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Non-noble Ni@NbO_x Catalyst for Selective Hydrodehydroxylation of 5-Hydroxymethylfurfural to 5-Methylfurfural

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ABSTRACT: Selective hydrogenation of substrates containing multiple unsaturated bonds (C=C, C=O) is a crucial catalytic process in the production of high-value chemicals. The development of non-precious metal catalytic systems is of importance for hydrogenation processes due to the high cost and scarcity of noble metals. In this study, we have developed a straightforward and versatile encapsulation technique for the synthesis of Ni@NbO_x catalysts, which enables highly selective hydrodehydroxylation of 5-hydroxymethylfurfural (HMF) to 5-methylfurfural (MF) under H₂. Mechanistic studies revealed that metallic Ni⁰ encapsulated within NbO_x facilitates hydrogen dissociation through an energy quasi-barrierless process (< 0.1 eV), while simultaneously avoiding the adsorption of furan or C=O groups over Ni nanoparticles, therefore enhancing the selective hydrodehydroxylation of HMF to MF. Furthermore, the Ni@NbO_x catalyst was tolerant to different conditions for selective hydrogenation, such as crude H₂ containing CO, substrates contaminated with various metal salts, etc.

KEYWORDS: Ni catalyst, NbO_x, selective hydrodehydroxylation, biomass conversion, metal encapsulation.

Synopsis: Non-precious metal Ni@NbO_x catalysts prepared using a simple and versatile method exhibit excellent 5-methylfurfural selectivity in the 5-hydroxymethylfurfural Hydrodehydroxylation reaction.

INTRODUCTION

It has long been known that supported catalysts have played a pivotal role in heterogeneous catalysis.¹ Researchers have explored various strategies to enhance catalytic performance by adjusting the composition, morphology, size, and

support of the catalyst.²⁻³ Additionally, the surface of supported catalysts acts as sites for substrate adsorption, activation, and hydrogenation reactions, making surface modifications highly promising for regulating the selectivity of target products.⁴⁻⁵

Modification strategies include surface ligand modification, multiple-site construction (such as single-atom alloys, bimetallic alloys, or the coexistence of isolated atoms, clusters, and nanoparticles), and metal encapsulation.⁶⁻⁸ Surface ligand modification and multiple-site construction allow for the alteration of electronic state, steric hindrance, and the adsorption/desorption properties of metal nanoparticles.⁹⁻¹⁰ However, the limited stability of certain ligands and segregation/aggregation/ostward ripening of multiple-site particles constrains their further extensive application.⁶ Metal encapsulation strategy impedes the migration and aggregation of metal nanoparticles and holds great promise in enhancing catalyst recyclability, and product selectivity.⁷⁻¹⁰

The direct conversion of 5-hydroxymethylfurfural (HMF) represents an innovative and environmentally friendly approach for the production of 5-methylfurfural (MF), a valuable and useful chemical.¹¹⁻¹⁴ Various noble metal-based catalysts have been applied in this transformation.¹⁵⁻¹⁹ In 2021, we first achieved this conversion process by using the isolated $\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-O}_\text{v}$ catalysts. While the single-atom catalysts are quite efficient and stable, it is difficult to synthesize them precisely and controllably.¹⁵ Following that, we developed the $\text{Pt@PVP}/\text{Nb}_2\text{O}_5$ catalytic system and it achieved a high MF yield of 92.0%.¹⁸ Nevertheless, the quite complex preparation process and extended reaction time presented some shortcomings. Chen et al. later prepared Au/TiO_2 catalysts with a diameter of 20 nm by incipient wetness impregnation for this conversion.¹⁷ However, the repeatability and stability of the wet impregnation method to control the 20-nm-diameter Au nanoparticles faced a tremendous

challenge. In our most recent work, we developed the nanoparticulate $\text{Pd}/\text{Nb}_2\text{O}_5\text{-500H}$ catalyst, where a strong interaction between Pd and Nb_2O_5 led to the formation of an NbO_x thin layer that surrounded the surface of Pd nanoparticles.¹⁹ This catalyst achieved an increase in MF selectivity from 6.4% to 81.0% compared to a similar supported $\text{Pd}/\text{Nb}_2\text{O}_5$ catalyst under the same conversion conditions.¹⁹ Despite these efforts made, these catalytic systems are limited to noble metal catalysts, heavily limiting the scalable industrial production of MF via this route. There exists an urgent requirement to develop efficient and selective non-noble-metal catalysts for the transformation. Most recently, Ahmad et al. explored co-quenching using graphene oxide and MnO_x at a high temperature of 900°C.¹⁶ The catalyst demonstrated excellent MF selectivity with an MF productivity of 1.2 mmol/ $\text{g}_{\text{cat}}/\text{h}$. Nevertheless, the catalyst preparation involved a series of complicated procedures for graphene oxide synthesis, expensive precursor materials, and energy-intensive consumption.¹⁶

In this work, using an encapsulation-reduction method, we developed a non-noble-metal Ni@NbO_x catalyst with Ni nanoparticles (NPs) encapsulated within NbO_x support. Despite the complexity of the reaction system due to the various potential pathways under the investigated conditions (Figure 1), this cheap Ni@NbO_x catalyst presented an MF selectivity of 91.8% at an HMF conversion of 94.3%, with an MF productivity of 2.7 mmol/ $\text{g}_{\text{cat}}/\text{h}$. A mechanistic investigation for the origin of unique hydroxylation performance was conducted using H_2/D_2 isotopic kinetic experiments and density functional theory (DFT) calculation.

