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Highly Selective Hydrogenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran at Low Temperature over a Co-N-C/NiAI-MMO catalyst

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Currently there is tremendous interest in the discovery of catalysts which can selectively hydrogenate biomass-derived 5hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF). Herein, a highly selective catalyst for this transformation was developed, by adsorption of a cobalt porphyrin (CoTAPP) onto a nickel-aluminium layered double hydroxide (NiAl-LDH) support, followed by a pyrolysis step at 500 °C under a N₂ atmosphere. The obtained catalyst (denoted here as Co-N-C/NiAl-MMO), comprising cobalt species (Co⁰ and CoOx) and N-doped carbon on a NiAl mixed metal oxide support, showed outstanding initial selectivity (99.9%) for the hydrogenation of HMF to DMF at 170 °C in tetrahydrofuran (THF). This is one of the highest selectivities reported to date for this reaction, with the reaction temperature being very mild. After 3 cycles of catalytic tests, with catalyst regeneration by heating at 300 °C in N₂ between tests, the HMF conversion efficiency and DMF selectivity of Co-N-C/NiAl-MMO had both decreased by >70% compared to the initial values. This deactivation resulted from the loss of surface basic sites needed for H₂ activation, as well as a change in the Co speciation on the catalyst surface (i.e. Co⁰ oxidation to CoOx). Results guide the development of improved catalysts for the selective conversion of HMF to DMF.

Introduction

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Today's chemical industry is heavily reliant on crude oil as its main carbon feedstock. The catalytic cracking of crude oil yields a diverse range of petrochemicals, which are further processed into fuels, solvents, plastics, and other industrial and consumer products. Over the past decade, total oil use has grown globally at a rate of 1.4% per year, whilst oil use for production of chemical feedstocks has grown at ~4.0% per year.¹ Since oil is a fossil fuel, its use in the energy and chemical manufacturing sector is not sustainable,²⁻⁶ motivating the search for new fuel and chemical manufacturing methods that are green and based around renewable sources.

Biomass resources, especially lignocelluloses, are attracting increasing attention as potential feedstocks for the synthesis of valuable commercial chemicals. 5-hydroxymethylfurfural (HMF) is a carbohydrate-derived product obtained by acid hydrolysis of sugars.^{7, 8} HMF represents an important intermediate for the synthesis of a wide variety of chemicals.^{9, 10} with 2,5-dimethylfuran (DMF) being a prized derived product as it is a liquid bio-fuel with properties comparable to gasoline. Compared to ethanol (a commonly used biofuel), DMF has a higher energy density (33.7 MJ/kg versus 26.9 MJ/kg

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for ethanol; c.f. 43.2 MJ/kg for gasoline), a higher boiling point (92-94 °C versus 78.4 °C for ethanol), and is insoluble in water (whereas ethanol is water soluble). 2,5-dimethylfuran thus holds great promise as a replacement for petroleum-derived gasoline.^{11, 12} Accordingly, finding efficient and stable catalysts for the selective hydrogenation of 5-HMF to DMF has become an imperative.¹³⁻¹⁵

Román-Leshkov et al. reported that a carbon-supported copper ruthenium catalyst (CuRu/C) produced DMF with a selectivity of 76-79% during the hydrogenation of 5-hydroxymethylfurfural.¹⁶ Ma et al. reported a 79.4% product yield of DMF using a bifunctional Ru–MoOx/C catalyst prepared by incipient wetness impregnation.¹⁷ Huang et al. reported that nickel-tungsten carbide nanoparticles supported on activated carbon were very active for the hydrogenation of HMF to DMF, with a DMF yield of 96% achieved.¹⁸ Nitrogen-doping of carbon nanotubes (CNTs) has been shown to enhance the stability and dispersed platinum (Pt) nanoparticles.^{19, 20} Jiang et al. decorated a N-doped graphene-modified Al₂O₃ support with Cu and Co nanoparticles, with the resulting catalyst showing excellent selectivity for the the conversion of HMF to DMF (DMF yield of 99.0% at 180 °C).²¹ N-doping improves the hydrophilicity of carbon supports, introduces basic sites, can create porphyrin-like metal single atom catalysts, provides anchor point for metal nanoparticles, and also inhibits metal aggregation.²²⁻²⁴ For the hydrogenation of HMF to DMF, basic surface sites are needed for H₂ activation, thus having domains of N-doped carbon on the catalyst surface would be advantageous. Also, it is desirable that catalysts developed for this reaction are noble metal free, prompting a rethink of catalyst design strategies for selective DMF synthesis.

