

# In situ formed MoO<sub>x</sub> and WO<sub>x</sub> for efficient conversion of lignin-derived phenols to alkylphenols in supercritical ethanol

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## Research Article

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# Abstract

The catalytic performance of *in situ* formed  $\text{MoO}_x$  and  $\text{WO}_x$  was studied in the hydroprocessing of lignin-derived phenols (guaiacol, phenol, anisole, and syringol) to alkylphenols (phenols- $\text{C}_n$ , where  $n = 2-10$ ) in supercritical ethanol under various reaction conditions. The general trend in the selectivity for phenols- $\text{C}_n$  depending on the substrate type varied following: anisole < < syringol < phenol < guaiacol. Additionally, the reaction pathways were studied in detail for guaiacol. It was concluded, that the presence of alkylguaiacols (guaiacols- $\text{C}_n$ , where  $n = 2-8$ ) in the reaction products indicates that alkylphenols are predominantly formed *via* direct alkylation of guaiacol followed by deoxygenation. According to the DEPT  $^{13}\text{C}$  spectra, ethyl substitutes predominate over the other alkyl substituents. However, the content of CH groups is about 6 – 8% for both catalysts and confirms the formation of isopropyl and sec-butyl substituents. It was shown, that the activity of *in situ*  $\text{MoO}_x$  and  $\text{WO}_x$  in deoxygenation and alkylation reactions is significantly higher compared to that of purchased  $\text{MoO}_3$  and  $\text{WO}_3$ . In the case of guaiacol hydroprocessing, the selectivity for alkylphenols decreased in the order: *in situ*  $\text{MoO}_x$  (97%) > *in situ*  $\text{WO}_x$  (79%) >  $\text{MoO}_3$  (73%) > >  $\text{WO}_3$  (30%).

## Introduction

In recent decades, transition metal compounds (phosphides, oxides, nitrides, and carbides) have proven to be highly active catalysts for the hydroprocessing of various feedstocks, including the processing of alternative ones (lignocellulosic biomass and plastic waste) [1 – 3]. Moreover, most works are devoted to study the catalytic performance of such catalysts in the hydroprocessing of lignin and its model compounds into high-value petrochemical products and fuel components. Depending on the type of catalytic system and the reaction parameters, the conversion of lignin and its model compounds can proceed *via* the following major pathways: 1) the full deoxygenation to the benzene-toluene-xylene fraction, 2) hydrogenation of aromatic fragments with subsequent partial or full deoxygenation to cyclohexanol or cyclohexane and their derivatives, 3) C-alkylation of phenolic substrates. Alkylphenols (the products of C-alkylation), particularly those with longer alkyl chains (phenols- $n$ , where  $n = 6 - 10$ ), are important intermediates for the production of surfactants, antioxidants, and fuel components [4 – 6]. Therefore, the direct alkylation of lignin-derived phenols is a promising route to the valorization of such renewable source as lignin.

It should be noted that molybdenum and tungsten oxides possess significant advantages as catalysts for lignin hydroprocessing compared to other transition metal compounds (sulfides, phosphides and etc.). First, transition metal oxide based catalysts are characterized by the presence of oxygen vacancies and acid (Brønsted and Lewis) sites, which play a key role in hydrodeoxygenation and alkylation reactions, respectively [7 – 9]. Moreover, the proposed catalysts are expected to exhibit high thermal and chemical stability, which is a crucial parameter for the processing of a complex feedstock such as lignin. In turn, transition metal phosphide and sulfide catalysts can undergo deactivation *via* their oxidation

during the hydroprocessing of oxygen-containing substrates. In the case of transition metal oxides, the catalysts are already in the oxide form [10].

In this work, *in situ* formed molybdenum and tungsten oxide catalysts are proposed for the selective conversion of phenols to alkylphenols in supercritical ethanol. The *in situ* formation of molybdenum and tungsten oxide catalysts in the reaction medium, during the hydroprocessing of lignin-derived phenols allows the elimination of a separate catalyst synthesis stage and promotes the formation of a catalytic system with a unique set of active sites. In turn, carrying out the reaction under supercritical conditions provides low viscosity, high diffusivity, and strong solvent power.

## Experimental section

### Materials

*In situ* MoO<sub>x</sub> and WO<sub>x</sub> were prepared using Mo(CO)<sub>6</sub> (LLC «Redkino experimental plant», Russia, 36.5–37.5 wt. % of Mo) and W(CO)<sub>6</sub> (LLC «Redkino experimental plant», Russia, 51–52 wt. % of W) as precursors, respectively. Purchased MoO<sub>3</sub> and WO<sub>3</sub> («Lenreactiv», Russia, pure) were used for comparison with the *in situ* MoO<sub>x</sub> and WO<sub>x</sub>. Ethanol (Reakhim, Russia, > 99%) was used as a solvent for conversion of lignin-derived phenols, and acetone (Component-reaktiv, Moscow, Russia, > 99.5%) was used for catalyst washing. The used gases were H<sub>2</sub> (Air Liquide, Paris, France, ≥ 98%) and Ar (Air Liquide, Paris, France, ≥ 98%). The chemicals used for NMR analyses: DMSO-d<sub>6</sub> (Solvex-D, Russia, 99.8%), trioxane (ChemCraft, Russia, > 99.5%), Cr(acac)<sub>3</sub> (ChemCraft, Russia, > 98%).

### Methods

The catalytic experiments were carried out in a stainless-steel autoclave reactor. MoO<sub>x</sub> and WO<sub>x</sub> catalysts were formed *in situ* from their carbonyls (Mo(CO)<sub>6</sub> or W(CO)<sub>6</sub>) during the reaction. Generally, a mixture of 2 g of a 10 wt.% solution of guaiacol in ethanol and metal carbonyl (Mo(CO)<sub>6</sub> or W(CO)<sub>6</sub>) was loaded into the autoclave. The molar ratio of substrate-to-metal was 5. The conversion of guaiacol was conducted at 300 – 350°C, 5 MPa H<sub>2</sub>, for 1 – 10 h, undergoing constant magnetic stirring (900 rpm).

After the catalytic tests, the autoclave was cooled to room temperature, and the liquid reaction products were separated from the catalysts by centrifugation (10000×g rpm). *In situ* obtained catalysts were washed with acetone, dried, and kept in an Ar atmosphere. The powder X-ray diffraction (XRD) pattern was obtained using a Rigaku Rotaflex RU-200 diffractometer (CuK<sub>α</sub> radiation).

