stable for the gas-phase hydrogenation of dimethyl oxalate to ethanol. Such a reaction proceeds mainly through ethylene glycol formation, whereas a pathway through methyl acetate (MA) formation also occurs. Catalyst activity and selectivity are primarily governed by the MoNi<sub>4</sub> nanoalloy but can be further improved by an MoO<sub>x</sub> modifier, due to the synergistic MoNi<sub>4</sub>-MoO<sub>x</sub> interaction that markedly promotes the MA hydrogenation to EtOH.

Ethanol (EtOH), a versatile commodity feedstock, has been extensively used as a solvent, chemical intermediate, disinfectant and so on.<sup>1</sup> In particular, EtOH is also considered as a promising clean fuel blending component because it can reduce CO, NO<sub>x</sub>, and SO<sub>x</sub> emission and prevent groundwater pollution caused by methyl tert-butyl ether additives.<sup>2</sup> Conventionally, EtOH is dominantly produced from the fermentation of edible agricultural carbohydrates and the hydration of oil-derived ethylene.<sup>3</sup> However, the fermentation process and hydration of ethylene are still facing great challenges owing to the lack of food supplies and the worldwide oil crisis, respectively.1c,2b Thus, it is necessary to explore new approaches to supplement the existing technologies and meet the increasing demand of EtOH. At present, an indirect EtOH synthesis from syngas that can be cheaply produced from diverse resources including natural gas, coal, inedible biomass and even organic wastes has drawn much attention.1c,4 Hydrogenation of syngas-derived acetate acid (HOAc, by carboxylation of MeOH) to EtOH has been extensively studied in the last decade.<sup>4</sup> The economy of this route is strongly dependent on the HOAc market; on the other hand, it suffers more severely from the corrosion problem as well as the lack of a high-performance catalyst.<sup>4</sup> EtOH can be synthesized through the MOR-zeolite-catalyzed carboxylation of DME to methyl acetate (MA) and the subsequent hydrogenation of MA to EtOH. Though the industrial demonstration of this process has been realized in China, a durable zeolite-based catalyst for the DME carboxylation still faces challenges.<sup>5</sup> In principle, EtOH can also be synthesized from syngas through a route named DMO-to-EtOH, consisting of CO coupling to obtain dimethyl oxalate (DMO) and subsequent DMO hydrogenation to form EtOH.<sup>6</sup> Notably, the first step was successfully commercialized in 2010.<sup>7</sup> Hence, the exploration of catalysts with high catalytic activity for DMO hydrogenation to EtOH is crucial for the industrial-scale DMO-to-EtOH process from syngas.

Currently, Cu-based catalysts are considered to be the most active materials for vapor-phase hydrogenation of DMO since Cu species can efficiently hydrogenate carbon-oxygen bonds but are relatively inactive for carbon–carbon bond hydrogenation.<sup>6,8</sup> For instance, the traditional Cu/SiO<sub>2</sub> catalyst<sup>8</sup> obtained by an ammonia evaporation hydrothermal method is capable of completely converting DMO with 83% EtOH selectivity at 280 °C and the Ce-Cu/SiO<sub>2</sub> catalyst<sup>9</sup> prepared by a urea-assisted gelation method offers 92% EtOH yield at 280 °C. Despite the above outstanding results over Cu-based catalysts, there are still many technical problems to be addressed in the practical applications. Most of all, in order to facilitate EtOH formation, the reaction is normally carried out at a high temperature (above 270 °C), which is quite a bit higher than the Hüttig temperature of Cu (134 °C), resulting in severe Cu agglomeration.<sup>1c</sup> Moreover, such a high temperature is favorable to form undesired C3-C4 diols (e.g., propanediol and butanediol) and ethers (e.g., 2-methoxyethanol and 2-ethoxyethanol) over the Cu/SiO2 catalysts, which severely deteriorate the selectivity of EtOH.<sup>10</sup> Furthermore, the local overheating due to the exothermic DMO hydrogenation to EtOH ( $\Delta H = -145.9 \text{ kJ mol}^{-1}$ ) and poor thermal conductivity of the oxide support easily aggravates the above problem.<sup>11</sup> Therefore, it is highly desirable to design a novel catalyst with an excellent EtOH yield, and especially long-term stability and enhanced thermal conductivity.