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In this work, we report the successful design and performance testing of a cobalt-based catalyst for the selective hydrogenation of HMF to DMF. A cobalt porphyrin (CoTAPP) was adsorbed onto a NiAl-LDH support, after which the resulting composite was pyrolysed at 500 $^\circ$ C for 5 h in N₂. The heat treatment converted the porphyrin into various Co species (Co⁰, CoOx) and N-doped carbon, and the NiAl-LDH into a NiAl mixed metal oxide (NiAl-MMO) (Scheme 1). The obtained low cost catalyst (denoted herein as Co-N-C/NiAl-MMO), benefitting from the basicity of the N-doped carbon, cobalt actives sites and thermal and chemical stability of the MMO support, demonstrated remarkable initial activity and selectivity for the hydrogenation of HMF to DMF in tetrahydrofuran at mild reaction temperatures (170 °C). Supporting characterization studies were used to pinpoint the origins of the excellent catalytic performance, and also provided a framework for understanding catalyst deactivation over successive catalyst testing/regeneration cycles.



Results and Discussion

Catalyst characterization



Figure 1. SEM images of (a) NiAl-LDH, (b) CoTAPP/NiAl-LDH, (c) Co-N-C/NiAl-MMO, and (d) Co-N-C.

The synthesis of the Co-N-C/NiAl-MMO catalyst was first examined through SEM and HRTEM investigations. **Fig. 1a** shows a SEM image of the NiAl-LDH sample, which possesses the nominal formulae $[Ni^{2+}_{0.67}Al^{3+}_{0.33}(OH^{-})_2]^{0.33+}$ [(NO³⁻, Cl⁻)_{0.33}·yH₂O]^{0.33-} and consists of positively charged sheets containing the NiO₆ and AlO₆ octahedra, with the charge stabilizing anions and water located in the gallery between the sheets. SEM showed the NiAl-LDH sample consisted of thin hexagonal platelets, a morphology typical for LDH materials. The CoTAPP/NiAl-LDH sample obtained by the adsorption of

CoTAPP was morphologically identical to the NiAl LDH Support (Fig. 1b). After the pyrolysis treatment @15001°C/60°S (0,3 KH sample morphology changed appreciably (Fig. 1c). The obtained catalyst, denoted herein as Co-N-C/NiAl-MMO, comprised small nanoparticles highly dispersed over thin sheets. Since the 500 °C pyrolysis step was expected to convert the NiAl-LDH into a NiAl mixed metal oxide (NiAl-MMO), some of the nanoparticles were likely NiO which has migrated from the NiAl-MMO to the surface (giving NiO/Al₂O₃). Thermal decomposition of the CoTAPP was expected to yield various Co nanoparticle species and N-doped carbon, which will also contribute the rich surface structure seen in Figure 1c. Fig. 1d shows the morphology of the Co-N-C nanoparticles obtained by direct pyrolysis of CoTAPP at 500 °C in N₂. The sample consists of sintered nanoparticles in the size range 50-120 nm.



Figure 2. (a) TEM and (b) HRTEM images of Co-N-C/NiAl-MMO. (c) SEM-EDS image and corresponding element maps for Co-N-C/NiAl-MMO.

To gain deeper insights about the structure of Co-N-C/NiAl-MMO, a TEM investigation was undertaken. Fig. 2a shows a TEM image Co-N-C/NiAl-MMO, showing the presence of many nanoparticles dispersed on a thin oxide support (the support is likely an amorphous NiAl oxide or amorphous Al₂O₃). The HRTEM image of Co-N-C/NiAl-MMO (Fig. 2b) showed nanoparticles with lattice fringes spacings of 0.205, 0.215 and 0.241 nm. These could readily be assigned to Co(111), CoO(200) and NiO(101) facets, respectively. The HRTEM study thus confirms that the Co(II) in CoTAPP is transformed to Co⁰ and CoO during CoTAPP/NiAl-LDH pyrolysis, whilst the NiAl-LDH becomes NiO/Al₂O₃ or a mixture of NiO/Al₂O₃ and NiAl-MMO (for simplicity, we will refer to the LDH-derived support as NiAl-MMO below). EDS elemental mapping analyses revealed a very homogeneous dispersion of Co, N, and C over the NiAl-MMO support (Fig 2c).

