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Tuning the adsorption energy of methanol molecules along Ni–Ndoped carbon phase boundaries via the Mott-Schottky effect for highly efficient dehydrogenation of gas-phase methanol

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Abstract: Engineering the adsorption of molecules on active sites is an integral and challenging part for the design of highly efficient transition-metal-based catalysts for methanol dehydrogenation. Here we report a Mott-Schottky catalyst composed of Ni nanoparticles and tailorable nitrogen-doped carbon-foam (Ni/NCF) and thus tunable adsorption energy for highly efficient and selective dehydrogenation of gas-phase methanol to hydrogen and CO even under relatively high weight hourly space velocities (WHSV). Both theoretical and experimental results reveal the key role of the rectifying contact at the Ni/NCF boundaries in tailoring the electron density of Ni species and enhancing the absorption energies of methanol molecules, which leads to a remarkably high turnover frequency (TOF) value (356 mol methanol mol⁻¹ Ni h⁻¹ at 350 °C), 10-fold outpacing the bench-marked transition-metal catalysts in the literature.

Activation of small molecules, such as methane, carbon dioxides and methanol, are important targets in modern catalysis science.^[1] Selective dehydrogenation of methanol to H₂ and CO by heterogenous catalysts is of great interests for both fundamental studies and practical applications.^[2] The noble-metal-based catalysts exhibit a high activity but suffer from a high price and a low tolerance to CO.^[3] The transition-metal-based catalysts promise great potentials as cheap and stable candidates for methanol dehydrogenation, although currently the relatively insufficient activity still restricts real-life applications.^[4] Despite great efforts,^[5] developing effective methods to significantly elevate the conversion and selectivity of the cheap transition metal based nanocatalysts for methanol dehydrogenation still remains a great challenge.

Considering the requirement of gas-solid heterogeneous systems when running high throughput gas reactions, we also paid our attention to the design of efficient nanostructured catalysts for the fast absorption of methanol molecules at high flow rates. Indeed, the adsorption energy for methanol molecules or the decomposed pathway intermediates on the surface of a metal catalyst has a volcano-shaped relationship with the final catalytic rate.^[6] As a result, an appropriately high adsorption energy of methanol is thus equally important to the lowered

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activation energy and also mass transfer barriers over specific metal centers for methanol dehydrogenation. It is thus reasonable for the more weakly binding transition metal species to enhance the adsorption of methanol molecules and intermediate species with lone-pair electrons ^[2a,7] onto their surface, a question which however is less touched at the moment as people are mostly not aware that this energy can be adjusted.

Herein, we described a direct way to modulate the adsorption of gas-phase methanol molecules on N-doped carbon-foamembedded Ni nanoparticles (Ni/NCF) for selective dehydrogenation into H₂ and CO via the Schottky effect with Ndoped carbon. We recently developed the concept and some series of Mott-Schottky catalysts composed of metallic nanocatalyst and semiconductive support with significantly promoted redox power due to the Mott-Schottky effect-induced band bending of the semiconductor part for specific reactions in the liquid phase.^[8] The Schottky barrier at the interface of metal and semiconductor can also be principally applied to modify the electron density of the Ni nanoparticle and thus the adsorption energy of methanol molecules on their surface. Indeed, textural and theoretical analysis in this work demonstrates the first example, as far as we know, of an on-demand tuning the absorption energy over a Mott-Schottky-type binary catalyst for high-throughput dehydrogenation of gas-phase methanol, resulting in a state-of-the-art turnover frequency among all reported Ni based catalysts in the literature.

