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Highly active and robust Ni–MoS₂ supported on mesoporous carbon: a nanocatalyst for hydrodeoxygenation reactions†

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NiMoS₂ nanoparticles supported on carbon, synthesized by a microemulsion method were used as a nanocatalyst for hydrodeoxygenation (HDO) of a lignin model compound – guaiacol. Two types of carbon supports – mesoporous carbon (CMK-3) and activated carbon (AC) with a predominantly microporous structure, were studied to investigate the role of porosity and nature of the porous structure in catalyst activity. The activity of NiMoS₂/AC resulted in the complete guaiacol conversion at 13 h of reaction time to produce phenol (31.5 mol%) and cyclohexane (35.7 mol%) as the two main products. Contrastingly, NiMoS₂/CMK-3 needed a much lesser reaction time (6 h) to attain a similar conversion of guaiacol but gave different selectivities of phenol (25 mol%) and cyclohexane (55.5 mol%). Increased cyclohexane production with NiMoS₂/CMK-3 implied better deoxygenation of MoS₂ and enhanced hydrogenation capacity of Ni since phenol is a partially deoxygenated product of guaiacol while cyclohexane is a completely deoxygenated and hydrogenated product. The superior catalytic activity and deoxygenating behavior of NiMoS₂/CMK-3 catalysts could be attributed to the organized mesoporosity of the CMK-3 support in relation to the improved active phase distribution and access to active sites that facilitate the conversion of the reaction's product. Recyclability study implied NiMoS₂/CMK-3 was more stable without significant changes in the catalytic activity even after three reaction cycles.

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Introduction

Lignin is the most abundant renewable aromatic resource in nature, however, it has been underutilized as a feedstock for biofuel production.^{1,2} Meanwhile, lignin is currently used mostly as plasticizers or low-grade fuel by burning.^{3,4} With the current depletion of non-renewable fossil fuels and the associated environmental issues of pollution, production of chemicals and fuels from lignin can be expected to gain more interest in the foreseeable future. Owing to the vast availability of lignin naturally in biomass or in the waste stream of pulp and paper industry, its transformation to useful products *i.e.* liquid fuel or

chemical feedstock *via*

is also critical to the reaction pathway of the HDO reaction. A study of guaiacol conversion using CoMo catalyst supported on carbon and γ -Al₂O₃ showed that the demethoxylation reaction pathway that produces higher phenol catechol ratio and less coke formation was favoured on CoMo/C as compared to CoMo/ γ -Al₂O₃,¹⁴ and found to be consistent with the report of Centeno *et al.*¹⁵ who observed that the rate of phenol formation is faster on CoMo supported on carbon.¹⁵ Among the widely used carbon support is activated carbon, nonetheless, its characteristic micropores can be easily blocked when using large reactant molecules which often leads to catalyst deactivation as was observed in our previous study of guaiacol conversion using MoS₂/C catalysts.¹⁶ In this context, the influence of surface porosity of carbon support on the activity of the catalyst for HDO reaction has yet to be explored. Mesoporous carbon is proven to be superior catalytic support because of its organised and controllable pore geometry that enables excellent distribution of active species, thus enhancing catalytic activity and stability.¹⁷ Moreover, the wide pores of mesoporous carbon are beneficial for the diffusion of reactants easily to reach the active sites of the catalysts.¹⁸ For example, improved cycling performance of MoS₂/CMK-3 nanocomposites as an electrocatalytic material was attributed to the large pores of CMK-3.¹⁹

Among the several methods that have been employed for the synthesis of metal nanoparticles, incipient wetness impregnation synthesis route is a widely used technique for preparing supported catalysts. This synthesis method adopts the concept of distribution of metal precursor over the support, followed by calcination. With this technique, nanosized metal particles could be obtained but difficult to achieve both the homogeneous and narrow particle size distribution of metal species in the carbon supports. Moreover, the aggregation of metal particles at the pore entrance and the loosely bound metal particles can leach out during the catalyst preparation step such as washing with a solvent. One of the synthesis technique to overcome this problem is microemulsion (ME), which has been utilized as a good strategy to synthesize nanoscale metal particles with narrow particle size distribution.²⁰ High dispersion of metals over the support, less synthesis time and *in situ* reduction of metals during synthesis are some other benefits associated with the microemulsion technique.²¹ Therefore, in this article, we utilise the ME method for the synthesis of NiMoS₂ nanocatalyst supported on two carbon supports with different surface porosity and pore structures. The catalytic activity of these nanomaterials was tested for the conversion of guaiacol, a lignin model compound. The selectivity of liquid products and the reaction mechanism were influenced by the type of carbon support used.