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Figure 3. XRD patterns for Co-N-C/NiAl-MMO and NiAl-MMO

Fig. S1 shows the XRD pattern of NiAl-LDH, which contains the characteristic (003), (006) and (110) reflections of a layered double hydroxide compound. The structures of Co-N-C/NiAl-MMO and NiAl-MMO (the product obtained by direct pyrolysis of NiAl-LDH at 500 °C) were also investigated by XRD (Fig. 3). The XRD patterns of NiAl-MMO and Co-N-C/NiAl-MMO show common peaks at 37.2, 43.3, and 62.8°, which can readily be assigned to the (111), (200) and (220) crystal planes, respectively, of NiO. These peaks are superimposed on a broad background, which can be attributed to amorphous alumina or a mixed NiAl oxide phase. The NiO formation was particularly evident for NiAl-MMO. Results are consistent with the following pyrolysis pathway: NiAl-LDH \rightarrow NiAl-MMO \rightarrow NiO/Al₂O₃. For, Co-N-C/NiAl-MMO, additional diffraction peaks were observed at 44.3° and 51.8°, which closely match the (111) and (200) planes of Co⁰ (JCPDS Powder Diffraction File No. 15-0806). No obvious diffraction peaks for CoO or Co₃O₄ were observed in the XRD patterns, though some CoO was seen by HRTEM. It is concluded that any cobalt oxide on Co-N-C/NiAl-MMO was highly dispersed and present at low loadings.²⁵



Figure 4. High resolution XPS spectra for Co-N-C/NiAl-MMO and NiAl-MMO. (a) Ni 2p region, (b) Al 2p region ,(c) Co $2p_{3/2}$ region (d) N 1s region, and (e) C 1s regions. Spectra for Co-N-C/NiAl-MMO are shown in black, those for NiAl-MMO in red.

X-ray photoelectron (XPS) was used to probe the metal and nonmetal speciation in Co-N-C/NiAl-MMO and NiAl-MMO. The XPS

survey spectra for Co-N-C/NiAl-MMO confirmed the presence of Ni, Al, Co, Ni, N and O. The Ni 2p spectra for 1961 To NYC/NGAH MMO and NiAl-MMO (Fig. 4a) were dominated by peaks due to Ni(II), showing peaks at 853.7 and 873.2 eV in a 2:1 area ratio. These can readily be assigned to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks of Ni(II) in NiO. The shake up satellites on the high binding energy side of the main Ni 2p peaks are also consistent with the presence of Ni(II).²⁶ The Al 2p spectra for Co-N-C/NiAl-MMO and NiAl-MMO show peaks at 73.9 and 74.6 eV respectively, typical for Al³⁺ in aluminas.²⁷ The slight shift between the Al 2p peak positions in Co-N-C/NiAl-MMO and NiAl-MMO will be due to the presence of the additional surface species in the former which will act as electronic modifiers. Fig. 4c shows the Co 2p_{3/2} XPS spectrum of Co-N-C/NiAl-MMO, which contains peaks due to Co^0 (Co $2p_{3/2}$ = 778.2 eV) and Co^{2+} (likely in the form of CoO, Co $2p_{3/2}$ = 780.0 eV with a corresponding shake-up satellite at higher binding energy).²⁸ Since the Co originated from CoTAPP, there is a possibility that Co single atom sites with a porphyrinlike coordination may also exist on the surface of Co-N-C/NiAl-MMO.²⁹⁻³¹ The high-resolution N1s spectrum of Co-N-C/NiAl-MMO (Fig. 4d) showed two nitrogen two states, pyridinic N (~397 eV) and pyrrolic N (~400 eV). These nitrogen sites will act as Lewis bases, stabilizing Co SACs and benefitting the immobilization of the Co nanoparticles.³²⁻³⁴ The C 1s spectrum of Co-N-C/NiAl-MMO (Fig. 4e) contained 3 components at 284.6, 285.1 and 286.2 eV, which can be attributed to C-C, C-N and C-O species, respectively.³⁵ The XPS data is thus consistent with the findings of the other techniques, indicating that the Co-N-C/NiAl-MMO catalyst contains surface Co⁰/CoO, NiO and Ndoped carbon on an oxide support (amorphous NiAl-MMO or Al₂O₃).



Figure 5. TG–DTA curves for CoTAPP/NiAl-LDH in $N_2.$ The heating rate was 10 $^{\rm o}\text{C/min}.$

Fig. 5 shows TG–DTA curves for CoTAPP/NiAl-LDH. A small mass loss was seen in the 30-230 °C region of the TGA curve, which can be attributed to the loss of surface physisorbed water and water from the LDH interlayer region. A much larger TGA mass loss was observed in the region 370-465 °C, which is consistent with the dehydroxylation of the NiAl-LDH layers and also decomposition of the interlayer NO³⁻ anions.³⁶ This coincides with the collapse of the LDH structure and the transformation of the support into a NiAl-MMO. A large exothermic peak was

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seen in the DTA curve in the same region, which can be attributed to the decomposition of both the LDH and surface adsorbed CoTAPP.³⁷ Accordingly, 500 °C was selected as the pyrolysis temperature for the synthesis of Co-N-C/NiAl-MMO catalyst in this work.