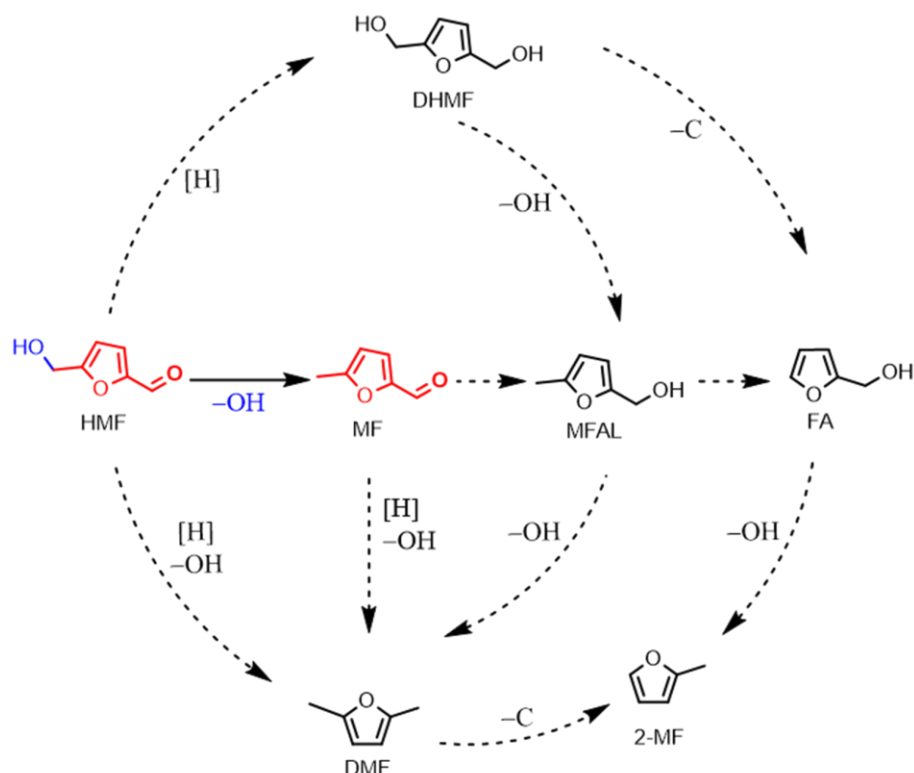


Figure 1. Reaction network for the hydrogenation of 5-hydroxymethylfurfural (HMF). [H] indicates hydrogenation, -OH indicates hydrodehydroxylation, and -C indicates C-C cleavage.

EXPERIMENTAL SECTION

Materials. Cetyl-trimethyl-ammonium bromide (CTAB, 99%, Sigma-Aldrich), Niobium(V) oxalate hydrate (99%, Acros), PdCl_2 (59% Pd, Acros), PtCl_4 (>99.0%, Acros), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (35-40% Ru, Acros), $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (38.5-45.5% Rh, Alfa), CuCl_2 (>98%, Alfa), CoCl_2 (99.7%, Alfa), and NiCl_2 (99%, Alfa). Tetrahydrofuran (AR), 5-hydroxymethylfurfural (AR), 2,5-dimethylfuran (AR), 5-methylfurfural (AR), and n-dodecane (AR) were procured from J&K and Sinopharm Chemical Reagent Co. Ltd. H_2 (>99.99%), Ar (>99.99%), D_2 (>99.99%), H_2/Ar (10%), and CO (>99.99%) were supplied by Beijing Analytical Instrument Company. Ultrapure water was utilized in all experiments. All chemicals were utilized without further purification.

Catalyst preparation. M@NbO_x ($\text{M} = \text{Pt}, \text{Ru}, \text{Rh}, \text{Pd}, \text{Ni}, \text{Cu}, \text{Co}$) catalysts were prepared via a hydrothermal-reduction approach utilizing

cetyltrimethylammonium bromide (CTAB) as the surfactant. Initially, a solution containing 2.69 g of niobium(V) oxalate hydrate, 0.5 g of CTAB, and 2.0 ml of 5.0 mg/ml $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (the mass concentration of Ni is 5.0 mg/ml) aqueous solution was added drop-wise into the suspension liquid under stirring. The additional amount of the other metal is also 10.0 mg. The resultant mixture was then transferred into a dried 100 ml Teflon autoclave at room temperature. Subsequently, hydrothermal treatment was conducted at 180 °C for 10 hours. Following cooling to room temperature, the precipitate was separated via centrifugation and washed three times with distilled water and ethanol. The resultant solid was then dried in an 80 °C oven for 6 hours. Subsequently, the dried powder was calcined at 500 °C for 4 hours in a tube furnace (Model TFFV-1200-50-I-220, Anhui Kemi Machinery Technology Co., Ltd.) under a reducing gas mixture (10% H_2/Ar) to obtain the M@NbO_x catalysts. The preparation of

the NbO_x catalyst aligns precisely with the M@NbO_x synthesis methodology, with the sole exception of the absence of the corresponding metal precursor.

Catalytic evaluation. In this investigation, a hydrogenation vessel equipped with a magnetic stirrer was utilized to carry out the experimental procedures. In a typical reaction, the 5-hydroxymethylfurfural (12.6 mg), catalyst (10.0 mg), dodecane (15.1 mg), and tetrahydrofuran (2.0 ml) were loaded into the kettle. The hydrogenation reactor employed in this setup is a robust, high-temperature, and high-pressure resistant container with a volume of approximately 16 ml. The high-purity hydrogen gas (1.0 MPa, > 99.99%, provided by Beijing Analytical Instrument Company) was employed to purge the reactor, eliminating any residual air. The reactor was subjected to three evacuation cycles and then pressurized to a specified hydrogen pressure before sealing. Afterward, the reactor was heated to the desired temperature, with continuous stirring at 800 rpm. Upon completion of the designated reaction duration, the reactor was removed from the heat source and immersed in an ice bath to cool to ambient temperature. The reaction gas was then released, and the liquid phase was separated from the solid catalyst through filtration. Liquid product analysis was conducted using an Agilent 6820 gas chromatograph (GC) equipped with a flame ionization detector (FID) and an Innovax capillary column (0.25 mm diameter, 30 m length). Conversion of HMF and selectivity towards the desired product, MF, were determined by employing dodecane as an internal standard based on the GC data. The initial molar amount of HMF before the reaction was denoted as n_0 , the molar amount after the reaction as n_1 , and the molar amount of the resultant product, MF, as n_2 . Calculation of HMF

conversion and MF selectivity was performed using the following formulas:

$$\text{Conversion (\%)} = \frac{(n_0 - n_1)}{(n_0)} \times 100\% \quad (1)$$

$$\text{MF Selectivity (\%)} = \frac{(n_2)}{(n_0 - n_1)} \times 100\% \quad (2)$$