The composition of gaseous reaction products was determined using a Chromos GH-1000 chromatograph equipped with a thermal conductivity detector; He was used as a carrier gas. The identification of the liquid reaction products was conducted using a gas chromatograph–mass spectrometer (GC-MS) (Thermo Scientific ISQ 7000 GC-MS) provided with a Restek 5XI-17SIL MS CAP

capillary column (30 m × 0.25 mm × 0.25 μm). He was used as a carrier gas. A gas chromatograph (Crystallux 4000 M) equipped with a flame ionization detector and a capillary column (Optima-1, 25 m × 0.32 mm × 0.35 μm) was used for quantitative analysis of liquid reaction products. The following equations were used to evaluate the conversion of substrates and product selectivity:

$$\text{Conversion (\%)} = \frac{\text{mole of substrate consumed}}{\text{initial mole of substrate}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{mole of product}}{\sum \text{moles of all products}} \times 100$$

In addition, the guaiacol conversion products were analyzed using the  $^{13}\text{C}$  NMR. In this case, the distortionless enhancement by polarization transfer (DEPT) spectra with final flip angles of 45°, 90°, and 135° recorded (DEPT-45, DEPT-90 and DEPT-135). All NMR spectra were acquired on a Bruker AVANCE III HD (400 MHz) spectrometer. Integrations and baseline correction were performed using MestReNova 15.0 software. Following this methodology [11] the relative contributions of the  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  were estimated. For quantitative  $^{13}\text{C}$  NMR, the following weights of chemicals were used: 60 – 70 mg of a sample, 5 mg/mL of the relaxation reagent  $\text{Cr}(\text{acac})_3$ , trioxane as an internal standard (mass ratio of sample/trioxane = 10), and 500 μl of  $\text{DMSO-d}_6$ . The  $^{13}\text{C}$  NMR spectra recorded employing an inverse gated decoupling pulse sequence (IG) (8096 scans, 2 s relaxation delay).

## Results and discussion

### 1. Hydroprocessing of lignin-derived compounds over *in situ* $\text{MoO}_x$ and $\text{WO}_x$

#### Hydroprocessing of guaiacol

The catalytic activity of *in situ* formed  $\text{MoO}_x$  and  $\text{WO}_x$  was investigated in the hydroprocessing of guaiacol in supercritical ethanol under various reaction parameters (300 and 350°C, 1 – 10 h) (Fig. 1 – 3). For both catalysts, the main reaction products were alkylphenols with different number of alkyl substituents (ethyl, propyl, butyl etc.) (phenols- $\text{C}_n$ , where  $n = 2 - 10$ ). According to the literature, guaiacol can be transformed to alkylphenols *via* three main pathways [12 – 14]. One pathway involves demethoxylation of guaiacol to phenol and its subsequent alkylation. The second route is direct alkylation of guaiacol followed by demethoxylation. In the third pathway, the deoxygenation of guaiacol to o-cresol and its subsequently alkylation.

To determine the predominant routes for guaiacol conversion using *in situ* formed  $\text{MoO}_x$  and  $\text{WO}_x$  catalysts, the experiments were carried out for different reaction durations (300°C, 5 MPa  $\text{H}_2$ , 1–10 h) (Fig. 1). For both catalysts, the formation of alkylphenols was already observed after 1 h of reaction with 71% selectivity over  $\text{MoO}_x$  and 52% over  $\text{WO}_x$ . The presence of alkylguaiacols (guaiacols- $\text{C}_n$ , where  $n = 2-8$ ) in the reaction products indicates that alkylphenols are predominantly formed *via* direct alkylation

of guaiacol followed by deoxygenation. Due to the presence of two strongly donating groups in the structure of guaiacol, direct alkylation of guaiacol is more favorable [12, 13]. In the case of  $\text{MoO}_x$ , the complete deoxygenation was observed after 6 h reaction time. In contrast, for the  $\text{WO}_x$  catalyst, guaiacols- $\text{C}_n$  were detected among the reaction products after 10 h with a selectivity of 7%. The value of substrate conversion was also higher in the case of  $\text{MoO}_x$  and exceeded 96% for 1–10 h. For  $\text{WO}_x$ , the conversion of guaiacol gradually increased from 82 to 100% as the reaction time increased from 1 to 10 h. The higher performance of  $\text{MoO}_x$  in deoxygenation reaction compared to  $\text{WO}_x$  can be related to the higher content of oxygen vacancies, as was shown in several of works [15, 16]. Using  $\text{MoO}_x$ , phenol, ethoxyphenol, ethoxyethylbenzene, and ethoxyethylphenol were designated as “others”. For *in situ*  $\text{WO}_x$ , the product composition of “others” slightly differed: ethoxyphenol, ethoxymethoxyphenol, diethoxyethylphenol, and ethoxyethylbenzene. It can be concluded that *in situ*  $\text{WO}_x$  promoted the formation of alkoxyphenols and alkoxybenzenes to a greater extent.

The transformations of ethanol over *in situ* formed  $\text{MoO}_x$  were studied in our previous work, and it was shown that not only ethanol but also its conversion products (alkenes and alcohols) can act as alkylating agents [17]. The formation of various alkenes and alcohols also led to the production of alkylphenols with a wide range of alkyl substituents. According to the GC-MS results, the formed alkylphenols contain 2–10 carbon atoms in the alkyl substituent and have various structures (ethyl, isopropyl, butyl, etc.). Alkylphenols with an even number of carbons prevails over the alkylphenols with an odd number of carbons in the alkyl group. It can be suggested that phenols- $\text{C}_2$ ,  $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_8$ , and  $\text{C}_{10}$  are mainly ethylphenols. In turn, phenols- $\text{C}_3$ ,  $\text{C}_5$ ,  $\text{C}_7$ , and  $\text{C}_9$  have the methyl or isopropyl alkyl substituents in their structure. To confirm these suggestions, the additional study (DEPT  $^{13}\text{C}$  NMR) was performed. The DEPT  $^{13}\text{C}$  spectra were recorded with 45°, 90°, and 135° final flip angles and are presented in Fig. 2. The signals in the range of 30–0 ppm in the  $^{13}\text{C}$  NMR spectrum correspond to carbon atoms in alkyl substituents linked to the aryl group. The relative contributions of the  $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  were estimated following this methodology [11] (Fig. 2b). According to the DEPT  $^{13}\text{C}$  spectra, it can be concluded that ethyl groups predominate over the other alkyl substituents. However, the content of the CH group is about 6–8% in the case of both catalysts. This result confirms the formation of, for example, isopropyl and sec-butyl substituents.