Herein, we attempt to use a promising foam-structured MoNi<sub>4</sub>-MoO<sub>x</sub> nanocomposite catalyst derived from NiMoO<sub>4</sub>

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**Fig. 1** (A) Schematic illustration of the fabrication of the representative  $MoNi_4-MoO_x/Ni$ -foam-400 catalyst. XRD patterns (B) of the samples collected at different stages. TEM image (C), XPS spectra (D), Raman spectrum (E), HAADF-STEM images (F and G), optical photograph (insert H), and SEM images (H and I) of the representative  $MoNi_4-MoO_x/Ni$ -foam-400 catalyst. (J) DMO conversion and EtOH selectivity against time on stream over the  $MoNi_4-MoO_x/Ni$ -foam-400 catalyst. Reaction conditions: 230 °C, 2.5 MPa, WHSV<sub>DMO</sub> of 0.22 h<sup>-1</sup>, and  $n(H_2)/n(DMO)$  of 180.

spinel directly grown on a Ni-foam (8.0 mm diameter; 1.5 mm thick; 100 pores per inch (PPI)), aiming to achieve a unique combination of high catalytic performance with enhanced heat/ mass transfer for application in strongly exothermic reaction processes,<sup>12</sup> such as the DMO-to-EtOH process. Fig. 1A schematically illustrates the synthetic route of our representative MoNi<sub>4</sub>-MoO<sub>x</sub>/ Ni-foam-400 catalyst engineered from macro- to micro-scales. The NiMoO<sub>4</sub>·xH<sub>2</sub>O nanorod arrays were initially grown onto the Ni-foam strut surface via a facile hydrothermal process. The as-obtained NiMoO<sub>4</sub> xH<sub>2</sub>O/Ni-foam could be transformed, for example, into the representative MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-400 catalyst after calcining at 350 °C (dehydrated to form NiMoO<sub>4</sub>/ Ni-foam) in air and reduction at 400 °C in H<sub>2</sub> (XRD, Fig. 1B). Notably, after reduction treatment, only one weak XRD peak is detected at  $2\theta$  of  $43.5^{\circ}$ , assigned to the (121) plane of MoNi<sub>4</sub> (JCPDS No. 65-5480) except Ni from the Ni-foam substrate (JCPDS No. 65-2865). The high-resolution transmission electron microscopy (HRTEM) image shows well-resolved lattice fringes with interplanar distances of 0.208 nm and 0.181 nm, which can be indexed to the MoNi<sub>4</sub> (121) plane and (310) plane, respectively (Fig. 1C).<sup>13</sup> Fig. 1D displays the X-ray photoelectron spectroscopy (XPS) spectra in the Mo3d region, which could be deconvoluted via a Gaussian peak fitting method into eight peaks. The peaks observed at 228.2 and 231.5 eV are assigned to Mo<sup>0</sup> species in MoNi<sub>4</sub>, and the peaks detected at 229.2/232.5, 230.5/233.8 and 232.1/235.4 eV are attributed to  $Mo^{4+}$ ,  $Mo^{5+}$  and  $Mo^{6+}$  in  $MoO_x$ , respectively.<sup>13,14</sup> The Raman spectrum shows five peaks at 147,