The detailed synthetic process for the large-scale fabrication of the Ni/NCF catalyst is illustrated in Figure 1a and described in the experimental section, Table S1 and Figure S2-9 of the supporting information. The high-resolution TEM (HRTEM) image (Figure 1c and d) indicates a highly integrated nanostructure of a layered carbon-coated Ni nanoparticle (~21 nm, Figure S7-9). Further high-angle annular dark-field (HAADF) and the corresponding energy dispersive X-ray spectroscopy (EDX) investigations (Figure 1e and f) directly confirm the homogenous distribution of the Ni nanoparticles inside the carbon-nitrogen matrix. X-ray diffraction (XRD) patterns (Figure S10) corroborate the coexistence of graphitic carbon and nickel as the main components of the Ni/N_xCF samples.^[9] X-ray photoelectron spectrum (XPS) results (Figure S11 and S12) and the Raman spectrum (Figure S13) further reveal the presence of pyridinic and graphitic N,[8b,10] and the gradually increased nitrogen contents in the Ni/N_xCF samples (x refers to the molar ratio of N and C) from Ni/N_{0.03}CF via Ni/N_{0.06}CF to Ni/N_{0.09}CF.-The Ni K-edge of X-ray absorption near-edge structure (XANES) of the Ni/N_{0.09}CF sample (Figure S14) demonstrates the metallic nature of the embedded Ni species. The corresponding Fourier transform (FT) extended X-ray absorption fine structure (EXAFS) of Ni K-edge in R-space (Figure S14) strikingly exclude the formation of Ni-O, Ni-C and Ni-N bonds in the Ni/N $_{0.09}$ CF sample, given as an example. The Ni

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loadings remained to be ca. 19 wt% for all samples as demonstrated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis results (Figure S15), which can be lowered by reducing the weight of the nickel sheet at fixed amount of DCDA (Table S1 and Figure S16).



Figure 1. Fabrication and structure. (a) Solid-state synthesis of Ni/NCF from nickel sheet and dicyandiamide (DCDA). (b) Transmission electron microscopy (TEM), HRTEM (c, d), HAADF images and the corresponding EDX mapping results (e, f) of typical Ni/N_{0.09}CF sample.

We initially tested the catalytic performance of all catalysts used in this work in typical fixed-bed reactor under a medium and widely used WHSV value of 15 h⁻¹. Blank reactions without a catalyst or by using metal-free nitrogen-doped carbon catalyst could not give detectable conversions of methanol (Figure 2a and S17). The workable light-off temperature in the conversion curve was ~200 °C with 100% selectivity to CO (Figure 2 and S18) with the addition of Ni/NCF catalysts. Methane and dimethyl ether were the only two detectable carbonaceous byproducts at even higher temperatures. The Ni loading is with 19 wt% optimal to offer the highest conversion for methanol dehydrogenation (Figure S16 and S18) and was thus used as the best-in-class Ni loading for further characterizations and applications.

The temperature dependency of methanol conversion over the Ni/N_xCF catalysts (Figure 2a) directly quantifies the support effect on catalytic activity. With the same Ni loading (Figure S15) and mesoscale structures (Figure 1 and S7-9), the Ni/N_xCF catalysts enable gradually increasing conversions of methanol (Figure 2a) along with the elevated concentrations of N dopants in the supports, whilst the selectivity to CO was not disturbed too much (> 90%, Figure 2b). A notable effect of surface area on the final catalytic activity can be excluded along with the fact that the Ni/N_{0.09}CF with a lowest specific surface area (37.1 m² g⁻¹) exhibits the best catalytic performance amongst the Ni/N_xCF samples (Figure S19). The highest conversion rate and also the lowest slope of Arrhenius plot (210–250 °C, Figure 2c) supplied by the Ni/N_{0.09}CF sample suggests that Mott-Schottky-type catalyst with higher nitrogen content provide a preferred activity for methanol dehydrogenation.



Figure 2. Study of reaction conditions. Temperature-dependent methanol conversions (a) and selectivity (b) of Ni/N_xCF samples with a WHSV of 15 h⁻¹ and corresponding Arrhenius plots (c). Catalytic stability test of Ni/N_{0.09}CF sample including the evolution in both conversions (d) and selectivity (e). (f) Temperature-dependent methanol conversions by the Ni/N_{0.09}CF catalysts with varied WHSV.