Figure 6 shows FT-IR spectra for CoTAPP, NiAl-LDH, CoTAPP/NiAl-LDH and Co-N-C/NiAl-MMO. As expected, the spectrum of CoTAPP/NiAl-LDH contains contributions from both CoTAPP and NiAl-LDH. The LDH shows band at 3496, 1633, 1345 and 400 cm⁻¹, which can be ascribed to O-H stretching modes of Brucite-layer hydroxyl groups and interlayer water (3496 cm⁻¹), bending vibrations of interlayer water molecules (1633 cm⁻¹), antisymmetric stretching mode (v_3) of interlayer carbonate (1345 cm⁻¹), and M–OH stretching vibrations in the brucite-like layers (400 cm⁻¹).³⁸ Interlayer nitrate in the LDHs can readily be exchanged for carbonate in aqueous solutions containing dissolved CO₂.³⁹ CoTAPP, shows many absorption peaks in the range 1600-1400 cm⁻¹ associated with stretching vibrations of the phenyl rings. C=N stretching vibrations of the porphyrin ring give rise to the 1345 cm⁻¹ peak, whilst the porphyrin ring skeleton vibrations produce the peak at 996 cm⁻ ¹. After pyrolysis at 500 °C for 5 h in N₂, the peaks characteristic of CoTAPP and NiAl-LDH disappeared, consistent with the transformation of CoTAPP/NiAl-LDH to Co-N-C/NiAl-MMO.

Catalyst	BET	BJH	BJH Pore	BJH Pore
	surface	surface	volume	diameter
	area	Area	(cm ³ /g)	(Å)
	(m²/g)	(m²/g)		
NiAl-MMO	53.32	52.91	0.0895	63.39
Co-N-C	41.53	40.50	0.0576	705.9

 N_2 physisorption at 77 K was used to probe the surface area and porosity of the Co-N-C/NiAl-MMO catalyst. These parameters have obvious implications for the catalytic properties of Co-N-C/NiAl-MMO, since a large area of surface will offer an abundance of actives sites for catalysis. Co-N-C/NiAl-MMO had a type IV adsorption isotherm, with a H₃-type hysteresis loop in 

H2-TPR experiments were subsequently carried out on NiAl-MMO and Co-N-C/NiAl-MMO, since the ability of these catalysts to adsorb hydrogen was very important to their function as hydrogenation catalysts. H₂-TPR curves are shown in Figure 8. For NiAl-MMO, an intense and broad reduction peak was observed in the temperature range 500-900 °C (maximum 677 °C), which is attributed to the reduction of NiO to Ni⁰ particles on the Al₂O₃ support.⁴¹ For Co-N-C/NiAl-MMO, a number of H₂ consumption peaks were observed in the 250-350 °C region. The first peak at 261 °C which is attributed to the reduction of Co₃O₄ to CoO, and the second reduction peak at 329 °C is attributed to the reduction of CoO to metal $Co^{0.42}$ Notably, the reduction peak of NiO shifted to the lower temperature compared with the NiAl-MMO sample, which is attibuted to hydrogen spillover from Co⁰ nanoparticles formed at lower reduction temperatures.43



HMF hydrogenation tests over various catalysts were conducted at 170 °C and 1.5 MPa H_2 over 6 h. The performance of the different catalysts are compared in the Table 2. The asprepared Co-N-C/NiAl-MMO catalyst showed a much higher catalytic activity (HMF conversion) than CoTAPP or the NiAl-MMO catalyst, whilst offering 100% selectivity to DMF. The 99.9% HMF conversion with 100% DMF selectivity after 6 h of reaction confirmed that Co-N-C/NiAl-MMO was an outstanding catalyst for this hydrogenation reaction.

 Table 2. Performance comparison of different catalysts for the selective hydrogenolysis of HMF.

Catalyst	Conversation %	Selectivity %		
		DMF	BHMF	MFA
Сотарр	8.8%	100%	-	-
NiAl-MMO	18.4%	91.0%	_	9.0%
Co-N-C/NiAl-MMO	99.9%	100%	_	_

Reaction conditions: HMF (0.25 g), tetrahydrofuran (THF, 10 mL), catalyst (0.1 g), T=170 °C, P(H_2)=1.5 MPa, 6 h.