As shown in Fig. 1, the selectivity for the target products (phenols- $\text{C}_n$ ) is higher using *in situ*  $\text{MoO}_x$  than  $\text{WO}_x$  at the same reaction conditions. For  $\text{MoO}_x$ , the selectivity for phenols- $\text{C}_n$  was 97% after only 6 h of reaction (300°C), and alkylguaiacols were not observed among the reaction products. In contrast, the intermediate products (guaiacols- $\text{C}_n$  and alkoxyphenols) were found with a total selectivity of approximately 17% using the  $\text{WO}_x$  catalyst at the same reaction parameters (300°C, 6 h). In this regard, it was of interest to study the possibility of increasing the extent of deoxygenation by raising the temperature from 300 to 350°C (Fig. 3). According to the results, increasing the reaction temperature had no significant effect on the conversion of substrate or the selectivity for the phenols- $\text{C}_n$  using *in situ*  $\text{MoO}_x$  catalyst. While for  $\text{WO}_x$ , the selectivity for phenols- $\text{C}_n$  increased from 79% to 93%, whereas the

selectivity toward alkylguaiacols decreased from 17% to 5% as the reaction temperature raised from 300 to 350°C. The full conversion of guaiacol was achieved using both catalysts at 300 to 350°C. It should be noted that an increase in the reaction temperature resulted in significant changes in the product composition. At the same reaction conditions, the use of  $\text{WO}_x$  catalyst led to higher selectivity for phenol- $\text{C}_8$  and phenol- $\text{C}_{10}$  compared to  $\text{MoO}_x$ . Thus, the total selectivity for the mixture of phenol- $\text{C}_8$  and phenol- $\text{C}_{10}$  was 49% using  $\text{MoO}_x$  and 79% for  $\text{WO}_x$  at 350°C (6 h, 5 MPa  $\text{H}_2$ ). This result is likely due to the higher acidity of tungsten oxide, which favors the alkylation reaction [1, 18]. Mai et al. also mentioned that the conversion of guaiacol using a  $\text{WO}_3/\text{HY}$  catalyst led to the predominant formation of pentaethylphenol (phenol- $\text{C}_{10}$ ) (30%) [12].

## Hydroprocessing of anisole, phenol, and syringol

Additionally, *in situ* formed  $\text{MoO}_x$  and  $\text{WO}_x$  catalysts were tested in the hydroprocessing of other model compounds (phenol, anisole, and syringol). The results of experiments are presented in Fig. 4, and the proposed transformation scheme for all substrates is shown in Fig. 5. The general trend in the selectivity for phenols- $\text{C}_n$  depending on the substrate type was as follows: anisole < syringol < phenol < guaiacol.

The presence of two donor groups (-OH and  $-\text{OCH}_3$ ) in the guaiacol structure facilitates the alkylation reaction, and as a result, the selectivity for alkylphenols was higher for guaiacol than for phenol [12, 19]. The transformations of phenol in ethanol involve C-alkylation to alkylphenols and O-alkylation to ethoxybenzene and ethoxyethylbenzene. In the case of both catalysts, the selectivity for C-alkylation products is predominant. However, there is some difference in the composition of phenols- $\text{C}_{10}$ . As was shown for guaiacol, the selectivity for phenol- $\text{C}_{10}$  was higher using  $\text{WO}_x$  (21%) compared to  $\text{MoO}_x$  (12%). Moreover, the selectivity for ethoxyethylbenzene was also higher in the case of  $\text{WO}_x$  that indicates the higher alkylation rate. Furthermore, the lower selectivity for alkylphenols in the case of phenol also confirms that the formation of alkylphenols proceeds *via* direct alkylation of the substrates followed by deoxygenation.

The selectivity for the alkylphenols was the lowest in the case of anisole conversion for both catalysts (Fig. 4). According to the results and literature data, there are the following pathways for anisole conversion in ethanol: 1) direct alkylation to anisoles- $\text{C}_n$  and 2) demethylation to phenol and its subsequent conversion *via* C-alkylation and O-alkylation. In the case of both catalysts, phenol, ethoxybenzene, ethoxyethylbenzene, and alkylanisoles were detected among the reaction products. For instance, the selectivity for phenol was 11% over  $\text{MoO}_x$  and 13% over  $\text{WO}_x$ . This result indicates that the conversion of anisole proceeds in parallel *via* two routes; that can be the reason for the lower selectivity for the target products. Although the deoxygenation of anisole to benzene is the predominant route in nonpolar solvents, the use of polar solvents promotes the conversion of anisole to phenol [20]. Mai et al. studied the hydrodeoxygenation of various lignin-derived phenols using  $\text{H}_2\text{WO}_4$  catalyst in ethanol and reported that the cleavage of the  $\text{C}(\text{sp}^3)-\text{OAr}$  bond is much easier than that for  $\text{C}(\text{sp}^2)-\text{OMe}$  [12]. The

lower selectivity for alkylphenols in the case of anisole and phenol compared to guaiacol was also mentioned in [12, 13].

Due to the presence of two methoxy groups, the scheme of syringol transformations is more complex. In the case of both catalysts, guaiacols- $C_n$  and benzenediols were detected among the reaction products, which indicates the parallel occurrence of two pathways: 1) demethoxylation to guaiacol followed by alkylation and 2) demethylation/demethoxylation to pyrocatechol with subsequent alkylation. It is possible that deoxygenation of both methoxy groups in syringol requires a longer reaction time to increase the selectivity for alkylphenols compared with guaiacol. The selectivity for alkylphenols was higher using  $MoO_x$ , that was also observed for other substrates. It should be noted that no fully deoxygenated products were detected in the case of all lignin-derived model compounds (phenol, anisole, guaiacol, and syringol). According to the literature data, the supercritical ethanol serves not only as a hydrogen donor but also as a capping agent that stabilizes highly reactive phenolic intermediates through successive alkylation steps [12].