Experimental section

Materials

Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (>98.5% purity), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) (81.0–83.0% purity MoO₃ basis), Brij 30, ammonium sulphide solution (20.0% in H₂O), tetraethyl orthosilicate (TEOS) (98.0% purity), sucrose (99.5% purity), sulphuric acid (99.9% purity),

dodecane (99.0% purity), guaiacol (99.0% purity), catechol (99.0% purity), anisole (99.7% purity), cyclohexanol (99.0% purity), cyclohexane (99.5% purity), cyclohexene (analytical grade), veratrole (99.0% purity), cresol (99.0% purity), pluronic P-123, activated carbon (norit SX ultra

concentrations of molybdenum and nickel were calculated to be 12 wt% and 3 wt%, respectively. MoS₂/AC and MoS₂/CMK-3 were also synthesised by the same procedure as mentioned above without the addition of the nickel precursor.

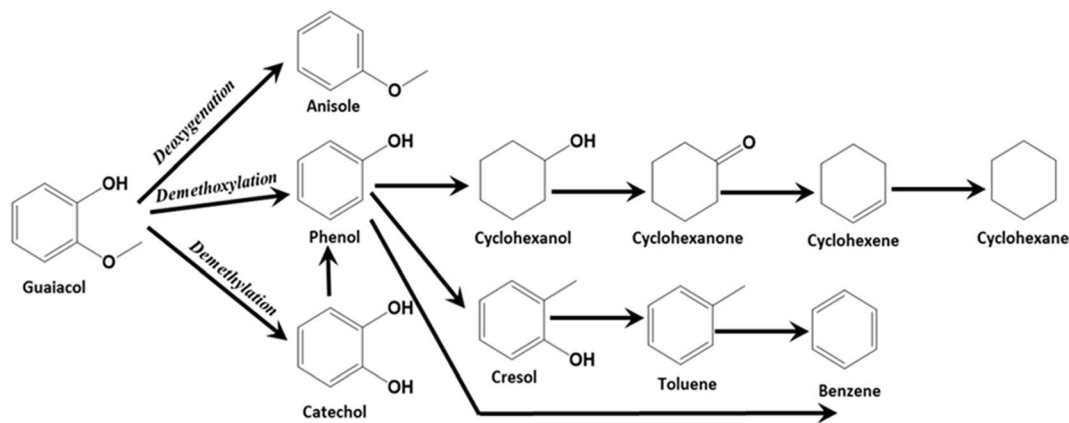
Catalyst characterization

X-ray diffraction (XRD) patterns of the used samples for this study were recorded using Rigaku Miniflex with monochromatic Co K α radiation (30 kV, 15 mA) for the range of $10^\circ \leq 2\theta \leq 90^\circ$ (step size of 0.1°) whereas Bruker radiation D8 advanced diffractometer with Cu K α radiation was used for the range of $1^\circ \leq 2\theta \leq 5^\circ$. Nitrogen adsorption-desorption isotherms were obtained at -196°C using a Micrometrics Tristar II 3020 system. The catalysts were degassed at 200°C overnight on a vacuum line, prior to analysis. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method and pore size distribution curve using the BJH model on the desorption isotherm curve. The chemical structure of the catalysts was analysed by Raman spectroscopy using Renishaw inVia Raman Microscope equipped with a Leica DM LM Microscope using a 514 nm HPNIR diode laser as an excitation source and 0.1 mW laser power. The Raman emission was collected by $50\times$ objective lens in a backscattering geometry in the region of $100\text{--}2000\text{ cm}^{-1}$ at 4 cm^{-1} resolution and acquisition time of 1.0 s. Transmission Electron Microscopy (TEM) JOEL 2100 microscope operated at 200 kV, fitted with energy dispersive X-ray (EDS) detector was used for morphology characterisation. Before TEM imaging, the samples were prepared by ultrasonically dispersing the particles in ethanol. The solution was settled on carbon-coated Cu grids to prepare the TEM samples. Inductively Coupled Plasma (ICP) analysis in a Varian Vista Pro ICPOES instrument was used for bulk elemental analysis. The samples were digested using a milestone Ethos

(CMK-3) supports along with the supported metal catalysts are discussed in ESI.†^{17,24–41}