Catalyst characterization. The metal loadings of all catalysts were quantified utilizing inductively coupled plasma-optical emission spectrometry (ICP-OES). High-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) images were obtained utilizing a JEOL-2100F electron microscope at 120 kV and a field emission transmission electron microscope JEM-F200 at 200 kV. Before analysis, the samples underwent dispersion in ethanol via ultrasonic treatment, and a droplet of the solution was deposited onto a copper grid supporting an ultra-thin carbon film. CO-probe Fourier transforms infrared spectroscopy (CO-FTIRS) measurements were executed using a FOLI10-R-T infrared spectrometer equipped with a DLaTGS detector supplied by INSA Co. Ltd. The measurements were conducted in transmission mode at a resolution of 4 cm⁻¹, with a scanning speed of one spectrum per minute. Preceding CO adsorption, all catalysts underwent treatment in 10% H₂/Ar at 200 °C for 60 minutes. After cooling to room temperature, the background spectrum was recorded. Subsequently, pure CO was introduced into the *in-situ* reaction cell, and spectra were continuously collected until no further changes were observed. Following this, pure Ar was introduced to eliminate any remaining gaseous CO, and spectra were recorded during this process. Structural characteristics of the samples were evaluated through nitrogen physical adsorption, and pore diameter measurements were conducted using a Micro 2020HD88 instrument (ASAP 2460 3.00). X-ray diffraction (XRD) patterns were obtained using a

Smart Lab X-ray diffractometer with Cu-K α radiation ($\lambda = 0.15$ nm), operating at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA) equipped with an Al K α excitation source (1486.8 eV). The C1s peak (284.8 eV) served as the standard reference. Depth profiling XPS for the 2000s with Argon GCIB (Gas cluster ion beams) was also performed on an X-ray photoelectron spectrometer (Thermo Fisher, USA). Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is employed for energy referencing. Ultralow-temperature CO-Fourier transforms infrared spectroscopy (LT-CO-FTIRS) was conducted at -150 °C using a CO pulse supply of 10^{-5} bar on the in-situ transient platform CRCP-7070 provided by Tianjin Xianquan company. Hydrogen temperature programmed desorption (H₂-TPD) was executed utilizing an Auto Chem HP 2950 instrument (Micromeritics Instrument Corporation, USA). Electron paramagnetic resonance (EPR) analysis was carried out using a Bruker A300-10/12 instrument.

Calculations. In this study, the modeling of NbO_x support was performed using Nb₂O₅ with oxygen vacancies. The nickel (111) and Nb₂O₅ (001) surfaces were modeled using four-layer slab models with a vacuum thickness of 15 Å, corresponding to a 2×2×1 k-point grid for each. Transition states (TS) were located using the constrained minimization method.²⁰ The valence electrons were expanded in a plane-wave basis set with a cutoff energy of 450 eV. Geometry optimization was carried out using the conjugate gradient method until the maximum force on each relaxed atom was less than 0.05 eV/Å. All density functional theory (DFT) calculations were performed using the VASP code,²¹ employing the Perdew-Burke-Ernzerhof (PBE) functional within the

framework of the generalized gradient approximation (GGA).²² The interactions between the valence electrons and atomic cores were described using the projector-augmented wave (PAW) method.²³

RESULTS AND DISCUSSION

The preparation and performance of the M@NbO_x catalyst. A hydrothermal-reduction method for the synthesis of M@NbO_x samples was developed and the process was illustrated in Figure 2a. In this method, niobium oxalate (C₁₀H₅NbO₂₀), cetyltrimethylammonium bromide (CTAB), and the respective metal precursor were mixed in an autoclave and subjected to a temperature of 180 °C for 10 hours to obtain the catalyst precursor. Afterward, the catalyst precursor was reduced at 500 °C in a flowing 10% H₂/Ar atmosphere to obtain M@NbO_x catalysts (M = Ru, Rh, Pd, Pt, Ni, Cu, Co). The contents of the metal in the prepared M@NbO_x catalysts, as determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), were detailed in Table S1.

High-resolution transmission electron microscopy (HRTEM) images of the obtained M@NbO_x samples (M = Ru, Rh, Pd, Pt, Ni, Cu, Co) were depicted in Figure 2b-f and Figure S1. Energy dispersive spectroscopy (EDS) images demonstrate the presence of Nb, O, and M elements, with each element represented in distinct colors, thereby confirming the successful synthesis of M@NbO_x catalysts. Moreover, taking Ni@NbO_x as an example, uniform dispersion of Nb and O elements throughout the entire structural framework, with Ni NPs observed. The interfacial structure of the M@NbO_x catalysts was affirmed by CO-Fourier transform infrared spectroscopy (CO-FTIRS) at room temperature, as depicted in Figure S2 and Figure S3. For instance, in the case of the Ni@NbO_x catalyst,

bands at approximately 2173 cm^{-1} and 2116 cm^{-1} were attributed to gaseous CO adsorption (Figure S2).²⁴⁻²⁸ Subsequently, no CO adsorption was detected after introducing argon to eliminate any residual gaseous CO. This observation suggests that the metal Ni is not exposed on the support's surface but rather encapsulated by NbO_x . The CO-FTIRS experimental results for the remaining M@NbO_x catalysts ($\text{M} = \text{Ru}, \text{Rh}, \text{Pd}, \text{Pt}, \text{Cu}, \text{Co}$) are consistent with those of Ni@NbO_x , affirming the universality of this catalyst preparation approach. The metals are encapsulated by NbO_x support, which effectively prevents their interaction with the $\text{C}=\text{O}$ functional groups of the HMF. Electron paramagnetic resonance (EPR) analysis indicates the presence of oxygen vacancies (O_v) across all M@NbO_x catalysts obtained (Figure S2f).