In order to probe the outstanding catalytic performance of Co-N-C/NiAl-MMO for HMF hydrogenation in more detail, the effects of reaction time, temperature and H₂ pressure were studied (Figure 9a-c, respectively). Fig. 9a shows the effect of reaction time on the hydrogenation of HMF over the asprepared Co-N-C/NiAl-MMO catalyst. The HMF conversion and DMF selectivity progressively increased over the first 3 h of reaction. The BHMF and MFA selectivity initially increased during the initial stages of the reaction (first 10-20 min), then decreased at longer reaction times. Results suggest that for the Co-N-C/NiAl-MMO catalyst, the hydrogenation of the C=O double bond in HMF leading to BHMF is dominant in the initial reaction stages, which is then followed by the hydrogenation of the C-O single bond in BHMF leading eventually to MFA and finally DMF. Tests were conducted at 150, 160, 170, 180, 190, 200 and 210 °C under 1.5 MPa H₂ for 6 h (Fig. 9b). The HMF conversion increased with temperature in the range 150-170°C, with the DMF selectivity also increasing in this range (again at the expense of 5-methyl-2-furanmethanol, the intermediate in

the formation of dimethyl furan). They remained rial most constant in the range 170-200 °C, though 品3220CY@C3%格 selectivity decreased due to the production of furfuryl alcohol (FA). At 210 °C, no intermediate product was formed. But the aldehyde side chain fracture of HMF produced FA, accompanied by the formation of CO. On the basis of these tests, the lower temperature of 170 °C was selected for due to the lower energy input requirement. Fig. 9c shows the effect of H₂ pressure on the hydrogenation of HMF. In the absence of H_2 , HMF conversion was almost negligible (5.5%), with 2-hexanol (HOL) being the main product formed. When the H₂ pressure was increased to 0.5 MPa, a 99.4% HMF conversion and 96.9% DMF selectivity were obtained. Clearly, the presence of H₂ promotes the hydrogenation of HMF, an intuitive result. On increasing the H₂ pressure to 1.5 MPa, the selectivity to DMF increased slightly owing to conversion of the MFA intermediate. No changes were seen at higher H_2 pressures (> 1.5 MPa), indicating that the H_2 pressure was no longer rate limiting. 1.5 MPa was identified as the optimal hydrogen pressure, and thus used in subsequent experiments.



Figure 9. Effect of (a) reaction time, (b) temperature, (c) H_2 pressure, and (d) catalytic test run on the HMF hydrogenation performance of Co-N-C/NiAl-MMO. Reaction conditions: (a) 0.1 g catalyst, 1.5 MPa, 0.25g HMF, 170 °C (b) 0.1 g catalyst, 1.5 MPa, 6 h, 0.25g HMF (c) 0.1 g catalyst, 0.25g HMF, 6h, 170 °C, and (d) 0.1 g catalyst, 1.5 MPa, 0.25g HMF, 6h, 170 °C.

Based on the above results, we offer a possible reaction mechanism for the catalytic hydrogenation of 5hydroxymethylfurfural to 2,5-dimethylfuran on Co-N-C/NiAl-MMO (Scheme 2). Firstly, the basic sites on the catalyst surface activate H₂ to form hydrogen atom species (involving the Co⁰ nanoparticles which have mild ability as hydrogenation catalysts). The carbonyl oxygen of HMF adsorbs on the electrophilic CoO sites. Then the hydrogenation of the carbonyl group occurs via reaction with activated hydrogen atoms via a spill over effect, leading to the formation of BHMF. Subsequently, the active hydrogen species attack the adsorbed BHMF, leading initially to the formation of 5-methyl-2furanmethanol (MFA). The hydroxyl group in MFA can also be hydrogenated by H transfer from Co⁰, resulting in the formation and desorption of DMF. The hydroxyl group in MFA is activated for hydrogenation through adsorption on oxygen vacancies of CoO.

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Scheme 2. Proposed mechanism for the hydrogenation of HMF to DMF over the Co-N-C/NiAl-MMO catalyst. The purple circles are N-doped carbon.