The catalytic activity at the complete conversion of guaiacol with MoS₂ supported on AC and CMK-3 is depicted in Fig. 1. Phenol was the major product of the reaction and was an intermediate for the formation of hydrogenated products such as cyclohexanol, cyclohexene and cyclohexane. The other products evolved during the reaction were anisole, catechol, veratrole, benzene, cresol and methanol. Almost all the products were partially/completely deoxygenated, except catechol and veratrole. However, these products are observed in minor quantities. H₂, CO and CH₄ were among the gaseous products observed. It is known that guaiacol produces phenol by two pathways as shown in Scheme 1; namely (i) demethoxylation (DMO) – direct production of phenol from guaiacol by cleaving the C–OCH₃ bond, producing methanol as a by-product^{7,42,43} and (ii) demethylation (DME) – where the guaiacol is first converted to catechol by cleaving O–CH₃ bond. Thus, the formation of catechol was also accompanied by the cogeneration of CH₄. The formation of catechol increases the coke formation by condensation reactions.⁴⁴ The acidity of the catalyst support was reported to be the key reason for catechol formation.⁴⁵ Bui

*et al.*⁴⁶ reported both catechol and methyl catechol to be the major products with CoMoS/γ-Al₂O₃ catalyst. However, interestingly with CoMoS/ZrO₂ catalyst, demethoxylation was the major pathway producing phenol directly. Irrespective of the slightly acidic nature of ZrO₂ support, the promoter effect of Co on ZrO₂ created a unique active site which promotes direct demethoxylation of guaiacol.⁴⁶ Hence, it is already concluded that acidity is not the only reason that favours catechol formation. Similarly, Ruiz *et al.*⁴⁷ examined the activity of MoS₂ supported on four different activated carb



Scheme 1 Reaction network of hydrodeoxygenation of guaiacol by carbon supported NiMoS_2 catalyst.

product selectivity was 44% of phenol and 19% of catechol. There is also a co-generation of 11% methanol formed as result of the direct deoxygenation of guaiacol to phenol. Methane which is coproduced during the formation of catechol was also observed in the gaseous product. The hydrogenation of phenol to cyclohexanol was observed from the start of the reaction (7%). The formation of cyclohexene from cyclohexanol occurs through the production of cyclohexanone which is an intermediate compound. As cyclohexanone was not detected in the reaction product, indicates a rapid conversion of cyclohexanone to cyclohexene (10.1%). The further hydrogenation of

cyclohexene to cyclohexane also occurred (4.6%) within 1 h reaction time. On the other hand, 35% guaiacol was converted at 1 h with $\text{NiMoS}_2/\text{CMK-3}$ catalyst. Contrastingly, the main products produced were phenol (25%), cyclohexanol (26%) and 20% cyclohexane respectively. On the other hand, it was also observed that 10% cyclohexene and 10% methanol were produced within 1 h reaction time. There was no trace of catechol detected by GC-MS. On NiMoS_2/C catalyst, increasing reaction time, the selectivity towards phenol constantly increased up to 4 h where it reached a 52% maximum, followed by a constant drop till the end of the reaction. The decrease in phenol selectivity was accompanied by an increase in cyclohexane and cyclohexene selectivity, which concludes that phenol was converted to cyclohexane. The catechol selectivity decreased sharply after 1 h, and the final product collected at the complete conversion of guaiacol showed no trace of catechol. The other products such as cresol, anisole, veratrole, benzene were produced at the onset of reaction but there was no increase in selectivity after 1 h of reaction. We can also infer from this reaction pattern that during the first hour, the kinetics of the reaction was fast for all deoxygenation, hydrogenation and methylation reactions that were taking place. After 1 h, the methylation reaction was suppressed. Looking into the reaction mechanism with $\text{NiMoS}_2/\text{CMK-3}$, there was no trace of catechol from the onset of reaction. However, methane was still detected in the gas product analysis, assuming that might be produced through decomposition of methanol.