These as-prepared M@NbO_x catalysts were used for the direct hydrodehydroxylation of 5-hydroxymethylfurfural (HMF) to 5-methylfurfural (MF) under hydrogen. As shown in Figure 3a, Ni@NbO_x catalyst presented an MF selectivity of 91.8% with an HMF conversion of 94.3% at $160\text{ }^\circ\text{C}$ for 4 h. When the reaction time was reduced to 2 h, the conversion of HMF was 58.1%, and the selectivity of MF was 88.1% over Ni@NbO_x . It was observed that when the type of metal in the catalyst varies, the conversion rates differ; however, the selectivity for MF remained consistently around 90% (Figure S4). The other non-noble metal Cu and Co catalysts showed poor MF yields of 7% and 12%, respectively. Their catalytic performance resembled that of the sole NbO_x acting as a catalyst ($\sim 6\%$). This can be attributed to the higher hydrogen activation

capacities of noble metals (Ru, Rh, Pd, Pt) and the non-precious metal Ni. In contrast, non-precious metals such as Cu and Co possess lower hydrogen activation capacities, resulting in reduced HMF conversion and MF selectivity. Due to the higher performance of Ni@NbO_x relative to other non-noble-metal catalysts, further optimization of reaction conditions (reaction temperature, time, solvent, and pressure) was conducted (Figure 3b-c, Figure S5-S6).

According to the Arrhenius equation, the apparent activation energy of the reactions was calculated to be $22.9 \pm 3.3\text{ kJ/mol}$ (Figure S7a). Within the investigated H_2 pressure range ($1.0\sim 4.0\text{ MPa}$), Figure S7b shows that the reaction rate remains relatively constant as the reaction pressure increases, indicating a zero-order reaction with respect to H_2 molecules. The reaction was conducted at a stirring rate of 800 rpm. At a reduced stirring rate of 400 rpm, the reaction rate decreased, whereas the rates at 800 rpm and 1000 rpm were similar. This suggests that a stirring rate of 800 rpm is adequate to mitigate any effects related to mass transfer (Figure S7c). The optimal MF production over Ni@NbO_x was achieved under the conditions of $160\text{ }^\circ\text{C}$ for 4 hours under 4 MPa of hydrogen using tetrahydrofuran as a solvent. Subsequently, we calculated hydrogen solubility ($1.0\sim 4.0\text{ MPa}$) in THF and studied its effect on the reaction rate, as shown in Figure S8. The reaction rate remained relatively constant with increasing hydrogen solubility, indicating that changes in solubility within this pressure range have little effect on the reaction rate.

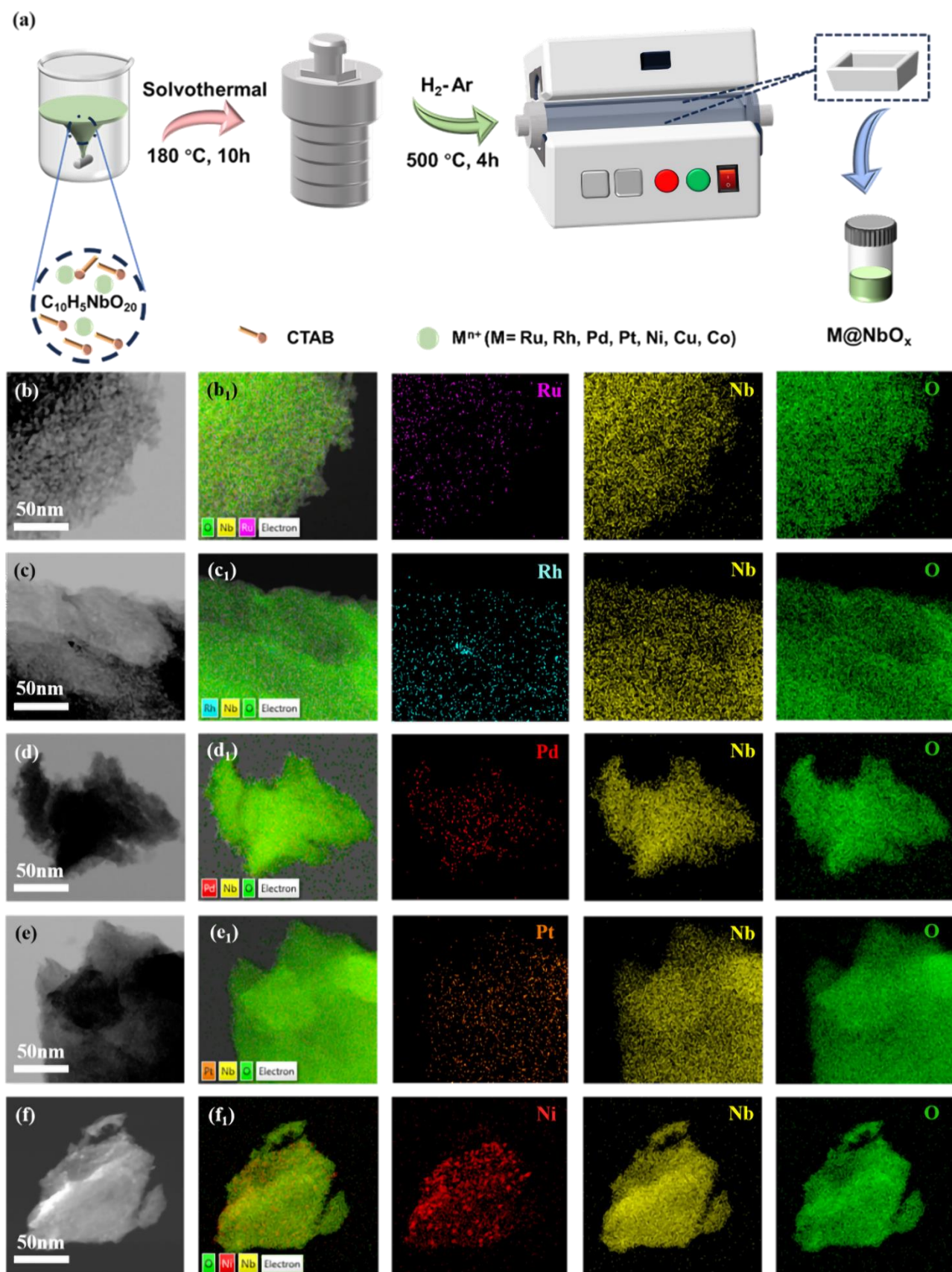


Figure 2. The synthesis of $M@NbO_x$. (a) Illustrative preparation process representation for $M@NbO_x$ catalyst used in this study ($M = \text{Ru, Rh, Pd, Pt, Ni, Cu, Co}$), HRTEM images and EDS mappings of M , O , and Nb elements of (b) $\text{Ru}@NbO_x$, (c) $\text{Rh}@NbO_x$, (d) $\text{Pd}@NbO_x$, (e) $\text{Pt}@NbO_x$, and (f) $\text{Ni}@NbO_x$.