## **2. Comparison of *in situ* and *ex situ* formed metal (Mo, W) oxide catalysts in the hydroprocessing of guaiacol.**

One of the important advantages of the *in situ* method of catalyst preparation is the formation of catalytic systems with a unique set of active sites [21]. In this regard, it was of interest to compare the catalytic activity of *in situ* and *ex situ* formed molybdenum and tungsten oxides in the conversion of guaiacol to alkylphenols in ethanol. It should be noted that  $MoO_3$  and  $WO_3$  were purchased and not synthesized in this work.

The phase composition of all samples (*in situ*  $MoO_x$  and  $WO_x$ ,  $MoO_3$  and  $WO_3$ ) was determined using XRD analysis (Fig. 6).  $MoO_x$  and  $WO_x$  samples were obtained *in situ* during guaiacol conversion in ethanol at 300°C, 5 MPa  $H_2$ , 6 h. The XRD patterns show the presence of  $MoO_2$  (PDF #50–739) and  $W_{18}O_{49}$  (PDF #71-2450) for *in situ*  $MoO_x$  and  $WO_x$ , respectively. It should be noted that some amorphous phases were detected for both *in situ*  $MoO_x$  and  $WO_x$  catalysts. In our previous work, the *in situ* formation of metal oxide from the corresponding metal carbonyls was studied during the hydroprocessing of diphenyl ether [15]. It was shown, that the full decomposition of metal (Mo, W) carbonyl to their oxides was already achieved at 300°C, 5 MPa and for 30 min. Thus, the catalyst phase was established very quickly relative to the reaction progress. According to the XRD results, the purchased metal oxides are crystalline, and all reflections are related to the  $MoO_3$  (PDF #5-508) and  $WO_3$  (PDF #71–131) phases. The catalytic performance of *in situ* and purchased metal (Mo, W) oxides was compared in the conversion of guaiacol in ethanol at 300°C, 5 MPa  $H_2$ , 6 h (Fig. 7). The substrate conversion was close to full for all catalysts; however, the product contribution and the selectivity for the target products differed. For example, the selectivity for phenol- $C_6$ ,  $C_8$ , and  $C_{10}$  was significantly higher in the case of *in situ*  $MoO_x$  (97%) compared to  $MoO_3$  (73%). For  $MoO_3$ , guaiacols- $C_n$  and alkoxyphenols were found with a total selectivity of about 30%. For tungsten-containing catalysts, the difference in activity was more

significant. The total selectivity for guaiacols- $C_n$  and alkoxyphenols was 70% for  $WO_3$  and 20% for *in situ*  $WO_x$ . Moreover, in the case of  $WO_3$ , the formation of O-alkylation products (alkoxyphenols) was observed with high selectivity. The selectivity for alkylphenols decreased in the order: *in situ*  $MoO_x$  > *in situ*  $WO_x$  >  $MoO_3$  >  $WO_3$ . Thus, the deoxygenation and alkylation abilities of *in situ*  $MoO_x$  and  $WO_x$  are significantly higher than those of  $MoO_3$  and  $WO_3$ .

Additionally, the *in situ* and *ex situ* formed metal oxides were tested in the conversion of ethanol to understand the reason for the above results. The all ethanol transformations over *in situ*  $MoO_x$  were discussed in detail in our previous study [17]. It was shown that various reactions (dehydrogenation, dehydration, and metathesis) yield alkenes and alcohols with different structures. Moreover, it was concluded that the formed alkenes and alcohols are also act as alkylating agents. As can be seen from Tables S1 and S2, the variety of ethanol conversion products over the *in situ* formed catalysts is significantly broader. In the case of  $MoO_3$  and  $WO_3$ , ethanol was predominantly converted to diethyl ether, as well as acetals and hemiacetals. Furthermore, the extent of ethanol conversion is also lower using purchased metal (Mo, W) oxide catalysts. Thus, the use of *in situ*  $MoO_x$  and  $WO_x$  promotes the formation of additional amounts of alkylating agents through the conversion of ethanol.

Several studies have been devoted to the conversion of lignin-derived phenols to alkylphenols using molybdenum- and tungsten-containing catalysts. In [22] an unsupported  $MoO_3$  catalyst was proposed for hydroprocessing of guaiacol to alkylphenols using ethanol as a solvent (280°C, 1 MPa  $H_2$ , 5 h). The selectivity for the target products was 86% at full substrate conversion. Valizadeh et al. reported on the processing of guaiacol over a 5Mo-20Ni/Ce catalyst with 66.1% selectivity for alkylphenols at the highest 95.6% conversion (340°C) [23]. In comparison, the processing of guaiacol at the same temperature (340°C) in supercritical ethanol over an activated carbon-supported  $\alpha$ -molybdenum carbide catalyst ( $\alpha$ - $Mo_{1-x}C/AC$ ) led to a total selectivity of 85% for phenol and alkylphenols [13]. Liu et al. highlighted that in the presence of the  $Mo_5Re_2/HBEA$  guaiacol was converted to alkylphenols with 85.6% selectivity (280°C, 4 h, 4 MPa  $N_2$ ) [14]. Alkylphenols were formed with 80.0% yield using the  $H_2WO_4$  catalyst (300°C) [12] and with 52% yield over a Y zeolite-supported tungsten oxide (280°C) [24]. The selectivity for alkylphenols in the case of all substrates over *in situ*  $MoO_x$  and  $WO_x$  is much higher compared to studies mentioned in the literature. Moreover, the *in situ* formation of  $MoO_x$  and  $WO_x$  does not require a separate synthesis stage, which significantly simplifies the process.

## Conclusions

The catalytic performance of *in situ* formed  $MoO_x$  and  $WO_x$  was studied in the hydroprocessing of lignin-derived phenols (guaiacol, phenol, anisole, and syringol) to alkylphenols (phenols- $C_n$ , where  $n = 2 - 10$ ) in supercritical ethanol under various reaction conditions. The general trend in the selectivity for phenols- $C_n$  depending on the substrate type varied as follows: anisole < syringol < phenol < guaiacol. The reaction pathways were studied in detail for guaiacol. It was concluded, that the presence of alkylguaiacols

(guaiacols- $C_n$ , where  $n = 2-8$ ) in the reaction products indicates that alkylphenols are predominantly formed *via* direct alkylation of guaiacol followed by deoxygenation. According to the DEPT  $^{13}C$  spectra, ethyl groups predominate over the other alkyl substituents. However, the content of CH groups is about 6 – 8% in the case of both catalysts and confirms the formation of isopropyl and sec-butyl substituents.