187, 288, 340 and 369 cm<sup>-1</sup>, which are well assigned to  $MoO_x$ (Fig. 1E).<sup>15</sup> The high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mapping in Fig. 1F and G visually illustrates the Mo-rich but Ni-barren locals (marked by dashed circles: orange for Ni, blue for Mo). The above results solidly evidence that the MoNi<sub>4</sub>-MoO<sub>x</sub> nanocomposite structure is derived from the NiMoO4 compounds. It is easy to understand that there is not enough Ni in the NiMoO4 for fully consuming the Mo atoms by forming an MoNi<sub>4</sub> alloy. As a result, during the reduction treatment, the Mo atoms in the NiMoO4 except the part alloying with Ni atoms extricated themselves to form MoO<sub>x</sub> segments around the MoNi<sub>4</sub> nanoalloys. Our representative MoNi<sub>4</sub>-MoO<sub>y</sub>/Ni-foam-400 catalyst is characteristic of the entirely open three-dimensional network structure (90 vol% voidage; lowmagnitude SEM image in Fig. 1H). Moreover, the flexibility of such a Ni-foam-structured catalyst permits the tailoring of its geometry on demand, for example, a circular chip (8 mm diameter by 1.5 mm thick; the optical photograph (insert) in Fig. 1H). The high-magnitude SEM image in Fig. 1I shows that the MoNi<sub>4</sub>-MoO<sub>x</sub> catalytic component mounted on the Ni-foam strut exhibits a nanorod (0.3 µm diameter) array morphology. As a result, the specific surface area (SSA) is increased from  $0.3 \text{ m}^2 \text{ g}^{-1}$  of the pure Ni-foam substrate to 39  $m^2 g^{-1}$  of the as-obtained catalyst. We are confident that the nanorod is MoNi<sub>4</sub> alloy, which is consistent with the XRD phase of only MoNi<sub>4</sub> (except Ni phase of Ni-foam; Fig. 1B). In addition, the  $MoO_r$  in the  $MoNi_4$ -MoO<sub>r</sub> is believed to be ultra-highly dispersed on the MoNi<sub>4</sub> nanorods, because of the fact of no MoO<sub>x</sub> diffraction (Fig. 1B) but a MoO<sub>x</sub>-enriched surface (Fig. 1D). Our foam-structured catalyst shows pleasing mechanical robustness: the nanorod arrays adhere firmly to the Ni-foam strut, evidenced by a low weight loss of 5.8 wt% (including the mass of Ni-foam, Fig. S1, ESI<sup>+</sup>) after an ultrasonic treatment in methanol even for 5 h. Undoubtedly, our approach works effectively and efficiently for engineering MoNi<sub>4</sub>-MoO<sub>x</sub> nanocomposites at a "nano-mico-macro" triple-scale level in one-step. Most importantly, the representative MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-400 catalyst is highly active, selective and stable in the DMO-to-EtOH process, being capable of fully converting DMO at a high EtOH selectivity of about 93%, and particularly, is stable for at least 220 h without any sign of deactivation at 230 °C and 2.5 MPa, using a H<sub>2</sub>/DMO molar ratio of 180 and a weight hourly space velocity (WHSV<sub>DMO</sub>) of 0.22  $h^{-1}$  (Fig. 1J and Table S1 for comparison with literature results, ESI<sup>†</sup>).

In general, the DMO-to-EtOH process comprises several sequential reactions, including DMO hydrogenation to methyl glycolate (MG) and MG hydrogenation to ethylene glycol (EG) followed by EG hydrogenation to EtOH as well as MG hydrogenation to methyl acetate (MA) followed by MA hydrogenation to EtOH (Fig. 2A).<sup>6c,9</sup> To determine which pathway the reaction dominantly follows over our MoNi<sub>4</sub>–MoO<sub>x</sub>/Ni-foam-400 catalyst, the reaction rates and apparent activation energies ( $E_a$ ) of the MG-to-EG, EG-to-EtOH, MG-to-MA, and MA-to-EtOH processes were calculated, with the results shown in Fig. 2. As shown in Fig. 2B, the MG-to-EG reaction rate is only slightly higher than that of the MG-to-MA process at each temperature, indicating that the above two reactions almost keep pace with each other.



