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Effect of DMSO on the catalytical production of 2,5-bis(hydroxymethyl)furan from 5-hydroxymethylfurfural over Ni/SiO₂ catalysts

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Hydroconversion of 5-hydroxymethylfurfural (HMF) to 2,5-bis(hydroxymethyl)furan (BHMF) was studied over mono- and bimetallic supported catalysts. It was found that monometallic Ni/SiO₂ catalysts exhibited superior performance with a total yield of BHMF of up to 99 wt.%. This excellent performance may be attributed to higher Ni dispersion and low acidity of the support. Dimethyl sulfoxide (DMSO) is often present in HMF, due to the route used for its synthesis. DMSO adsorption caused a clear reduction of Ni/SiO₂ performance for the HMF hydrodeoxygenation reaction. Characterization of the spent catalysts were performed using HAADF-STEM-EDX, Raman, ICP, and XPS spectroscopies, and showed the presence of sulfur and graphitic carbon, which could explain the deactivation.

Consequently, BHMF may also contribute to the development of hydrodeoxygenation processes to produce other platform chemicals. Different by-products can be obtained due to over hydrogenation which is considered as the key challenge to control the selectivity of this process. To address this issue, heterogeneous catalysts have received considerable attention. In this light, the efficiency of several noble metals (including Pt, Pd, Ru and Rh) for the catalytical production of BHMF has been demonstrated. Recently, HMF was hydrogenated to BHMF with complete conversion and 98.9% selectivity using a Pt/MCM-41 catalyst in an aqueous medium. It was also reported that HMF was converted to BHMF in water over Au sub-nano clusters supported on γ-Al₂O₃ with 96% yield being achieved at 120 °C in 2 h under an initial H₂ pressure of 65 bar. A higher selectivity of 99% of BHMF was obtained using an Ir-ReOₓ catalyst in water.

Previous studies indicate that the metal species strongly affects the selectivity of the products, while the nature of the support influenced significantly the activity of the catalysts. The metal species effect and control of the products distribution on various supports were investigated by Cai et al. The results showed that the Pd/γ-Al₂O₃ and Pd/SiO₂ did not enhance the catalytic activity of BHMF compared to Pd/TiO₂ and Pd/C. However, the yield of THFDM was higher for Pd/γ-Al₂O₃ and Pd/SiO₂ than those of Pd/C and Pd/TiO₂, indicating that the product selectivity is sensitive to the choice of support. By selecting the proper metal species and support, BHMF selectivity was further enhanced to 95.4 % over Ir/TiO₂ catalyst, indicating that the metal catalyst exhibits the

Introduction

The utilization of renewable resources and development of effective processes for their conversion are critical future developments for the chemical industry. 5-hydroxymethylfurfural (HMF), produced from dehydration of cellulose and hexoses, is a renewable platform candidate for achieving significant production of high value-added intermediates such as 2,5-bis(hydroxymethyl)furan (BHMF), 2,5-dimethylfuran (DMF), 5-methyl-2-furanmethanol (MFM), 1,6-hexanediol (HD), tetrahydrofuran-2,5-dimethanol (THFDM), and caprolactone. Despite its potentially versatile application, HMF production has some economic challenges, such as raw materials availability and cost.

Besides the effectiveness of the catalyst for achieving higher yield and selectivity, this process also requires separation and purification of the HMF from high boiling solvents such as DMSO, by-products, and unreacted fructose. However, efficient separation is costly. If there are residues of the solvent DMSO after separation, it may affect the activity and stability of the metal catalysts used for the downstream processing of HMF.

Among these promising intermediates, the BHMF molecule can be formed by selective hydrogenation of the C=O bond in HMF.

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potential for selectively hydrogenating the carbonyl group while leaving the C=O bond unchanged to form BHMF 22.

Non-noble metal catalysts have been examined and constitute an attractive solution in terms of their abundance, good stability and high cost-effectiveness. Efficient hydrogenation of HMF into BHMF was performed using a Cu/SiO₂ catalyst, obtaining as high as 97% BHMF yield 23. It was also reported that 94.8% of BHMF selectivity and 97.5% conversion were obtained over a CuO-Fe₂O₃/AC bimetallic nanocatalyst supported on activated carbon at 150 °C for 5 h 26. Zhang et al showed that Ni catalysts were effective for the hydrogenation of HMF. A high yield of BHMF was obtained at 160 °C for 24 h, with a selectivity of 94% with HMF conversion of 93.6% using 10% Ni/hydrothermal carbon 27. More recently, Yu et al. disclosed that Ni-Fe/CNTs bimetallic catalysts in carbon nanotubes were active and totally converted HMF, with a selectivity to BHMF of 96.4 % at 120 °C for 3 h 28.