Moreover, the catalytic activity of *in situ* and *ex situ* formed molybdenum and tungsten oxides was compared in the conversion of guaiacol. In the case of guaiacol hydroprocessing, the selectivity for alkylphenols decreased in the order: *in situ*  $MoO_x$  (97%) > *in situ*  $WO_x$  (79%) >  $MoO_3$  (73%) >  $WO_3$  (30%). Thus, the activity of *in situ*  $MoO_x$  and  $WO_x$  in deoxygenation and alkylation reactions is significantly higher compared to that of  $MoO_3$  and  $WO_3$ . It should be noted that, the selectivity for alkylphenols for all substrates over *in situ*  $MoO_x$  and  $WO_x$  is much higher compared to reported in the literature. Moreover, the *in situ* formed  $MoO_x$  and  $WO_x$  catalysts are characterized by a lower cost compared to noble metal doped catalysts and do not require a separate stage for their synthesis.

## Abbreviations

XRD powder X-ray diffraction;

GC-MS gas chromatography–mass spectrometry;

DEPT distortionless enhancement by polarization transfer;

DO direct deoxygenation;

DM demethylation;

DMO demethoxylation;

Alk alkylation.

## Declarations

## Supplementary Information

The online version contains supplementary material available at...

## Ethics and Consent to Participate

The authors are dedicated to maintaining the integrity of the scientific record and fully adhering to the Committee on Publication Ethics (COPE) guidelines during the preparation and submission of this paper.

# Consent for Publication

All authors have read and approved the final manuscript and consent to its publication in this journal.

## Competing Interest

The authors declare no competing interests.

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## Author Contribution

Mariyam Mukhtarova: Writing – original draft, Writing – review & editing, Validation, Formal analysis, Visualization, Investigation, Conceptualization. Maria A. Golubeva: Writing – review & editing, Validation, Project administration, Supervision. Anton L. Maximov: Project administration, Supervision.

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## Availability of data and materials

No data was used for the research described in the article.

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## Figures

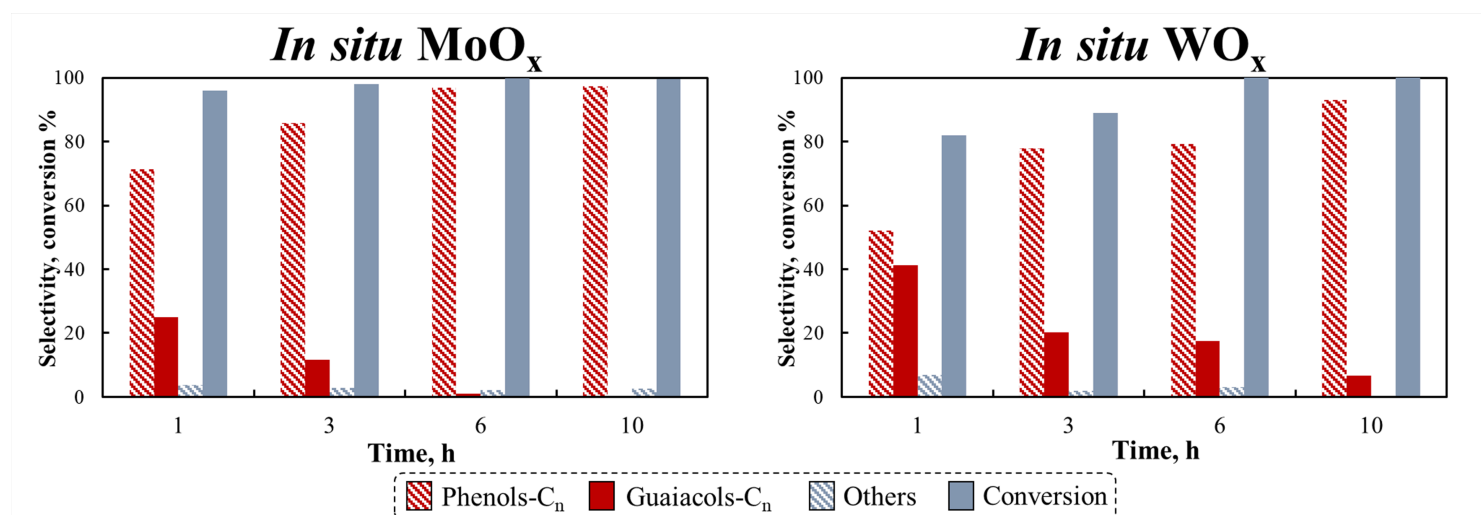


Figure 1

The hydroprocessing of guaiacol to alkylphenols using *in situ* MoO<sub>x</sub> and WO<sub>x</sub>. Reaction conditions: 300 °C, 5 MPa H<sub>2</sub>, 1–10 h