The Mott–Schottky barrier formation also significantly improves the stability of the Ni based nanocatalysts, which is of pivotal importance for industrial applications. The long-term durability of Ni/N_{0.09}CF catalyst for methanol dehydrogenation for over 3 days (Figure 2d) was excellent, keeping the high conversions and a constant selectivity to CO (Figure 2e). More than 90% of activity was maintained for more than 24 h at 350 °C. Both structure and chemical composition of the used Ni/N_{0.09}CF catalysts were found to be structurally stable after the long-term durability test (Figure S20-23).

High throughput conversions of gas molecules in gas-solid heterogeneous systems is the key challenge for the extended

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application of potential catalysts in industry. The Ni/N_xCF based Mott-Schottky catalyst with modified electron affinity may principally enhance the pre-adsorption of methanol molecules even at high flow rate. Indeed, the best-in-class Ni/N_{0.09}CF catalyst can provide excellent to good conversions of methanol and high selectivity to CO and H₂ even at significantly elevated WHSV (Figure 2f and S24), rendering a considerable reaction rate of more than 424 mmol methanol g⁻¹ catalyst h⁻¹ at 300 °C and WHSV of 45 h⁻¹. Such a reaction rate for methanol dehydrogenation at a relatively low temperature is close to or even higher than those of classical noble-metal nanocatalysts (Table S2).



Figure 3. DFT calculation of a model unit of a Ni/N_xCF Mott-Schottky catalyst. (a) The calculated band structures of N_xCF supports along Γ -M-K- Γ . The models were built on the basis of experimental results. The energies are measured with respect to the Fermi level. (b) CDD stereograms (side view) of Ni/N_xCF after the introduction of metallic Ni clusters. Blue and red represent electron depletion and accumulation, respectively; color arrows are draw to guide the eye. (c) CDD stereograms after the adsorption of a CH₃OH molecule onto the Ni/N_xCF models. (d) The calculated adsorption energy of CH₃OH molecules adsorbed on the Ni/N_xCF catalysts. Insets of d: corresponding structures of the CH₃OH and the active centers.

Density functional theory (DFT) calculations were applied to quantify the Mott-Schottky effect in promoting the methanol dehydrogenation reaction, confirming the support effect to tune the adsorption energy of gas-phase methanol molecules on the surface of the catalysts. The band gap (Figure 3a and S25-26) of the carbon support is gradually enlarged by increasing the concentrations of nitrogen dopant,^[10d] especially the pyridinic nitrogen, resulting in a valence band edge close to the Fermi level and thus a *p*-type semiconductive structure.^[11] The electron deficient area of the loaded Ni nanoparticles and electron rich

area of the carbon support were also enlarged in the nitrogen-rich sample Ni/N_{0.09}CF as marked with the blue and red arrows respectively in the charge density difference (CDD) stereograms (Figure 3b and S27), demonstrating the formation of a rectifying Mott-Schottky heterojunction.^[8a]

Indeed, the electron-deficient Ni nanoparticles in Ni/N_xCF catalyst exhibit strong interaction with methanol molecule, which is believed to be the descriptive factor to enhance the possibility of the O-H bond scission on the surface of Ni nanoparticles and thus accelerate the methanol dehydrogenation reaction.^[2a,6b,7] As illustrated in the CDD stereograms (Figure 3c and S28), the methyl group is totally embedded in the electron-rich region. The increasing surface electron density (Figure 3c left) of the carbon support as nitrogen concentration increases, significantly attracted the -CH₃ group to the surface. The equilibrium distance between the carbon surface and the adjacent hydrogen of the methanol over the Ni/N_{0.09}CF catalyst is only 2.7 Å, further suggesting the even stronger interaction between the electron deficient methyl group and the electron rich region of carbon surface, which can be also expresses as a partial bonding of the hydride to be eliminated from the methyl group. Due to this secondary binding, the calculated adsorption energy of methanol on the surface of Ni/N_{0.09}CF is the most negtive value among all the models, with the C-H bond thereby weakened by at least 0.3 eV.