Recently, Luo et al 29,30 highlighted the importance of using a flow reactor to show the initial hydrogenation of HMF using 1-propanol. By varying the space time in the reactor, HMF reacted first to furfuryl ethers and other partially hydrogenated products, which then formed DMF with different selectivity depending on the metal catalyst 29,30. It is important to note that these reactions are applicable to specific solvents. Various alcohol solvent effects were studied and it was shown that BHMF can be etherified to 2,5- bis(alkoxy)methyl)furfurans (BAMFS) through simple addition of a proton donor 25,31-33.

We start this study by comparing different noble and non-noble metal catalysts. We found Ni/SiO₂ to be the most selective catalyst in addition at lower costs than the noble metal catalysts. We therefore continued the studies using this catalyst, examining the effect of metal content. Moreover, HMF contains some residuals of DMSO solvent, which due to its sulfur content can result in catalyst deactivation 17,18. However, to the best of our knowledge, there are no available studies where the effect of DMSO has been disclosed for the catalytic activity of HMF hydrogenation. In this work we therefore examine the effect of DMSO on the selective hydrogenation of HMF to BHMF over Ni/SiO₂ using both high pressure reactor experiments as well as catalyst characterization in order to study the poisoning effect.

Experimental

Materials

HMF (≥ 99% purity), DMF (≥ 98% purity), DMSO (≥ 99.5% purity), THFDM (98% purity), n-butanol (99% purity) were purchased from Sigma Aldrich. BHFDM (≥ 98% purity) was procured from BIOSYNTH Carbonsynth. γ-Al₂O₃ (Puralox SCCa 150/200, Sasol), SiO₂ (>99.0%, Catalyst support, Alfa Aesar), Amorphous SiO₂-γ-Al₂O₃ (Sigma Aldrich, grade 135), Ni(NO₃)₂·6H₂O (99.99%, Sigma Aldrich), Co(NO₃)₂·6H₂O (99.99%, Sigma Aldrich), Ru(NO)(NO₃)₂ (1.8% Ru solution, Strem Chemicals), and Pd(NO₃)₂ (quality level 100, Sigma Aldrich) were used to prepare the catalysts for BHMF hydrogenation. A commercial catalyst Pd/C (5 wt.% Pd loading, Sigma Aldrich) was compared to catalysts prepared. Further analysis of HMF as received from the supplier using ICP analysis (ALS Scandinavia AB, Luleå, Sweden) revealed that it contained 0.5 wt.% DMSO.

Catalyst synthesis

Metal-loaded catalysts were synthesized by an incipient wetness impregnation route. Firstly, γ-Al₂O₃, SiO₂, Alumina-Silica (Al-Si) supports were calcined in air at 550 °C for 4 h. The SiO₂ pellets were ground and sieved to a particle size ≤ 250 µm. Then, the calcined supports were impregnated with aqueous solutions of Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Ru(NO)(NO₃)₂, Pd(NO₃)₂ and Pt(NO₃)₂. The impregnated catalysts were dried at 110 °C overnight. The amounts of active metals, and supports are summarized in Table 1.

Hydrogenation reactions

Hydrogenation of HMF was carried out in a 450 mL autoclave supplied by Parr Instruments Co. USA. Prior to hydrogenation reactions, 1 g of each catalyst was reduced with 25 bar H₂ at 450 °C for 6 h. Then, the reduced catalyst was passivated under 2% O₂/Ar at a flow rate of 25 ml/min for 1h at room temperature. In a typical experiment, a mixture of 1 g reduced catalyst, and 5 g HMF dissolved in 80 g of n-butanol were loaded into the reactor. After sealing the reactor, it was subsequently flushed 3-5 times with nitrogen to expel the air and then purged with hydrogen three times. After leak testing, the reactor was pressurized and heated up to a designated temperature. The time zero and stirring at 700 rpm were set once the desired reaction temperature and pressure were reached.