**Fig. 2** (A) The reaction pathways for the DMO-to-EtOH process. The reaction rates for (B) the MG-to-EG and MG-to-MA and (C) the EG-to-EtOH and MA-to-EtOH processes over the MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-400 catalyst. (D) Activation energies of this catalyst for reaction steps involved in the DMO-to-EtOH process.

However, the reaction rate of the EG-to-EtOH process is quite a bit higher than that of the MA-to-EtOH process in the whole temperature range studied (Fig. 2C), revealing that hydrogenation of EG to EtOH is easier than MA to EtOH. Furthermore, the  $E_a$  of the MG-to-EG process (40 kJ mol<sup>-1</sup>) is close to that for the MG-to-MA process (42 kJ mol<sup>-1</sup>), whereas the  $E_a$  of the EG-to-EtOH process is much lower than that for the MA-to-EtOH process (40 kJ mol<sup>-1</sup>  $\nu s$ . 63 kJ mol<sup>-1</sup>; Fig. 2D). Clearly, the formation of target EtOH is achieved through the hydrogenation of intermediate EG and MA, but the latter is more difficult to proceed over our catalyst.

We then attempted to explore the synergistic catalysis of the MoNi<sub>4</sub>-MoO<sub>x</sub> mounted on the Ni-foam, on the basis of the above elucidated reaction pathway. Fig. 1 clearly shows the coexistence of Ni, MoNi<sub>4</sub> and MoO<sub>x</sub> on our catalyst. Thus, to shed light on the role of each species, four model catalysts including Ni/SiO<sub>2</sub>, MoO<sub>x</sub>/SiO<sub>2</sub>, MoNi<sub>4</sub>/SiO<sub>2</sub> and MoNi<sub>4</sub>-MoO<sub>x</sub>/ SiO<sub>2</sub> (XRD in Fig. S2, ESI<sup>†</sup>) were prepared and examined in the DMO-to-EtOH reaction. The Ni/SiO2 and MoOx/SiO2 deliver low DMO conversion of less than 34% with trace EtOH formation under identical reaction conditions (Table S2, ESI<sup>†</sup>), indicating that neither Ni nor  $MoO_x$  is active and selective for the DMO-to-EtOH reaction. In contrast, the MoNi<sub>4</sub>/SiO<sub>2</sub> shows markedly improved activity and selectivity, being capable of almost fully converting DMO with EtOH/MA selectivity of 74.3%/19.8% (Table S2, ESI<sup> $\dagger$ </sup>). Most notably, once the MoO<sub>x</sub> is formed together with MoNi<sub>4</sub> formation on the SiO<sub>2</sub> support, the asobtained MoNi<sub>4</sub>-MoO<sub>x</sub>/SiO<sub>2</sub> becomes more selective and active in comparison with the MoNi<sub>4</sub>/SiO<sub>2</sub>, achieving a 99.9% DMO conversion with further improved EtOH selectivity of 84.4% while leading to a remarkable reduction of MA selectivity to 10.1%. Nevertheless, the MoNi<sub>4</sub>-MoO<sub>x</sub>/SiO<sub>2</sub> is still inferior to that of our preferred MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-400 catalyst (93% EtOH selectivity with full DMO conversion under identical reaction conditions). It is rational to infer from the above results that the MoNi<sub>4</sub> nanoalloy plays a key part in the DMO-to-EtOH process and the MoO<sub>x</sub> modification leads to a further improvement in EtOH selectivity. A possible explanation for such improvement in the EtOH selectivity is that the MA-to-EtOH reaction is markedly promoted by MoO<sub>x</sub> modification, evidenced by a significant reduction of MA selectivity.