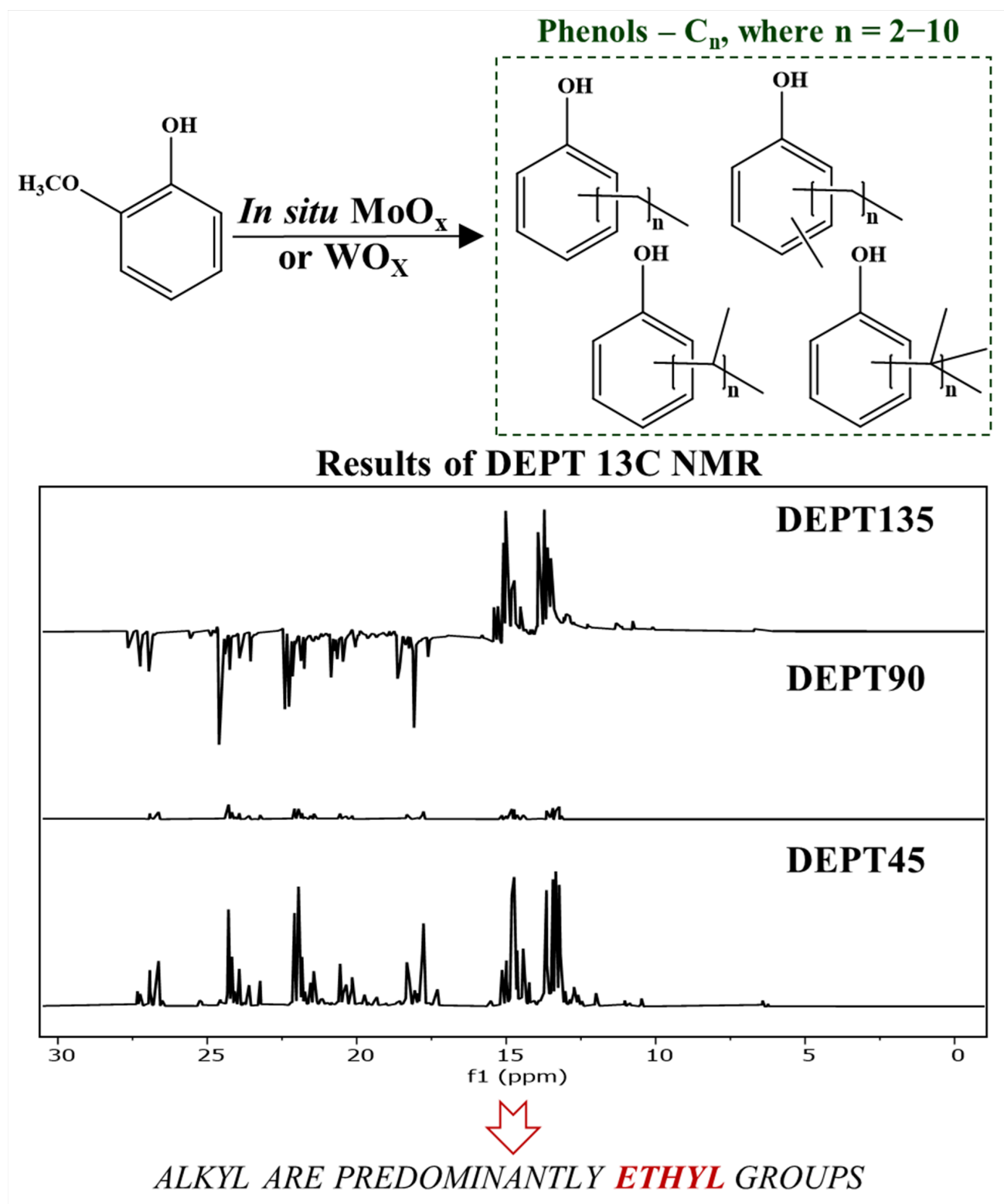


**Figure 2**

DEPT <sup>13</sup>C spectra of the reaction products obtained during the conversion of guaiacol using *in situ* MoO<sub>x</sub> and WO<sub>x</sub>. Reaction conditions: 300 °C, 5 MPa H<sub>2</sub>, 6 h

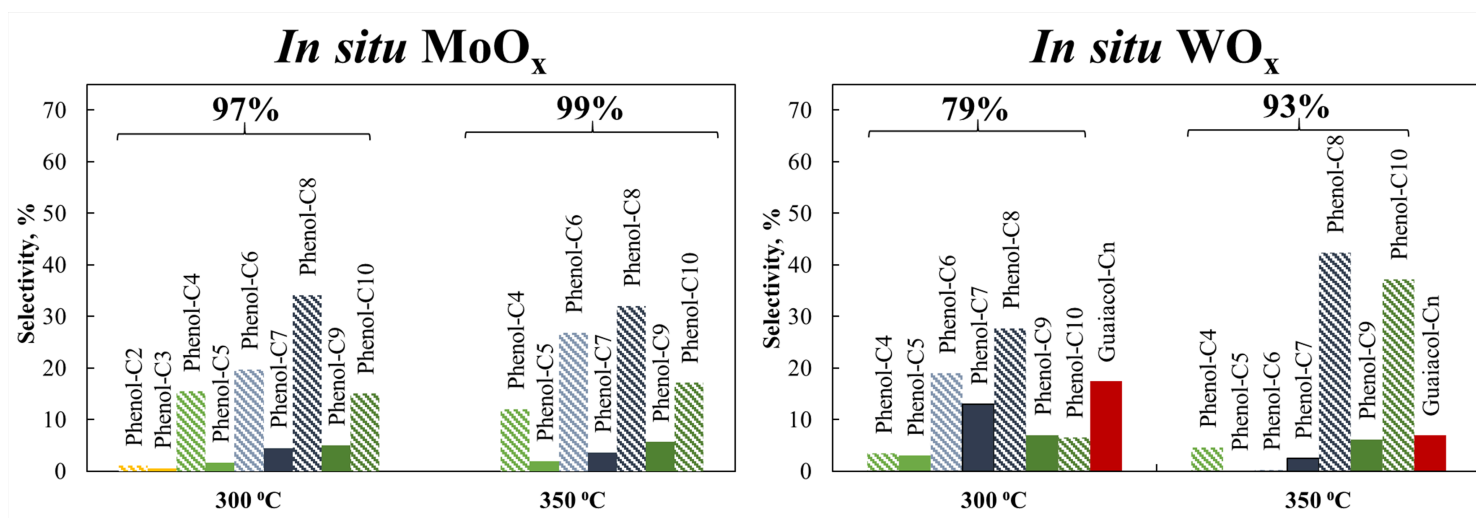
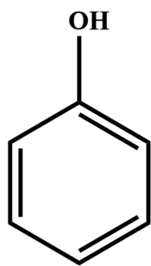
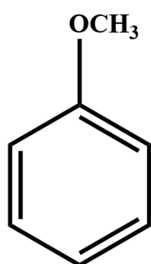
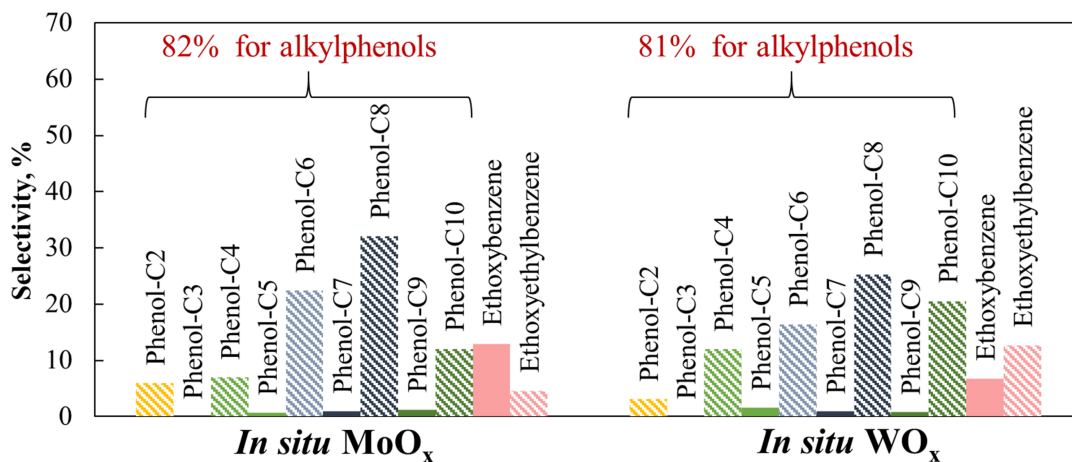