The prepared monometallic and bimetallic catalysts (Table 1) were screened by experiments at 130 °C and 40 bar H₂ for 6 h. Subsequently, the most selective of these catalysts was further investigated with different metal loadings at 180 °C and 75 bar for 6 h. Under similar conditions, the effect of DMSO was examined for HMF hydrogenation over the 15Ni/SiO₂ catalyst using a series of DMSO concentrations (0.08 g, 0.16 g and 0.4 g DMSO). Note that the first point (0.025g) is the HMF as received, since it contains 0.5 wt.% of DMSO. Samples were collected every 1 h during reaction, and the final sample was taken directly just before cooling the reactor to room temperature. Afterward, the catalysts were separated from the reaction mixture using a PTFE membrane filter, then washed and stored under ethanol.

Catalyst Characterization

The textural properties of silica supported Ni catalysts such as specific surface area, pore volume, and pore size were measured by N₂-physisorption using a TriStar 3000 gas adsorption analyzer. Prior to N₂-physisorption, 300 mg of samples were degassed under vacuum at 250 °C for 4 h. After drying, the N₂-physisorption isotherms were collected at -195 °C under a reduced pressure. The specific surface area was calculated by the
Table 1. Summary of relevant properties of the catalysts used in this study.

| Catalysts      | Metal loading, wt.% | Support, wt.% | Notation    |
|----------------|---------------------|---------------|-------------|
|                | Ni  | Pd  | Co  | Ru  | Al₂O₃ | SiO₂ | Al-Si | C |
| Ni/SiO₂        | 5   | -   | -   | -   | -     | 95   | -     | - | 5Ni/SiO₂ |
|                | 10  | -   | -   | -   | -     | 90   | -     | - | 10Ni/SiO₂ |
|                | 15  | -   | -   | -   | -     | 85   | -     | - | 15Ni/SiO₂ |
| Ni/Al₂O₃       | 20  | -   | -   | -   | 80    | -    | -     | - | 20Ni/Al₂O₃ |
| Ni-Pd/SiO₂     | 8   | 2   | -   | -   | -     | 90   | -     | - | 8Ni-2Pd/SiO₂ |
| Ni-Pd/Al₂O₃    | 15  | 2   | -   | -   | -     | 83   | -     | - | 15Ni-2Pd/Al₂O₃ |
| Ni-Pd/Al-Si    | 15  | 2   | -   | -   | -     | 83   | -     | - | 15Ni-2Pd/Al-Si |
| Ni-Co/Al₂O₃    | 5   | -   | 5   | -   | -     | 90   | -     | - | 5Ni-5Co/Al₂O₃ |
| Ru/Al₂O₃       | -   | -   | -   | 2   | 98    | -    | -     | - | 2Ru/Al₂O₃ |
| Pd/C           | -   | 5   | -   | -   | -     | -    | -     | 95| 5Pd/C |

40 kV and 40 mA using Cu Ka radiation (λ=1.542 Å) with the 2θ range of 15-70° and the scan speed of 1°/min.

The size and dispersion of Ni particles on the silica support were determined by CO chemisorption using an ASAP2020 Plus instrument (Micromeritics). The measurements were performed on the as-prepared materials. Approximately 100 mg of the sample was degassed in He, evacuated in vacuum at 110 °C and reduced in H₂ at 450 °C for 4 h.

The sample was then flushed and cooled to 35 °C in He. After that, sample was evacuated to vacuum before conducting the first total isotherm in the pressure range from 100 to 600 mmHg (intervals of 25 mmHg). When the first isotherm was completed, the sample was evacuated to remove physically adsorbed CO before the second isotherm was repeated in the same way as the first measurement. The difference between the two isotherms provides the chemisorbed CO. The intercept of a linear regression curve fit from the isotherm of chemisorbed CO was assigned to the amount of adsorbed CO on a monolayer of the metal surface. The stoichiometry factor Fₛ was determined with equation (2):

\[
F_s = \frac{101}{D_M(\text{nm})} 
\]  

(2)

The Ni and sulfur contents of the fresh and spent Ni/SiO₂ catalysts were measured by inductively coupled plasma and sector field mass spectroscopy (ICP-SFMS) by ALS Scandinavia AB, Luleå, Sweden. The STEM images of the spent catalysts were acquired using a FEI Titan 80-300, operating at 300 kV. Prior to STEM, samples were kept in ethanol to preserve their reduced/sulfided states.