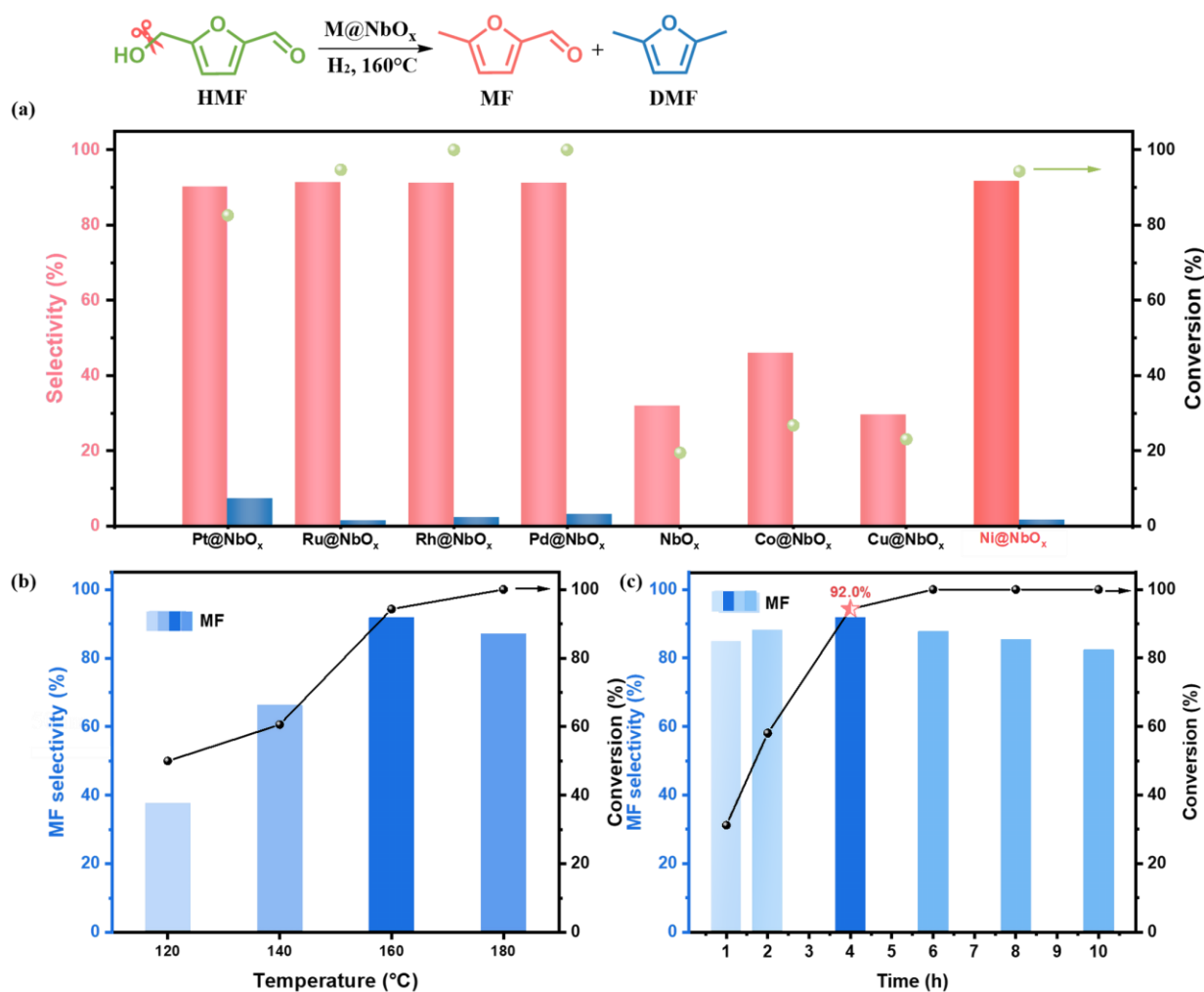


Figure 3. Chemoselective production of MF from HMF conversion. Performance of (a) the noble and non-noble metal catalysts, (b) temperature-dependent and (c) time-dependent evolutions over Ni@NbO_x. Reaction conditions: substrate (12.6 mg), catalyst (10.0 mg), THF (2.0 ml), dodecane (15.1 mg), H₂ (4.0 MPa), 160 °C, 4 h.

Catalyst characterizations and mechanistic investigations. To elucidate the origins of the high catalytic efficiency of the Ni@NbO_x catalyst, comprehensive catalyst characterizations, and mechanistic investigations were undertaken. Nitrogen adsorption-desorption measurements revealed that the Ni@NbO_x sample exhibited type IV isotherms with a hysteresis loop, indicative of mesopores (Figure S9), with a pore size centered around 5 nm (Figure S10). The specific surface area of Ni@NbO_x, determined using the Brunauer-Emmett-Teller (BET) method, was found to be 201.6 m²/g. Powder X-ray diffraction (PXRD) patterns for

Ni@NbO_x catalyst revealed a diffraction peak at 44.5°, corresponding to the (111) crystal planes of the cubic phase of Ni (JCPDS card no. 70-0989), indicating the presence of Ni NPs (Figure S11). Additionally, HRTEM and EDS images of Ni@NbO_x samples confirmed the presence of Ni NPs.