To further verify the promotion effect of MoO<sub>r</sub> by synergistic interaction with MoNi<sub>4</sub>, a series of MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam catalysts, with tuned contents of MoNi<sub>4</sub> and MoO<sub>x</sub>, were prepared from the NiMoO<sub>4</sub>/Ni-foam precursors by varying the H<sub>2</sub>-reduction temperature from 350 to 500 °C. Notably, all catalysts present similar SEM surface morphology (Fig. S3, ESI<sup>†</sup>). The MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-350 catalyst (*i.e.*, reduced at 350 °C) possesses the highest specific surface area (SSA) of 92 m<sup>2</sup> g<sup>-1</sup>, whereas the SSAs of the other catalysts reduced at 400 °C, 450 °C and 500 °C are almost identical (38–42 m<sup>2</sup> g<sup>-1</sup>; Table S3, ESI<sup> $\dagger$ </sup>). Moreover, as shown in Fig. 3A (deduced from deconvoluted XPS spectra in Fig. S4, ESI<sup>†</sup>), the MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-350 catalyst possesses the highest surface  $MoO_r$  content but an extremely low  $Mo^0$ content of 1.8 at%, indicating that the reduction temperature of 350 °C is too low to sufficiently reduce NiMoO<sub>4</sub> spinel to form an MoNi<sub>4</sub> alloy, which is consistent with the observation of a clear XRD peak of NiMoO<sub>4</sub> on this sample (Fig. S4C, ESI<sup>†</sup>). Not surprisingly, this catalyst delivers a very low DMO conversion of 19.6% with an EtOH selectivity of only 3.1% (Fig. 3B). In contrast, when increasing the catalyst reduction temperature to 400 °C, the DMO conversion and EtOH selectivity are dramatically improved to 100% and 93%, in line with the full transformation of NiMoO<sub>4</sub> into MoNi<sub>4</sub>–MoO<sub>x</sub> (Fig. 3 and XRD in Fig. S4C, ESI<sup>†</sup>). In this case, Ni in the NiMoO<sub>4</sub> is fully transformed into MoNi<sub>4</sub> alloy, confirmed by the Mo<sup>0</sup>/Ni<sup>0</sup> atom ratio of 0.26 (close to 1/4 for the MoNi<sub>4</sub>; Table S4, ESI<sup> $\dagger$ </sup>) and a Mo<sup>0</sup>/Mo<sup>n+</sup> atom ratio of 0.30 (close to 1/3, one Mo alloyed with four Ni atoms to form one MoNi<sub>4</sub> and release three  $Mo^{n+}$  during NiMoO<sub>4</sub> reduction; Fig. 3A and Table S4, ESI<sup>+</sup>). Interestingly, by further increasing the catalyst reduction temperature to 500 °C, the EtOH selectivity is sharply decreased to 77.1% and the MA selectivity is reversely increased to 21.3%, whereas the full conversion of DMO is retained (Fig. 3B). On such as-obtained



**Fig. 3** (A) Surface atom fraction occupied by MoO<sub>x</sub> and Mo<sup>0</sup> in total surface Mo atoms for the Ni-foam-structured MoNi<sub>4</sub>–MoO<sub>x</sub> catalysts with varied H<sub>2</sub>-reduction temperatures, determined by XPS. (B) Conversion and selectivity for the DMO-to-EtOH reaction against the catalyst reduction temperature. Reaction conditions: 2.5 MPa, WHSV<sub>DMO</sub> of 0.22 h<sup>-1</sup>,  $n(H_2)/n(DMO)$  of 180, 230 °C.

Table 1 Activation energies of the  $MoNi_4-MoO_x/Ni$ -foam catalysts for the reaction steps involved in the DMO-to-EtOH process against the catalyst reduction temperature

|                      | $E_{\rm a}$ (kJ mol <sup>-1</sup> ) |       |         |       |         |
|----------------------|-------------------------------------|-------|---------|-------|---------|
| Reduction temp. (°C) | DMO-MG                              | MG-EG | EG-EtOH | MG-MA | MA-EtOH |
| 400                  | 38                                  | 41    | 40      | 43    | 63      |
| 450                  | 38                                  | 42    | 43      | 45    | 75      |
| 500                  | 39                                  | 41    | 43      | 46    | 89      |