X-ray photoelectron spectroscopy (XPS) measurements were done to investigate the chemical state of the Ni phase of the catalysts using a PHI 5000 Versa Probe III–Scanning XPS Microprobe™ system. Samples were placed on carbon rubber pads situated on a sample holder. The XPS spectra were collected using a monochromatic Al Kα source with a binding energy of 1486.6 eV. Sample charge neutralization was done on all samples. The C 1s contamination line with a binding energy of 284.6 eV was taken as a reference for all obtained spectra. The Ni 2p core level spectrum includes Ni 2p1/2, Ni 2p3/2, and shakeup satellites were deconvoluted by fitting a Gaussian – Lorentzian function with a Shirley background. The peak positions and areas were optimized until the standard deviation (δx) stabilized to a minimum at 0.3.
carbon recovery reached 91.6-98.5% (Figure 1b), which is similar
in sharp contrast, the 2Ru/Al2O3 and 5Ni-5Co/Al2O3 catalysts did not produce BHMF, instead, they were more selective towards hydrogenolysis of the C=O bond of the aldehyde group of HMF to produce MFM (C in Scheme 1). MFM could also possibly be produced sequentially, where the BHFHM is dehydrated to form MFM (dehydration of alcohols, B in scheme 1). Some THFDM (E in Scheme 1) was also observed for noble metal and alumina supports, such as 2Ru/Al2O3, which could be explained by hydrogenation of the BHMF. It is important to mention that higher selective BHMF catalysts Ni-Pd/SiO2, Ni/SiO2, 2Ru/Al2O3, Ni-Pd/Al-Si, and Pd did not form MFM product.

Moreover, comparing Ni-Pd/Al2O3 with Ni-Pd/Al-Si, which contain the same amount of Ni and Pd, it is clear that the more acidic Ni-Pd/Al2O3 produces more MFM and no DMF (D in Scheme 1). However, DMF was further produced over Ni-Pd/Al-Si and Pd/C that may be due to conversion of MFM on acid sites associated with the carbon and Al/Si supports and Pd. These findings indicated that the type of supports correlated with metal had a synergistic effect on the catalytic activity and selectivity. In fact, the results in Figure 1a reveal that all alumina supported catalysts displayed higher selectivity towards the production of MFM. This implies that the reactions catalyzed by alumina are typical acid catalyzed such as the dehydration of alcohols and cyclohexene 38–39. Therefore, the acid sites may convert partially or totally the intermediate BHMF formed to the MFM product via a deoxygenation of the C—OH bond of the alcohol group of BHMF. Conversely, the weak acidic nature of silica supported catalysts, 15Ni/SiO2 and 8Ni-2Pd/SiO2, showed the highest selectivity towards hydrogenation of the aldehyde group of HMF to produce BHMF, with close to 100% selectivity for Ni/SiO2. It is noteworthy to mention under the performed conditions using 1-butanol as the solvent, that neither ether compounds nor ring-opened products were formed. Hence, the development of efficient catalyst systems, based on different Ni loadings over SiO2, are promising for selective hydrogenation of HMF to BHMF.

Effect of Ni loadings for Ni/SiO2.

Table 2 presents the nickel content and textural properties of silica supported Ni catalysts. The ICP analysis showed that the measured Ni contents of the catalysts were close to the intended Ni content values. The N2 physisorption results show that an increase in the nickel content resulted in a slightly decreased specific surface area, and pore volume of the Ni/SiO2 catalysts. This could be explained by some pore blockage due to the addition of Ni.

The average crystallite size and dispersion of Ni particles on the as-prepared Ni/SiO2 catalysts were measured by using CO chemisorption (Table 2). Note that the as-prepared materials were simultaneously calcined and reduced by the pretreatment step before the measurements. A trend of decreasing dispersion with an increase of the Ni loading was observed, although the dispersion of Ni remained relatively high, i.e. 87.1 and 58.6% for 5 and 10 wt.% Ni, respectively. However, a further increase in Ni loading to 15 wt.%
caused a substantial decrease in the dispersion to 8.6%. Notably, the relationship between the loading and the dispersion of Ni fits well with a linear regression (Figure 2a).