The encapsulation structure of Ni NPs within NbO_x was confirmed by low-temperature CO-Fourier transform infrared spectroscopy (LT-CO-FTIRS) at -150 °C. As shown in Figure 4a, bands at approximately 2173 cm⁻¹ and 2116 cm⁻¹ were attributed to gaseous CO.²⁴⁻²⁸ Subsequent introduction of helium to eliminate residual gaseous

CO resulted in no other signals of CO adsorption. It was challenging to distinguish the valence state of Ni from the extremely weak signals obtained from X-ray photoelectron spectroscopy (XPS) due to the encapsulation of Ni NPs by NbO_x support (Figure S12). To address this issue, depth profiling XPS was employed to assess the valence state of Ni atoms after cluster etching for 2000 seconds. In Figure 4b, Ni@NbO_x displayed a prominent peak at a binding energy of 852.6 eV, characteristic of metallic Ni⁰, along with a minor peak at 855.6 eV, indicating the minor presence of divalent Ni²⁺.²⁹ These observations suggest that Ni predominantly exists in the form of metallic Ni⁰ within Ni@NbO_x.

In situ Fourier-transform infrared spectroscopy (FTIRS) surface reactions were carried out to observe the reaction process. The FTIRS experiments were performed at 160 °C under a hydrogen flow (Figure S13). As the reaction time increased, the peaks corresponding to the C-OH functional group diminished and eventually disappeared, while the C=O peaks remained nearly unchanged. This indicates the conversion of HMF to MF.

Hydrogen activation is crucial for hydrogenation reactions; thus, hydrogen temperature programmed desorption (H₂-TPD) was conducted to assess hydrogen sorption behaviors on both Ni@NbO_x and NbO_x materials. As indicated in Figure 4c, the Ni@NbO_x catalyst exhibited a 40 °C lower temperature desorption of hydrogen compared to sole NbO_x, implying that the presence of Ni metal enhances hydrogen activation and desorption. Quantitative analysis further revealed that the hydrogen desorption capacity of the Ni@NbO_x catalyst is approximately 1.3 times greater than that of the NbO_x catalyst. Combining these results, it can be inferred that the metallic Ni⁰ NPs within NbO_x

serve as the primary active sites for hydrogen activation.

The H₂/D₂ kinetic isotope effects (KIE) were investigated to gain insights into the dynamics of hydrogen or proton transfer in chemical reactions.³⁰ Under optimized reaction conditions, H₂/D₂ kinetic experiments revealed a kinetic rate constant ratio (k_H/k_D) of 2.45 (Figure 4d). When the reaction was conducted at atmospheric pressure, a KIE value of 1.98 was observed (Figure S14), indicating that the impact of hydrogen pressure on the KIE is minimal, as the KIE remains close to 2. These results suggest that the transfer of hydrogen or protons is likely the rate-determining step in the hydrogenolysis of HMF to MF.

To further understand the effects of hydrogen adsorption and activation on the reaction process, density functional theory (DFT) calculations of the reaction paths on NbO_x and Ni@NbO_x materials were performed (Figure 4e). The energy distribution plot across the entire reaction pathway for NbO_x support revealed that the transition state for hydrogen dissociation on the niobium oxide carrier (TS1) occupied the highest energy position at 0.53 eV. This indicates that hydrogen dissociation serves as the rate-determining step on NbO_x support throughout the reaction process. Conversely, the incorporation of Ni can reduce the hydrogen dissociation energy barrier to 0.1 eV, lowering the energy barrier of the rate-determining step observed with NbO_x.

DFT calculations were employed to determine the most favorable adsorption configuration for HMF activation on NbO_x support. As shown in Figure S15, the calculations confirm that Ov sites facilitate the adsorption of HMF. Figure S16a illustrates that the presence of Ov sites enables the cleavage of the C-OH bond with an energy barrier of only 0.21 eV,

which is significantly lower than the energy barrier for CHO hydrogenation ($E_a = 0.87$ eV). This finding indicates that O_v plays a critical role in facilitating the cleavage of the C-OH bond. The adsorption structure shown in Figure S16b reveals that HMF preferentially adsorbs on NbO_x via interaction between the OH terminus and O_v . During this adsorption process, the C-OH bond elongates from its initial length of 1.414 Å to 1.708 Å, suggesting the effective activation of the C-OH bond. In contrast, the C=O bond of CHO adsorbed on O_v elongates from 1.229 Å to 1.387 Å, demonstrating the less effective activation compared to the C-OH bond, thereby limiting the formation of CHO-H.

Subsequent dissociated hydrogen on Ni overflowed to NbO_x support to form an active NbO_x -H site. HMF substrate demonstrated a preference for adsorption onto O_v sites of NbO_x support via the OH group over the CHO group. Following the dissociation of the CH_2 -OH bond of HMF over O_v sites, the hydrogenation of $-CH_2$ via active H bonded with NbO_x was completed with an energy barrier of 1.08 eV, followed by desorption and production of MF. This confirms that the hydrogenation steps of $-CH_2$ species facilitated by spillover H on the support are the rate-determining steps in the $Ni@NbO_x$ catalyst, consistent with the results from H_2/D_2 KIE experiments.

Robustness of $Ni@NbO_x$ catalysts. The cost of ultrahigh-purity hydrogen is nearly double that of industrial-grade crude hydrogen. Given industrial crude H_2 typically contains trace amounts of CO, developing a CO-resistant catalyst capable of effectively catalyzing hydrogenation reactions using crude hydrogen possesses substantial industrial utility. Herein, we performed the catalytic hydrogenation reaction of HMF using CO-contaminated hydrogen. As shown in Figure 5a,

despite CO exposure, the $Ni@NbO_x$ catalyst showed nearly no fall in both HMF conversion and MF selectivity. The CO-resistant behavior of $Ni@NbO_x$ is similar to that of the sole NbO_x support in the absence of Ni. Furthermore, $Ni@NbO_x$ catalyst was employed for the direct conversions of HMF-rich crude biomass hydrolysate or HMF solutions contaminated with different metal salts (NaCl, Na_2SO_4 , KCl, and K_2SO_4). As shown in Figure 5b, approximately 70-80% yields of MF were obtained for all the HMF solutions investigated. These results demonstrate that $Ni@NbO_x$ catalyst with the encapsulation structure exhibit robust stability under harsh reaction conditions.