Figure 4. Schematic of Mott-Schottky contact (a). The measured work functions (Φ) via UPS analysis (b) and Ni 2p XPS spectra (c) of Ni/N_xCF catalysts. (d) The CO₂-TPD results of Ni/N_xCF samples and the acid-etched sample Ni/N_{0.09}CF-H⁺. The activation energies (e) and TOF values (f) for the methanol dehydrogenation over Ni/N_xCF catalysts.

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All the DFT calculation (Figure 3a-b and S29) and XPS results indicate that more electrons of metallic Ni nanoparticles were transferred to the nitrogen-doped carbon support (Figure 4a) of the Ni/N_{0.09}CF, which has a higher work function (Figure 4b and S30) and an even lower valance band position (Figure S31-S33) in the carbon support as demonstrated by the ultroviolet photoelectron spectroscopy (UPS) results.^[12] Typical XPS peaks of nickel gradually shift to a higher binding energy with the increase of nitrogen dopants (Figure 4c), whilst N 1s XPS peaks (Figure S34) shift to a lower binding energy values. The gradually enhanced electron enrichment of the carbon support, as directly reflected by their Lewis basicity, of the Ni/N_xCF samples with more nitrogen dopants could be also experimentally confirmed by the temperature-programmed desorption (TPD) analysis results (Figure 4d). A mild acid treatment of the Ni/N_{0.09}CF sample could not obviously change the nitrogen content (Figure S35) but significantly temporarily knocks-out its Lewis base sites (Figure 4d), rather supporting our picture of the source of the catalytic activity.

Most importantly, the strong interactions of methanol molecule with the electron-rich carbon support and the electron-deficient Ni principally facilitate substrate polarization and thus selective dehydrogenation process following the manner of the frustrated Lewis pairs in homogeneously catalytic systems. As expected, the activation energy of methanol molecules, estimated from Arrhenius plots, decreased gradually from Ni/N_{0.03}CF via Ni/N_{0.09}CF to Ni/N_{0.09}CF sample (Figure 4e). The best-in-class Ni/N_{0.09}CF Mott-Schottky catalyst provides a high TOF of 356 mol methanol mol⁻¹ Ni h⁻¹ at 350 °C for methanol dehydrogenation, far exceeding the values of the reported benchmark Ni-,^[4b,5e] Co-^[5a] or Cu-based^[5b] heterogeneous catalysts (Figure 4f).

In summary, we present here the ability of the Ni/NCF-based Mott-Schottky binary catalysts to change the adsorption energy of methanol molecules for highly efficient and selective dehydrogenation of methanol in a gas-solid heterogeneous catalytic system. The rectifying contact at the Ni/nitrogen-dopedcarbon interface was theoretically and experimentally demonstrated to take the crucial role in promoting the adsorption and further activation of methanol molecules, thus efficiently boosting the methanol dehydrogenation. The facile strategy created here can be easily extended to fabricate other functional nanocatalysts with different abundant and sustainable transition metal components, creating unique, previously not accessed properties. Moreover, this study paves the way towards the development of high-performance, durable, real-world catalysts for sustainable gas phase transformations in heterogeneous catalytic systems.

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Active boundaries: the ability of the Mott-Schottky-type nanocatalysts to change the adsorption energy of methanol molecules for highly efficient and selective dehydrogenation of gas-phase methanol was achieved by constructing Ni nanoparticle/N-doped carbon-foam catalyst. The electron redistribution along the Ni–N-doped carbon phase boundaries via the Mott-Schottky effect significantly and generally promotes the adsorption and further activation of methanol molecules, thus efficiently boosting the methanol dehydrogenation reaction.