It is also important to consider a trade-off between the metal loading and the dispersion of the particle. In this regard, the sample 10Ni/SiO$_2$ had the greatest surface area of metallic Ni per gram of catalyst, 39.8 m$^2$ g$^{-1}$ (Table 2), which was approximately four-fold higher than that of the 15Ni/SiO$_2$ catalyst. Such high dispersion of Ni in the 5Ni/SiO$_2$ and 10Ni/SiO$_2$ catalysts resulted in small average Ni particle sizes of 1.2 and 1.7 nm, respectively. Thus, the 10Ni/SiO$_2$ that had both a high dispersion and a high Ni loading had the highest exposed metal surface. However, the 15Ni/SiO$_2$ with a high loading of Ni had significantly larger crystallite size (11.8 nm), which caused a very low exposure of surface Ni sites, even though the total Ni weight was the largest. We suggest that the direct reduction of the impregnated Ni/SiO$_2$ materials plays an important role in the high dispersion of Ni in the resulting catalysts as reported in the literature $^{39}$.

After CO chemisorption measurements, the catalysts were characterized with XRD and the results are shown in Figure 2b. Apart from a broad peak around $2\theta = 22.5^\circ$ for the amorphous silica support $^{40}$, metallic Ni reflections were observed on the samples with a significant difference in the intensity. The Ni reflections on the 5Ni/SiO$_2$ sample almost vanished, indicating highly dispersed Ni particles. Note that XRD measurement is usually not effective to detect crystallites smaller than 3 nm $^{41}$. By contrast, the Ni reflections were the most intense for the 15Ni/SiO$_2$ sample. The crystallite size calculated by the Scherrer equation for the main reflection at $2\theta = 44.5^\circ$ was approximately 12.6 nm. These results agree well with the data obtained from the CO chemisorption measurements, where a particle diameter of 11.8 nm was found (see Table 2).

Table 2. Textural properties, elemental and ICP analysis of Ni content of Ni/SiO$_2$ catalysts

| Samples     | 5Ni/SiO$_2$ | 10Ni/SiO$_2$ | 15Ni/SiO$_2$ |
|-------------|-------------|--------------|--------------|
| BET surface area (m$^2$/g) | 100.1 | 96.4 | 93.3 |
| Average pore size (Å) | 121.3 | 114.5 | 109.3 |
| Pore volume (cm$^3$/g) | 0.37 | 0.33 | 0.31 |
| Ni (wt.%)$^*$ | 5.1 | 10.2 | 15.9 |
| Ni dispersion (%) | 87.1 | 58.6 | 8.6 |
| Metallic surface area (m$^2$ g$^{-1\text{metal}}$) | 579.5 | 390.2 | 57.0 |
| Metallic surface area (m$^2$ g$^{-1\text{cat}}$) | 29.5 | 39.8 | 9.1 |
| Ni crystallite diameter (nm)$^*$ | 1.2 | 1.7 | 11.8 |

$^*$ Inductively coupled plasma and sector field mass spectroscopy (ICP-SFMS). * hemisphere shape

Figure 2. Relationship between the loading and the dispersion of Ni on the Ni/SiO$_2$ catalysts (a), the XRD patterns of the Ni/SiO$_2$ materials after CO chemisorption measurements (b).

Figure 3. XPS spectra of the Ni 2p (a), O 1s (b) and Si 2p (c) of the reduced Ni/SiO$_2$.

Scheme 1. Reaction network for HMF hydrodeoxygenation using various catalysts.
Initially, from 1 to 3 h reaction, HMF conversion was achieved with 100% selectivity to BHMF. This suggests that BHMF, as the main product, was produced via hydrogenation of the aldehyde group of HMF, suppressing the formation of other byproducts. Despite that the total HMF conversion was maintained beyond 4 h, a minor decrease in BHMF selectivity along with formation of small amounts of DMF and MFM was observed. In comparison to the moderate reaction temperature at 130 °C (Figure 1a), higher reaction temperature 180 °C along with increased residence time may be the reason that generation of small amounts of byproducts was observed. Our results are consistent with previous reports, where higher temperature suppress BHMF production. However, for our case the DMF production was only minor.

The excellent performance of the 10Ni/SiO₂ catalysts for HMF hydrogenation might be due to a combined outcome of excellent dispersion of Ni nanoparticles (<2 nm) on the surface (Table 2) and the low acidic silica support, which makes it extremely effective as well as selective for HMF hydrogenation towards BHMF. The main reason for the activity of the Ni nanoparticles can be considered an association between the surface of Ni and the furanic ring of HMF in which C=O functional group of the furan ring is bonded to the Ni surface via both its C and O atoms which leads to the highly selective formation of BHMF.