The recyclability of the Co-N-C/NiAl-MMO catalyst for HMF hydrogenation to DMF was subsequently examined. Experiments were conducted under the standard test conditions. Between cycles, the catalyst was washed and heated to 300 $^\circ\text{C}$ under N_2 to remove organic species from the catalyst. Results are presented in Fig. 9d. The Co-N-C/NiAl-MMO catalyst maintained good performance over the first two runs, after which the HMF conversion and DMF yield dropped sharply. The catalyst retained only 31.7% of its initial activity during the third run. In order to explain sharp drop in the HMF conversion rate during the third run, the Co content in the aspreapred Co-N-C/NiAl-MMO catalyst and Co-N-C/NiAl-MMO-3 catalyst (i.e. catalyst after the thrid run) were determined by ICP-AES to probe a possible loss of the active Co component during the tests. The content of Co in Co-N-C/NiAl-MMO (1.43 wt %) was higher than that in Co-N-C/NiAl-MMO-3 (1.18 wt %), indicating that some Co was lost during repeated use of the catalyst. XPS was used to examine the form of various elements in Co-N-C/NiAl-MMO-3. As shown in Fig. S2, the valence states of Ni (Fig. S2a), Al(Fig. S2b) and N(Fig. S2d) in the catalyst did not change significantly during the tests, with the data for Co-N-C/NiAl-MMO-3 being comparable to that of the Co-N-C/NiAl-MMO catalyst. However, the Co 2p3/2 XPS spectrum (Fig. S2c) for Co-N-C/NiAl-MMO-3 showed the predominance of Co²⁺, indicating the loss of Co⁰. The total amount of nitrogen in the Co-N-C/NiAl-MMO-3 by XPS was lower than in Co-N-C/NiAl-MMO, indicating that lot of loss of N during the HMF hydrogenation tests. This was expected to alter the basicity of the catalyst and hydrogenation performance, consistent with experimental observations across runs 1-3.

To gain deeper insights about the changes in surface properties of the Co-N-C/NiAl-MMO catalyst that occurred during the HMF hydrogenation tests, NH_3 -TPD was applied to probe the surface acidity of Co-N-C/NiAl-MMO and Co-N-C/NiAl-MMO-3 (the catalyst after the third run). The TPD profiles for each catalyst are shown in **Fig. 10a**. The analysis reveals that there were two acid centers on the surface of the Co-N-C/NiAl-MMO



Figure 10. Characterization of surface acidity of the different catalysts. (a) NH_3 -TPD (b) Py-IR spectra for Co-N-C/NiAl-MMO and Co-N-C/NiAl-MMO-3.

Co-N-C/NiAl-MMO catalyst, a weak acid site and a strong acid site. However, the catalyst did not adsorb very much with (indicating that there were very few acid sites on the asprepared catalyst surface). In contrast, the Co-N-C/NiAl-MMO-3 catalyst had only a single strong acid site, but this enabled a very large amount of NH₃ adsorption. The acidity data for each catalyst determined by NH₃-TPD is summarized in Table 3. Pyridine adsorption IR (Py-IR) spectra were also collected for each catalyst to further probe the nature of the acidic sites (Fig. **10b**). For each catalyst, bands were observed at 1446 cm⁻¹ and 1491 cm⁻¹, consistent with pyridine adsorbed on Lewis acid sites. A further weak adsorption band at 1599 cm⁻¹, which is characteristic of pyridine interacting with OH groups through hydrogen bonding interactions (i.e. Bronsted acid sites), was observed for each catalyst.44 Based on the catalytic tests and surface acidity measurements (NH₃-TPD, pyridine adsorption studies), it can be concluded that acid sites are detrimental to HMF hydrogenation to DMF (instead an abundance of basic sites are beneficial for achieving high HMF conversions).

Table 3. Surface acidity data for different catalysts from NH ₃ -TPD profiles.							
	NH₃ desorption amount (mmol NH₃/g)						
	170°C	689°C	702°C				
Co-N-C/NiAl-MMO	0.801	8.31	_				
Co-N-C/NiAl-MMO-3*	-	_	22.0				

*following 3 cycles of HMF hydrogenation, with catalyst regeneration at 300 $^\circ\text{C}$ in N_2 between cycles.

CO₂-TPD measurements were carried out to obtain direct information on the surface basicity of NiAl-MMO, Co-N-C/NiAl-MMO and Co-N-C/NiAl-MMO-3 catalysts. As shown in Fig. 11, a very small CO₂ desorption peak centered at 556 °C was observed for NiAl-MMO. Co-N-C/NiAl-MMO showed a large desorption peak at 511°C, indicating the presence of a strong basic site. For Co-N-C/NiAl-MMO-3, an intense CO₂ desorption peak was seen at 703 °C, attributed to a very strong basic site.⁴⁴ Clearly, the strength of the basic site is important for efficient HMF hydrogenation. In the case of Co-N-C/NiAl-MMO, the basic sites allowed HMF adsorption via the carbonyl, but were not too strong that they prevented desorption of products. In comparison, the super strong basic sites on Co-N-C/NiAl-MMO-3 were not conducive for the desorption of adsorbed species, thus lowering the catalytic activity.