The organized mesopore structure of CMK-3 can facilitate the better distribution of active species (Ni and MoS_2) that enhances the contact time of guaiacol with the catalyst active phases. On the other hand, on NiMoS_2/AC , larger metal species are deposited on the micropores of activated carbon reducing the active surface area of the catalyst that can be noticed from Table S1.[†] Hence, we may conclude that the active metal species are deposited on the surface of the AC support, wherein interaction of the reactants with active species occurs mostly at the surface level. The channel-like pores of the CMK-3 act as a nanoreactor containing the active catalyst species. Thus, guaiacol has easy accessibility to get in contact with the active metal sites, as illustrated in Fig. 3. Ferrari *et al.*³⁴ concluded that

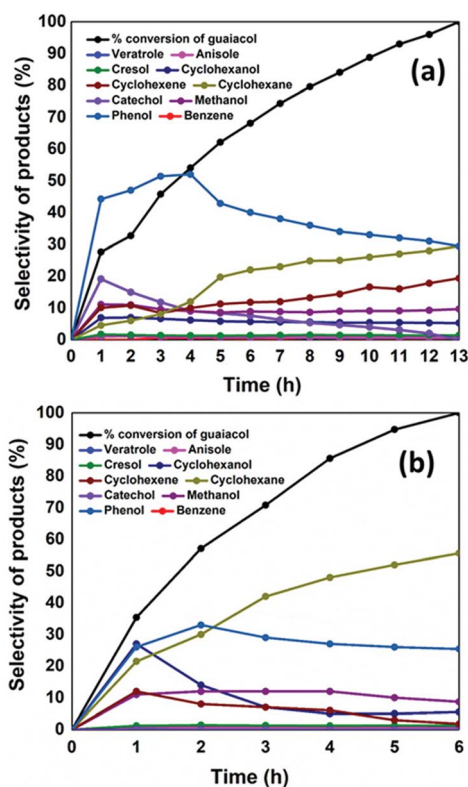


Fig. 2 Conversion (mol%) of guaiacol and selectivities of liquid products produced (mol%) with respect to increase in reaction time with (a) NiMoS_2/AC and (b) $\text{NiMoS}_2/\text{CMK-3}$ catalysts.



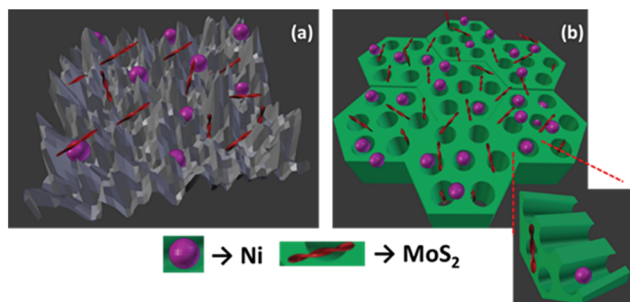


Fig. 3 Figure illustrating the Ni and MoS₂ active phase distribution over (a) activated carbon (b) CMK-3 supports.

the dispersion of catalytic metal species and the accessibility of active sites are the crucial steps in guaiacol conversion. This observation was strongly supported by Ghampson *et al.*⁵³ who have used four different activated carbons as support for Mo₂N catalyst.

While testing these catalysts for the conversion of guaiacol, they noticed that the support with high mesopore content possessed the highly exposed active sites for reaction. Lee *et al.*⁵⁴ proposed that CoMoS/nanoporous carbon exhibit higher activity for HDS reaction when compared to alumina and activated carbon supported catalyst. The high surface area and the organized pore geometry are the main reasons for the enhanced activity. They noted similar observation while evaluating the activity of Pt/mesoporous carbon for methanol oxidation. The superior activity is attributed to the high dispersion of Pt species in the pores, the orientation of nanochannels and easy accessibility of the pores by the reactant.⁵⁵

Catalyst recyclability – NiMoS₂/CMK-3

The catalyst after being used for the reaction was recovered by filtration, washed with ethanol and dried overnight at 50 °C. Afterwards, was reduced before each recyclability test. The reactions were conducted for 13 h and 6 h with NiMoS₂/AC and NiMoS₂/CMK-3 catalysts, respectively. These are the times that the catalysts attained complete conversion at the first catalytic run. The selectivity of liquid products (mol%) and the

conversion of guaiacol by NiMoS₂/AC and NiMoS₂/CMK-3 catalysts for three cycles is depicted in Fig. 4.