**Effect of DMSO on HMF hydrogenation to BHMF**

During HMF production, DMSO is often used as a solvent. Indeed, our purchased HMF contained 0.5 wt.% DMSO. Since DMSO contains sulfur, and sulfur is known to be a catalyst poison, it is important to study the effect of the DMSO present in the HMF. We have therefore doped the feed for the reaction, with additional DMSO. The most optimum catalyst, i.e. 10Ni/SiO₂, exhibited over 80% conversion in the first data point and over 90% in the second point (Figure 4a), which makes it difficult to properly study the deactivation over time due to the very high activity. In order to study the effect of DMSO, we therefore chose 15Ni/SiO₂ so that the effect of DMSO during the whole experiment of 6 h could be examined.

![Figure 4. HMF hydrogenation conversion over Ni loadings for Ni/SiO₂ catalysts (a), and the product yield distributions for HMF hydrogenation over 10Ni/SiO₂ (b). The reactions were performed at 180 °C, 40 bar H₂, 6 h.](image)

Figure 4a presents the HMF conversion and product yields during the hydrogenation reactions over the silica supported Ni catalysts. The experiments were performed at 180 °C, under 75 bar of H₂ for 6 h. A complete HMF conversion was achieved after 3 h reaction over the 10Ni/SiO₂ catalyst. The reaction with 5Ni/SiO₂ and 15Ni/SiO₂ catalysts reached full conversion within 6 h (Figure 4a). It was observed that HMF conversion and selectivity to BHMF increased as the Ni loading increased from 5Ni/SiO₂ to 10Ni/SiO₂. While a further increase in metal loading (>10%) led to slower hydrogenation kinetics with lower conversion rates. This may be due to lower Ni dispersion (see Figure 2a). Since, the 10Ni/SiO₂ catalyst showed the highest activity with complete conversion of HMF, the selectivity to BHMF was also examined to assess the reaction pathways (Figure 4b).

![Figure 5. HMF conversion of the hydrogenation reaction with different concentration of DMSO over 15Ni/SiO₂ catalyst. Operating conditions: 180 °C, 75 bar H₂, for 6 h.](image)
Figure 5 presents the effect of DMSO doping on the conversion of HMF using 15Ni/SiO₂. The results clearly show a poisoning effect when the concentration of DMSO increased from 0.5 wt.% to 8.5 wt.%. Moreover, after 6 h reaction, the experiment with the lowest amount of DMSO (0.5 wt.%) showed the highest HMF conversion (98%), whereas the lowest HMF conversion of only 56% was observed at the highest amount of DMSO (8.5 wt.%). Similar trends of HMF conversion were observed for all experiments during the reaction time. This trend is consistent and having the same functional dependence on DMSO concentration which potentially affects the activities of the catalysts, particularly at the initial period of the reactions.

It has previously been reported that DMSO can be decomposed to produce hydrogen sulfide over solid catalysts and in the presence of hydrogen. Then, the produced hydrogen sulfide can act as a sulfur poison for most metal catalysts. To evaluate such a hypothesis, the sulfur contents of the spent catalysts were measured by ICP-SFMS, XPS and STEM-EDX analysis. The ICP analysis showed the presence of sulfur in the spent catalysts. The sulfur content increased from 0.13 wt.% to 0.5 wt.% when the DMSO concentration increased from 0.5 wt.% to 8.5 wt.%. The XPS analysis of the spent catalysts did not show any sulfur contamination since the sulfur content of the spent catalysts, previously measured by ICP-SFMS, was lower than the XPS instrument detection limit of 1 %. The Ni loading of the catalysts was 15 wt.%, therefore, a low sulfur contamination of less than 1 wt.% may not be the only reason for the observed drastic inhibition of the hydrogenation.