**Figure 3**

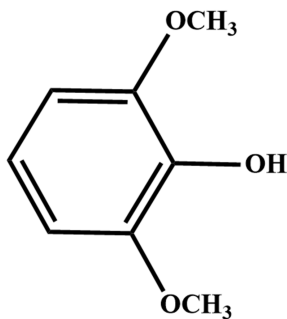
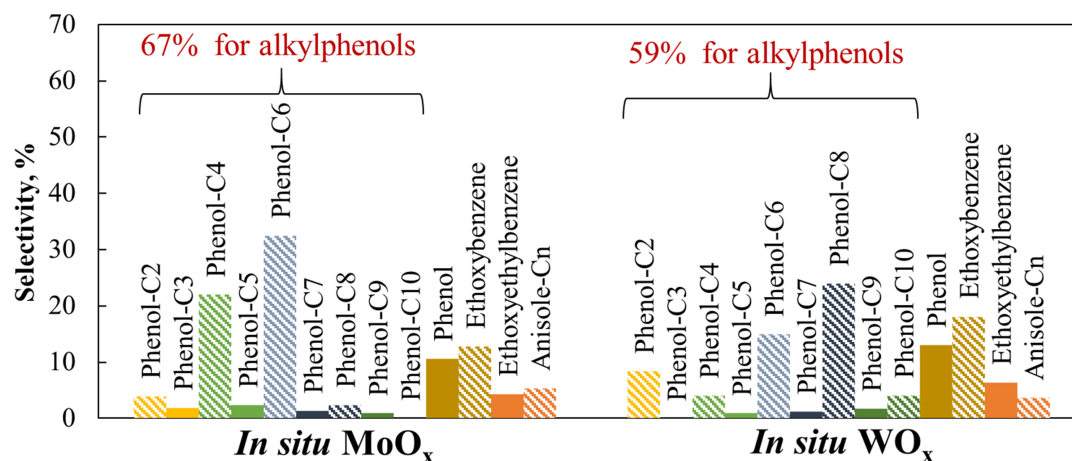
The hydroprocessing of guaiacol to alkylphenols using *in situ* MoO<sub>x</sub> and WO<sub>x</sub>. Reaction conditions: 300 and 350 °C, 5 MPa H<sub>2</sub>, 6 h



The full conversion over both catalysts



The conversion was 99% over MoO<sub>x</sub> and 90% over WO<sub>x</sub>



The full conversion over both catalysts

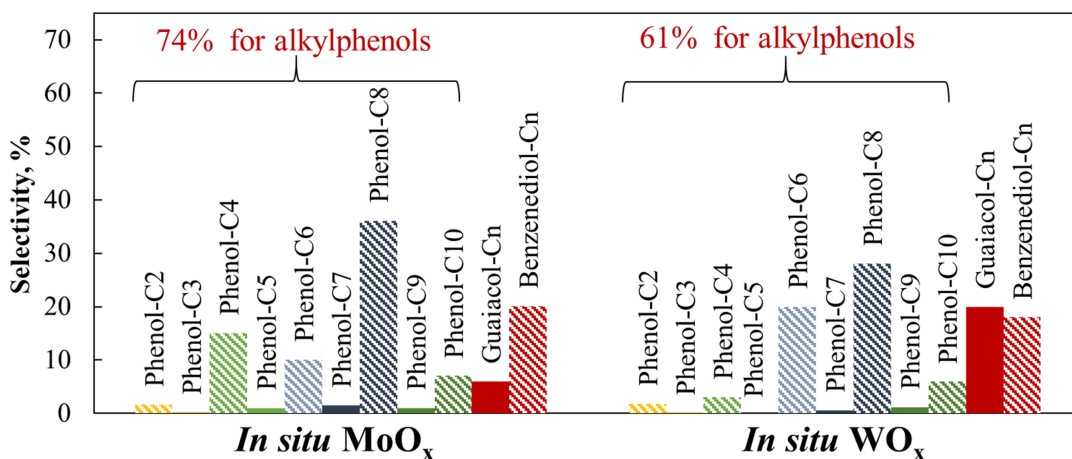


Figure 4

Hydroprocessing of phenol, anisole and syringol over *in situ* MoO<sub>x</sub> and WO<sub>x</sub>. Reaction conditions: 300 °C, 5 MPa H<sub>2</sub>, 6 h