During the recyclability experiment, there was a drastic drop in the catalytic activity with NiMoS₂/AC catalyst. 93.2% guaiacol was converted during the second cycle which was further reduced to 88.6% during the third cycle in 13 h of reaction time. Further discussing on the selectivity of products, the selectivity towards phenol decreased from 31.4% to 25.8% respectively after the third cycle which is an overall 18% decrease in selectivity. Similarly, the cyclohexane selectivity decreased from 35.7% to 28%. On the other hand, the methylated product increased from 3.9% to 4.9% by third cycle. We have already reported that the increase in methylated products was mainly due to the formation of MoO_x species which was also noticed by MoS₂/AC catalyst recyclability test.¹⁶ It can also be supported by the decrease in the S : Mo ratio in bulk (2.05 : 1 to 1.95 : 1) and surface (1.92 : 1 to 1.79 : 1) as estimated by ICP and XPS analyses (Table 1). There was also a decrease in catalyst surface area from 153 m² g⁻¹ to 102 m² g⁻¹ after third cycle accounting for a 33% loss in active surface area. From the current result, we can infer that one of the main reason for the catalyst deactivation could be the loss of catalyst surface area available for catalytic reaction. Zanuttini *et al.* also described rapid deactivation of Pt/zeolite, for the conversion of *m*-cresol due to the micropore blockage of the support.⁵⁶ The coke formation in the catalyst was also calculated using CHNSO analysis and the amount of coke formed after 3 cycles was found to be 1.1%. Generally, carbon supported catalyst were reported to produce less coke when compared to acidic catalysts such as alumina, ZrO₂ *etc.* which was attributed to the neutral/less acidic nature of carbon.^{57,58}

Regarding the activity of NiMoS₂/CMK-3, the complete guaiacol conversion was achieved within 6 h even after 3 reaction cycles. Considering the selectivity, the selectivity towards phenol decreases from 25.4% after first cycle to 23.9% after third cycle, which is a 5.9% selectivity difference. It is noteworthy to mention that the selectivity towards cyclohexane was not affected even after the third cycle.

The characterisation of spent catalyst in Table 1 shows interesting results. A similar decrease in S : Mo ratio was noticed with NiMoS₂/CMK-3 also as previously noticed with

Table 1 Surface and bulk sulphur composition, S : Mo ratio, BET surface area and pore volume of spent NiMoS₂/C catalyst after cycle 1, 2 and 3

Catalyst	Amount of sulphur (at%)		S/Mo (at. ratio)		BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Coke deposition ^b (%)
	Surface ^a	Bulk ^b	Surface ^a	Bulk ^b			
NiMoS ₂ /AC – fresh	9.8	3.2	1.92 : 1	2.05 : 1	153	0.21	0
NiMoS ₂ /AC – cycle-1	9.9	3.0	1.88 : 1	2.02 : 1	135	0.19	0.6
NiMoS ₂ /AC – cycle-2	9.7	2.9	1.82 : 1	1.99 : 1	119	0.17	1.0
NiMoS ₂ /AC – cycle-3	8.7	2.7	1.79 : 1	1.95 : 1	102	0.17	1.1
NiMoS ₂ /CMK-3 – fresh	9.1	3.3	1.92 : 1	1.98 : 1	453	0.33	0
NiMoS ₂ /CMK-3 – cycle-1	8.9	3.2	1.90 : 1	1.97 : 1	448	0.27	0.3
NiMoS ₂ /CMK-3 – cycle-2	8.9	3.0	1.87 : 1	1.97 : 1	441	0.24	0.6
NiMoS ₂ /CMK-3 – cycle-3	8.7	2.8	1.85 : 1	1.92 : 1	437	0.21	0.7

^a Analyzed by XPS. ^b Analyzed by CHNS elemental analyzer.



NiMoS₂/AC. This data supports correlate with an increase in methylated product from 2.4% – cycle 1 to 3.9% – cycle 3. Surprisingly the mesopore surface area decrease after third cycle was only 3.5%. It is to be noted that the pore volume decreased from 0.33 cm³ g⁻¹ to 0.21 cm³ g⁻¹; with an amount of coke deposited of 0.7%. Hence, we can conclude that the coke formed were deposited inside the pores which reduced the pore volume of the catalyst, however coke did not block the mesopore of the catalyst and hence only 3.5% of the surface area was decreased. Hence, the remarkable activity of the NiMoS₂/CMK-3 catalyst could then be attributed to the mesoporosity of the CMK-3 support.

Discussion

The influence of the difference in carbon surface porosity was not in an appreciable amount for the conversion of guaiacol with MoS₂/C. Notably, when Ni was introduced as a promotor the selectivity of products changed significantly. For example, the use of NiMoS₂/AC produced phenol (31.5%) and cyclohexane (35.7%) as the major products compared to the MoS₂/AC where phenol (62.2%) was produced to MoS₂/AC predominantly followed by cyclohexane (7.6%) (Fig. 1).