The results in Table 2 showed a Ni dispersion of 8.6% and a particle size of 11.8 nm for 15Ni/SiO₂. An estimate of the S/Ni surface atom ratio (sulfur from ICP of spent catalyst, and Ni surface atoms based on ICP and dispersion) was made assuming that all sulfur was bound to Ni (see next paragraph for STEM-EDX that supports this assumption). This resulted in a ratio of 0.095, 0.10, 0.11 and 0.37, respectively. Thus it is clear that not all Ni surface atoms were blocked by sulfur species, but that part of the deactivation is likely originating from sulfur inhibition. These results are consistent with observations that an organosulfur agent can react with hydrogen over a catalyst to generate hydrogen sulfide and thereby act to sulfide the catalyst. These results are also in agreement with the S-Ni diagram presented by Wand and Liu and confirmed by Lakhapatri and Abraham suggesting that the sulfur compounds decompose to hydrogen sulfide, which adsorbs dissociatively on the metal surface, thereby forming a sulfur layer. The Ni-surface layer inhibits chemisorption of small molecules leading to catalyst deactivation.

Figure S1 presents a HAADF-STEM micrograph and the corresponding EDX spectra of the 15Ni/SiO₂ catalyst that was spent from the HMF hydrogenation reaction using 8.5 wt.% DMSO. The EDX spectra identified Ni particles supported on the silica support (Figure S1b). After reaction with 8.5 wt.% of DMSO in the feed, presence of sulfur in the vicinity of Ni particles was confirmed. Furthermore, no sulfur on silica support was observed as can be seen in the EDX analysis at positions 2 and 4.

The existence of carbon deposits on the catalyst surface was confirmed by Raman spectroscopy. Figure 6 represents the Raman spectra of carbon deposition on the spent 15Ni/SiO₂ catalysts exposed to 8.5 and 0.5 wt.% DMSO. The G band which appears at 1565 cm⁻¹ corresponds to planar vibrations of carbon atoms present in graphite-like materials, whereas the D band which appears at 1350 cm⁻¹ is due to structural defects in graphite-like carbons. The relative intensity of D and G-bands (Iₐ/I₀) indicates higher crystallinity due to a higher contribution of formed carbonaceous species (graphitization).

When comparing the Iₐ/I₀ for the spent catalyst using 8.5 and 0.5 wt.% DMSO, it is clear that the sample exposed to the highest DMSO concentration has significantly higher Iₐ/I₀, thus undergoing more graphitization. These results are consistent with a previous report where steam reforming of sulfur-containing dodecane were studied over Rh-Pt catalysts. Zheng et al. found that the degree of carbon deposition due to graphitization on the spent catalyst, during the course of the reaction, increased with increasing sulfur concentration, which is mostly responsible for deactivation, as it acts like a shell covering the active sites.
The high concentration of Ni for the metal particle, associated with the silica support, is evident. Sulfur deposition for the spent catalysts was clear with a S/surface Ni molar ratio of 0.1-0.4. This formed sulfur may be due to the decomposition of DMSO to produce hydrogen sulfide over Ni under the reduced conditions. Based on the analysis performed for the reduced and spent Ni/SiO$_2$ catalysts, we suggest that the presence of sulfur at the nickel catalyst surface not only results in catalyst poisoning but also in carbon deposition. The Raman study on the spent catalyst revealed that graphitic carbon was dominant after increasing the concentration of DMSO. In addition, XPS spectra of the spent catalyst, reveal small shifts (~1-2 eV) in the binding energies of the Ni 2p3/2 and Ni 2p1/2 main peaks (Figure 7). These results indicate that the reaction with HMF in the presence of DMSO partially changes the nickel species and this is accompanied with a decrease of dehydration in the deoxygenation of HMF.

**Conclusions**

In summary, several metal supported catalysts were prepared and evaluated for HMF hydrogenolysis and hydrogenation to BHMF. Among the prepared catalysts, the 10Ni/SiO$_2$ catalyst exhibited excellent performance in terms of complete conversion of HMF along with the highest selectivity of 99% to BHMF. This is mainly due to a combined outcome of well dispersed Ni nanoparticles on silica and weak acidity of the catalyst support. In addition, the effect of DMSO on HMF hydrogenation activity was also investigated. The overall conversion rate of HMF was decreased by nearly 57% when the concentration of DMSO increased to 8.5%. Various characterization results shown in this study clearly demonstrate that DMSO can profoundly affect the carbon deposition. The sulfur and carbon deposition covered the Ni catalysts and inhibited HMF hydrogenation, which is believed to be the major reason causing its drastic inhibition by the presence of DMSO.

**Conflicts of interest**

There are no conflicts to declare.

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