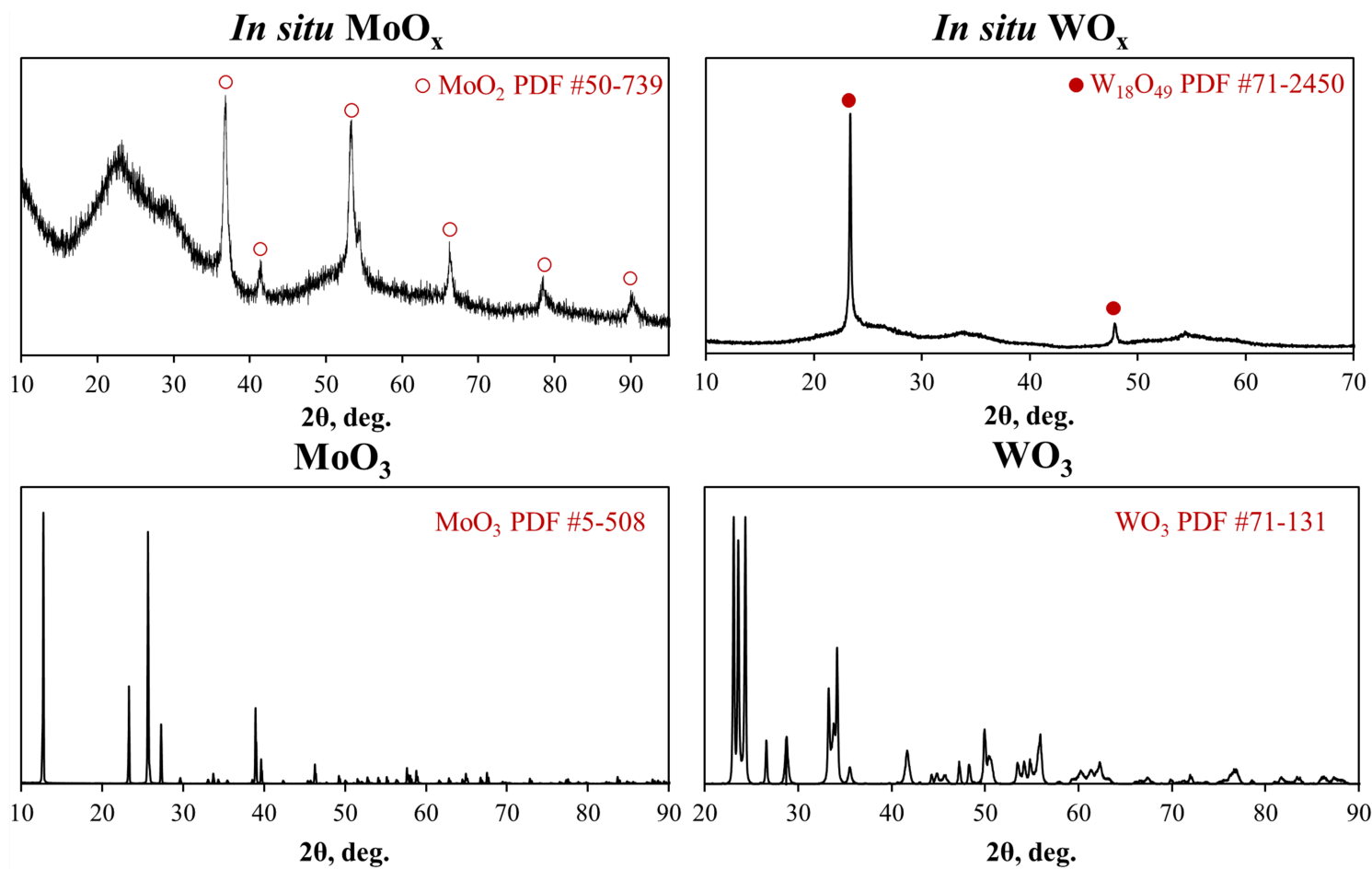


Figure 6

XRD patterns of *in situ* and *ex situ* formed molybdenum and tungsten oxides. Reaction conditions *in situ* formation MoO<sub>x</sub> and WO<sub>x</sub>: 300 °C, 5 MPa H<sub>2</sub>, 6 h

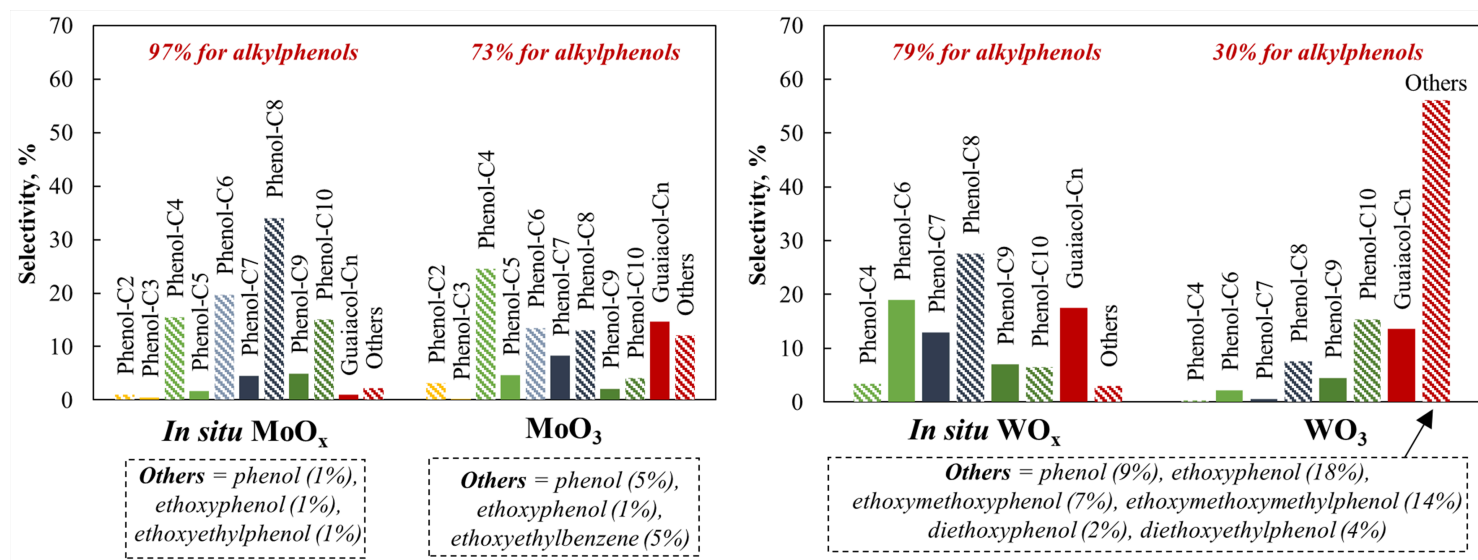


Figure 7

The comparison of *in situ* and *ex situ* formed metal (Mo, W) oxides in the hydroprocessing of guaiacol.  
Reaction conditions: 300 °C, 5 MPa H<sub>2</sub>, 6 h

## Supplementary Files

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