MoNi<sub>4</sub>-MoO<sub>x</sub>/Ni-foam-500, as shown in Fig. 3A, the surface Mo<sup>0</sup> content (in total surface Mo atoms) is increased to 42 at%, much higher than the theoretical value of 25 at% (according to one MoNi<sub>4</sub> formed from one NiMoO<sub>4</sub>). This observation indicates that the catalyst is over-reduced at 500 °C, *i.e.*, some MoO<sub>x</sub> is reduced to free Mo<sup>0</sup> (no more Ni for alloying) thereby leading to a decline of the surface MoO<sub>x</sub> content to 58 at% (Fig. 3A). On the basis of the above results, we are thus confident that the catalyst activity and selectivity are primarily governed by the MoNi<sub>4</sub> nanoalloy but the selectivity can be further improved by an MoO<sub>x</sub> modifier with suitable amount.

However, it is still not clear whether the  $MoO_x$ -related EtOH selectivity improvement is owing to the MG-to-MA reaction being inhibited or the MA-to-EtOH being promoted. To seek the answer, the apparent activation energies of the catalysts reduced at 450 and 500 °C were also calculated for all reaction steps involved in EtOH formation (including MG-to-EG, EG-to-EtOH, MG-to-MA, and MA-to-EtOH), with the results shown in Table 1 and Fig. S5 (ESI<sup> $\dagger$ </sup>). As we can see, the  $E_a$  for only the MA-to-EtOH reaction step is strongly dependent on the catalyst reduction temperature, with an ordered sequence of 89 kJ mol<sup>-1</sup>  $(500 \ ^{\circ}\text{C}) > 75 \text{ kJ mol}^{-1} (450 \ ^{\circ}\text{C}) > 63 \text{ kJ mol}^{-1} (400 \ ^{\circ}\text{C})$ . In nature, this order links to the MoO<sub>x</sub> content in the MoNi<sub>4</sub>-MoO<sub>x</sub> mounted on the Ni-foam: the higher the  $MoO_x$  content, the lower the  $E_a$ for the MA-to-EtOH reaction is. In addition, the reaction rate for each reaction step involved in the DMO-to-EtOH process was measured at 210 °C using the model catalysts of MoNi<sub>4</sub>/SiO<sub>2</sub> and MoNi<sub>4</sub>-MoO<sub>x</sub>/SiO<sub>2</sub>, with the results as shown in Table S5 (ESI<sup>†</sup>). As expected, both of them achieved a similar reaction rate for each reaction step of DMO-to-MG, MG-to-EG, EG-to-EtOH and MG-to-MA; however, for the step of MA-to-EtOH, the MoNi<sub>4</sub>- $MoO_x/SiO_2$  catalyst achieves a reaction rate of 0.55 mmol g<sup>-1</sup> h<sup>-1</sup> almost 2 times as high as that (0.28 mmol  $g^{-1} h^{-1}$ ) of the MoO<sub>x</sub>-free MoNi<sub>4</sub>/SiO<sub>2</sub> catalyst. Such similarity observed on both model catalysts further confirms the conclusion that the MoO<sub>x</sub> modification makes the catalyst much more active for the MA-to-EtOH reaction step without impact on other reaction steps.

In summary, a Ni-foam-structured  $MoNi_4-MoO_x$  nanocomposite catalyst derived from NiMoO<sub>4</sub>/Ni-foam, with high thermal conductivity and high permeability, is developed for the strongly exothermic DMO-to-EtOH reaction. The preferred catalyst is capable of fully converting DMO into EtOH with a high selectivity of 93%, and particularly, is stable for at least 220 h. The MoNi<sub>4</sub> nanoalloy primarily governs the activity and selectivity while the MoO<sub>x</sub> modifier works synergistically with  $\rm MoNi_4$  to further improve the EtOH selectivity by speeding up the MA-to-EtOH reaction step.

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#### Conflicts of interest

There are no conflicts to declare.

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