Finally, the cycle experiments were performed to assess the recyclability of $Ni@NbO_x$. Consistent selectivity was maintained over four cycles under optimal reaction conditions, despite a gradual decrease in the conversion rate (Figure 5c). Comfortingly, after the regeneration treatment at 500 °C with 10% H_2/Ar after the fourth cycle, conversion was recovered in the fifth cycle. Depth profiling XPS analysis of the reacted catalyst, following cluster etching for 2000 seconds, indicated that Ni predominantly existed in the form of Ni^0 (Figure S17). Similarly, depth profiling XPS analysis of the regenerated catalyst after 2000 seconds of cluster etching revealed that Ni was also primarily present as Ni^0 (Figure 5d). Additionally, the CO-FTIRS experimental result of the regenerated catalyst exhibited no adsorption peaks associated with Ni^0 , suggesting the Ni^0 was still encapsulated by NbO_x support (Figure S18). XRD analysis of both fresh and regenerated catalysts indicated no discernible differences. (Figure S19).

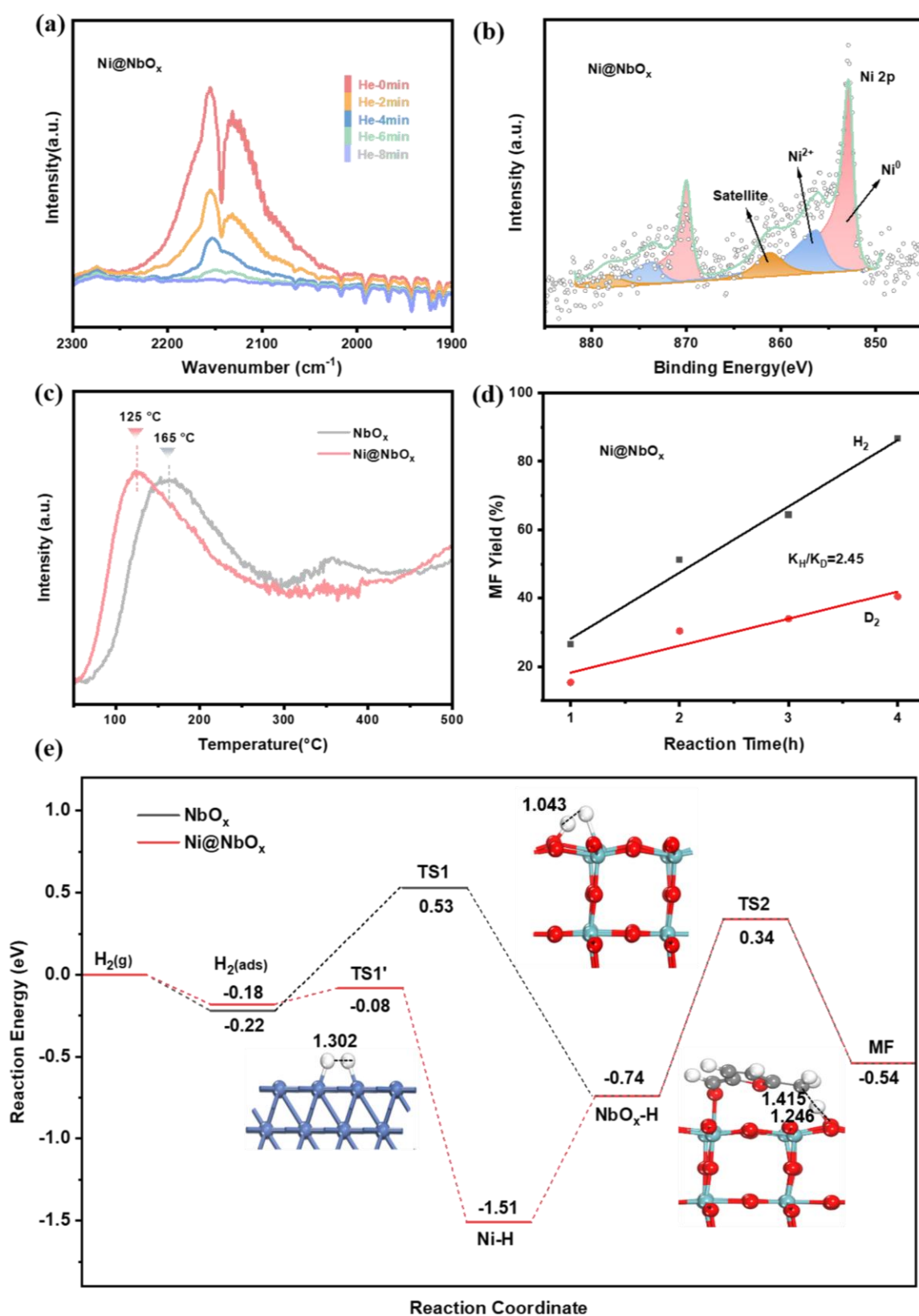


Figure 4. Reaction mechanism investigations. (a) Low-temperature CO-pulse FTIRS spectra at -150 °C, (b) Depth profiling X-ray photoelectron spectroscopy following cluster etching for 2000 seconds, (c) Hydrogen temperature programmed desorption (H₂-TPD), (d) The kinetic isotope effect observed for Ni@NbO_x in selective hydrodehydroxylation. (e) Calculation of hydrogen adsorption, dissociation, and hydrogenation reaction pathway diagrams. (The hydrogen dissociation (TS1-NbO_x), the hydrogen dissociation (TS1'-Ni), and the hydrogenation reaction (TS2). TS: transition state. Blue: Ni, white: H, red: O, green: Nb.