To further probe the changes in the Co-N-C/NiAl-MMO catalysts resulting from the HMF tests, a SEM examination of Co-N-C/NiAl-MMO-3 was undertaken (**Fig. S3**). After the third run, the catalyst retained a sheet-like structure though the nanoparticles on the surface of the catalyst were less abundant. This suggested nanoparticle loss by sintering during the regeneration step or loss of nanoparticles during catalytic reaction or the subsequent washing step. The XRD pattern for Co-N-C/NiAl-MMO-3 is shown in **Fig. S4**. The Co⁰ peaks were retained, but new peaks due to CoO appeared, indicating that partial conversion of Co⁰ to CoO occurred during the catalytic tests. The decrease in the amount of Co⁰ explains the loss in activity for HMF hydrogenation over the 3 cycles to tests. The appearance of CoO also enhances the Lewis acid acidity of surface, which again is detrimental to catalyst performance.

Conclusions

A Co-N-C/NiAl-MMO catalyst was successfully prepared by pyrolysis of a CoTAPP/NiAl-LDH precursor at 500 °C in N₂ for 5 h. The as-prepared Co-C-N/NiAl-MMO catalyst offered remarkable activity for 5-hydroxymethylfurfural hydrogenation to 2,5-dimethylfuran in THF under mild reaction conditions (170 °C, 1.5 MPa H₂, reaction time = 6h). Under these optimized testing conditions, 100% HMF conversion was achieved with a DMF yield of 99.9%. However, the stability of the catalyst was modest, with a sharp drop in activity observed on a third cycle of catalytic testing. This loss in activity was due primarily to Co⁰ oxidation to CoO, which reduced the surface sites for H₂ dissociation. If the active Co⁰ sites could be stabilized, the Co-N-C/NiAl-MMO catalyst would be an excellent all-round catalyst for HMF hydrogenation to DMF under mild conditions.

Experimental

Materials

Dimethylformamide (C_3H_7NO , $\geq 99.5\%$), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, >98%) and cobalt chloride hexahydrate (CoCl₂·6H₂O, $\geq 99\%$) were purchased from TianJing KaiTong Chemical Reagent Co. Ltd. Aluminum nitrate nonhydrate (Al(NO₃)₃·9H₂O, >97%) was purchased from BASE Chemical Trading Co. Ltd (TianJin, ChinH).¹⁰ BER2aldeffyde (C₆H₅CHO, >98.5%), Propionic acid (CH₃CH₂COOH, \geq 96.0%) and pyrrole (C₄H₅N, 99%) were purchased from Macklin Chemical Reagent Co. Ltd. Distilled deionized water was utilized through the experiments. The hydrogen gas used had a purity of 99.9%.

Synthesis of 5,10,15,20-tetra(4-pyridyl)-porphyrin

Pyrrole (6.7 g) was dissolved in 30 mL of propionic acid, which was then added dropwise into a solution of benzaldehyde (10.6 g) in propionic acid (200 mL) at 130 °C under continuous magnetic stirring. After the addition of the pyrrole solution, the reaction was maintained at 130 °C for 1 h. After cooling the reaction vessel to room temperature, 100 mL of water was added and the vessel placed in the refrigerator at 4 °C for 24 h to allow the 5,10,15,20-tetra(4-pyridyl)-porphyrin product to crystallize. The product was collected by filtration and washed several times with water, then air dried.

Preparation of cobalt 5,10,15,20 tetrakis (4-aminophenyl)-21H, 23H-porphine (CoTAPP)

The method used to synthesize CoTAPP was as follows. 5,10,15,20-tetra(4-pyridyl)-porphyrin (1 g) was added to 100 mL of N,N-dimethylformamide and the solution heated to reflux. Next, $CoCl_2 \cdot GH_2O$ (3 g) was added to the mixture and resulting solution refluxed for 1 h. After cooling to room temperature, 100 mL of water was added to the solution, and the flask containing the CoTAPP placed in a refrigerator for 12 h to crystallize the product. The product was collected by vacuum filtration, washed with ethanol, then air dried.