The main influence of Ni to MoS₂ was the increase in deoxygenation and hydrogenation activity. So, the deoxygenation of guaiacol and the hydrogenation of phenol occurred simultaneously which increased the conversion of phenol and selectivity of cyclohexane. Also, comparing the other hydrogenated compounds such as cyclohexene (10.6%) and cyclohexanol

(6.3%) were similar for NiMoS₂/AC (14.4% – cyclohexene, 5.3% – cyclohexanol). Hence, we can conclude that promotion of MoS₂ by Ni, increases the hydrogenation tendency. On the other hand, a similar trend was not observed with CMK-3 supported catalyst. The selectivity of cyclohexene was 10.6% for MoS₂/CMK-3 which reduced to 1.8% on NiMoS₂/CMK-3 but accompanied by increased cyclohexane (50%) which is a product of intense hydrogenation. Thus, the promotion of Ni to MoS₂/CMK-3 increases the hydrogenation as well as the deoxygenation of guaiacol to a greater extent. The kinetic diameter of guaiacol was calculated to be 0.0668 nm.⁵⁹ Since most of the pores of activated carbon falls in the micropore region, the diffusion of guaiacol into the pores of activated carbon was limited. Hence, the conversion of guaiacol mostly occurred at the surface level. On the other hand, the high surface area of CMK-3 along with its mesoporosity (3.85 nm pore size) facilitates better dispersion of the active sites both within and outside of the pore channels of the support. As a result, there is an improved contact of the reactant with the catalytic active sites, thus increasing the rate of the reaction and hence, the complete conversion of guaiacol was achieved in 6 h with NiMoS₂/CMK-3 which was much quicker than the 13 h required for NiMoS₂/AC to achieve a similar conversion. This fact is supported by XPS data (Table S2†) that shows that Ni species are predominantly deposited inside the pores of CMK-3 (surface_{Ni/Mo} = 0.16) whereas, for AC (surface_{Ni/Mo} = 0.31), Ni was deposited mostly on the catalyst surface.

Conclusions

In summary, the microemulsion technique has been used for the successful synthesis of NiMoS₂ nanocatalyst supported on two different carbon materials containing different surface porosity. The catalysts were tested for HDO of guaiacol. Phenol and cyclohexane were produced as the major products. The selectivity of products was influenced by the pore geometry of the carbon supports which is ascribed to the distribution of Ni and MoS₂ active species. The Ni–Mo–S phase, along with the easy accessibility to the active phases by guaiacol in the NiMoS₂/CMK-3 catalysts exhibited superior deoxygenation and hydrogenation activity than the activated carbon supported catalyst. Mesoporous carbon is a perfect choice to be used as support for hydrodeoxygenation reaction for their mesoporosity and pore geometry. Hence, the use of the high surface area, mesoporous materials as support for HDO reactions are highly recommended.

Conflicts of interest

There are no conflicts to declare.

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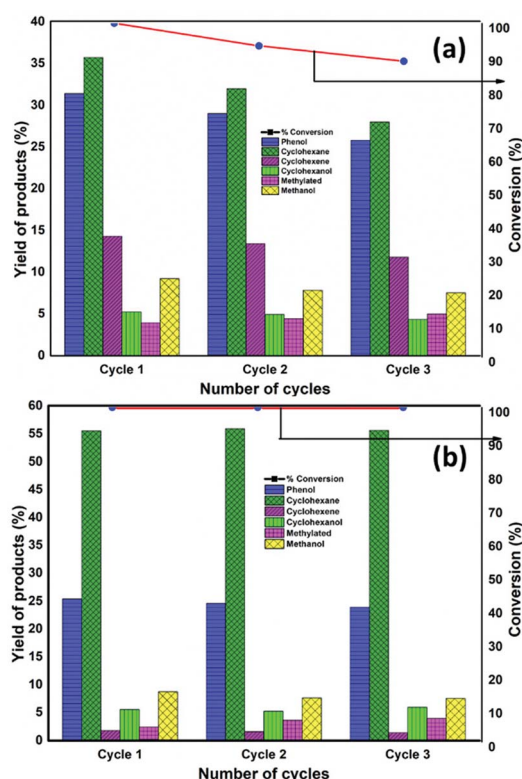


Fig. 4 The selectivities of liquid products (mol%) and the conversion of guaiacol by NiMoS₂/AC and NiMoS₂/CMK-3 catalysts for three cycles.



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