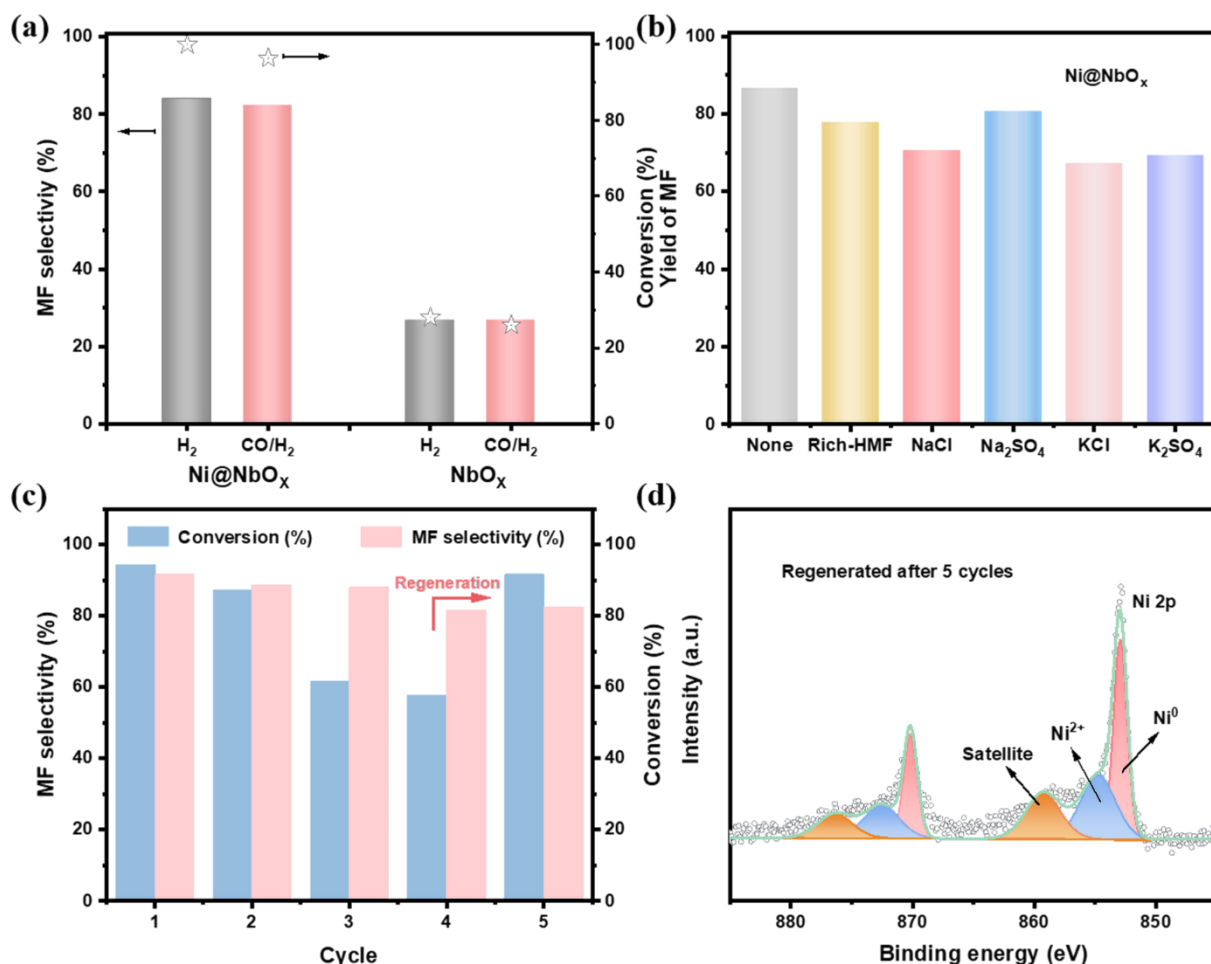


Figure 5. The robustness of Ni@NbO_x. (a) CO-resistant catalytic performance. (b) Direct conversion of HMF-rich crude biomass hydrolysate or HMF solutions suffering from various metal salts. (c) Cycle performance and (d) Depth profiling XPS patterns of the regenerated after the 5th reaction. Reaction conditions: substrate (12.6 mg), catalyst (10.0 mg), THF (2.0 ml), 160 °C, 4h, H₂ (4.0 MPa), dodecane (15.1 mg).

CONCLUSIONS

In this study, we have successfully developed a facile and universal encapsulation strategy for the construction of M@NbO_x (M = Ru, Rh, Pd, Pt, Ni, Cu, Co) catalysts. Notably, the earth-abundant Ni@NbO_x catalyst achieved a selectivity of 91.8% for MF with the near-complete conversion of HMF under optimized reaction conditions. Experimental and DFT calculations evidence that Ni⁰ within NbO_x serves as an active site in the dissociation of hydrogen, and transfers to NbO_x support to undergo the hydrogenation following the cleavage of the CH₂–OH bond of HMF, yielding MF. Furthermore, the Ni@NbO_x catalyst maintains approximately 70-

80% yields of MF even when using HMF-rich crude biomass hydrolysate and HMF solutions contaminated with various metal salts. This straightforward, widely applicable, and efficient metal encapsulation strategy provides valuable insights for catalyst design and preparation in heterogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information.

Characterizations of catalyst, catalytic performance, reaction kinetics, in-situ FTIRS experiments, and complementary figures and tables.

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Notes

The authors declare no competing financial interest.

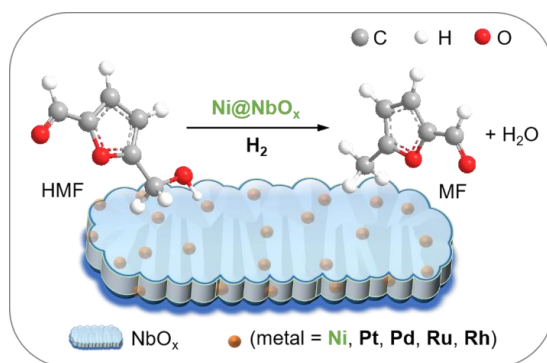
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Graphical Abstract