Preparation of Co-N-C/NiAl-MMO

The NiAl-LDH was prepared by a co-precipitation method that used urea. Briefly, 0.02 mol of Ni(NO3)2·6H2O, 0.01 mol of $Al(NO_3)_3 \cdot 9H_2O$ and 0.1 mol of urea were dissolved in water (50 mL), then the resulting solution heated at 120 °C for 24 h. The NiAl-LDH product was collected by vacuum filtration, washed with water, and then air dried. CoTAPP (0.2 g) was dissolved in 50 mL of ethanol, then the resulting solution sonicated for 2.5 h. Next, NiAl-LDH (0.2 g) was added and the resulting dispersion stirred for 5 hours at room temperature. The resulting dispersion was then evaporated to dryness under a flow of N₂. After drying, the solid product was transferred to a quartz boat and then heated in a tube furnace from room temperature to 500 °C at 5 °C/min under N₂. After heating at 500 °C for 5 h (under an N₂ atmosphere), the sample was cooled to room temperature. The product obtained here is denoted as the Co-N-C/NiAl-MMO catalyst. A NiAl-MMO reference catalyst was prepared by heating NiAl-LDH at 500 °C for 5 h under N₂.

Catalytic Tests

The hydrogenation of 5-hydroxymethylfurfural catalytic tests were carried out in a stainless reactor with a 50 mL Teflon sleeve. In a typical experiment, the reactor was loaded with 5-hydroxymethylfurfural (HMF, 0.25 g), tetrahydrofuran (THF, 10 mL) and catalyst (0.1 g), then sealed and purged three times with H_2 . The reactor was then pressurized to 1.5 MPa with H_2 .

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The hydrogenation reaction was conducted at 170 $^{\circ}$ C over 6 h using a stirring speed of 500 rpm. Following the reaction, biphenyl was added to the reaction mixture as an internal standard, after which the reaction mixture was analyzed by using a Shimadzu GC-2010 gas chromatograph equipped with a AE-SE-54 column and a flame ionization detector (FID).

Catalyst Recycling Tests

For the catalyst recycling tests, the catalyst was collected after the HMF hydrogenation reaction, washed three times with ethanol, dried at 80 °C under vacuum, then finally heated in N_2 at 300 °C for 3 h.

Characterization

SEM analyses were carried out on a NoVaTM Nano SEM 430 scanning electron microscope (FEI, USA) operating at an electron acceleration voltage of 20 kV. AFM images were collected on a Multimode Nanoscope IIIa atomic force microscope (Veeco, USA) operating in tapping mode. High resolution transmission electron microscopy (HRTEM) images were collected on a FEI Tecnai G20 (USA) instrument operating at an accelerating voltage of 300 kV. XRD patterns were obtained at a scanning rate of 2 °/min on a Rigaku Smartlab SE XRD diffractometer, equipped with a Cu K α source (λ =0.154 nm, 40 kV). TGA analyses were carried out in air on a thermogravimetric analyzer (TA SDT Q600). The air flow rate was 100 mL/min and the heating rate was 10 °C/min. FT-IR spectra were collected over the range 4000 to 400 cm⁻¹ on a Thermo Scientific Nicolet 380 spectrometer (USA). Spectra were acquired at a resolution of 4 cm⁻¹, with 32 scans co-added to produce each spectrum. XPS measurements used a K-Alpha XPS system (Thermo Fisher Scientific, USA) equipped with a monochromatic Al K α source (h ν = 1486.6 eV). The binding energy scale was corrected using the C 1s signal of adventitious hydrocarbons (284.8 eV). N₂ adsorption-desorption isotherms were collected at 77 K on a Tristar3000 instrument (Micromeritics Instrument Corp). Samples were degassed at 533 K prior to the acquisition of the isotherms. The surface area and pore volume of samples were calculated using BET and BJH methods, respectively. Temperature programmed desorption of NH₃ (NH₃-TPD) experiments were conducted on the AutoChem II 2920 V5.02 instrument (Micromeritics Instrument Corp). For the NH₃-TPD experiments, samples (80 mg) were pretreated under an argon atmosphere at 300 °C for 2 h to remove surface adsorbed species. The samples were then cooled to 50 °C, after which they were exposed to a 2000 ppm NH_3/Ar atmosphere for 2 h to achieve NH_3 adsorption saturation. Next, the catalyst was exposed to an Ar flow (50 mL/min) for 1 h. Finally, the sample was heated from 50 °C to 800 °C at a heating rate of 10 °C/min and NH₃ evolved as a function of temperature recorded. Pyridine-infrared (Py-IR) spectra were recorded on a PE Frontier FT-IR Spectrometer (PerkinElmer). Samples were degassed under vacuum at 350 °C for 2 h, after which pyridine vapor (saturation vapor pressure) was adsorbed at room temperature for 0.5 h. The FT-IR spectrum of the samples were then collected to determine the

amount of pyridine adsorbed on each sample_{Vi} E_{00} T_{ci} H_{20} Three analyses, catalysts were heated at 300 °C for 20 H H_{20} $H_{$

Conflicts of interest

There are no conflicts to declare.

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