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Vibrational spectroscopic characterization of glycerol reaction pathways over metal-modified molybdenum carbide surfaces

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Abstract

As the production of biodiesel increases, it is economically preferable to upgrade the excess byproduct, glycerol, into value-added products. Metal-modified molybdenum carbide (Mo₂C) is a class of promising catalysts for this application due to their promising hydrodeoxygenation (HDO) activity. In this work, Pt, Fe and Cu were used to modify the Mo₂C surface and tune the product selectivity of glycerol. Pt/Mo₂C showed reforming activity to produce syngas, Fe/Mo₂C cleaved all the C-O bonds of glycerol to produce propylene, while Cu/Mo₂C broke only one C-O bond of glycerol to form acetol. Consecutive temperature-programmed desorption (TPD) experiments demonstrated an enhanced stability of all surfaces when compared to Mo₂C. High-resolution electron energy loss spectroscopy (HREELS) characterization indicated that the Fe/Mo₂C surface weakened the C-O bonds of glycerol, while the Pt/Mo₂C surface showed no activity towards C-O bond cleavage. This study demonstrated that the Pt/Mo₂C, Fe/Mo₂C and Cu/Mo₂C surfaces were active, selective and stable for converting glycerol into syngas, propylene, and acetol, respectively. The combination of TPD and HREELS also served as an example of utilizing surface spectroscopy to identify the reaction pathways and intermediates on model catalyst surfaces. This should, in turn, provide insights to guide the design of metal-modified carbide catalysts for the upgrading of biomass-derived oxygenates.

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1. Introduction

The upgrading of biomass-derived molecules has attracted significant research attention recently.^{[1]–[7]} Among the pathways to convert biomass, biodiesel production is a promising approach for mitigating current environmental issues and reducing dependence on fossil fuels.^[8] In biodiesel production, glycerol is generated as a major by-product. For every 100kg of biodiesel, 10kg of glycerol is produced.^[9] As biodiesel production continues to increase,^[10] it is economically preferable to convert the excess glycerol to value-added products. Various reactions have been studied to explore the utilization of glycerol.^[11] The reforming reaction breaks the C-H and C-C bonds of glycerol to form syngas (CO + H₂) for methanol production and Fisher-Tropsch synthesis.^{[12]–[14]} The complete hydrodeoxygenation (HDO) reaction can cleave all the C-O bonds of glycerol to produce propylene, an industrially important building block.^{[15]–[17]} The propylene produced from glycerol can contribute to the on-purpose production to fill the current gap between propylene market demand and supply.^[18] On the other hand, the selective HDO reaction can break one or two C-O bonds of glycerol to produce value-added C3 oxygenates such as acetol.^{[19][20]} propanediol,^{[21][22]} and propanol.^[23] To upgrade glycerol on an industrial scale, it is necessary to design low-cost catalysts with high stability, activity, and selectivity. There have been many research efforts on the upgrading of glycerol, but spectroscopic studies on the reaction pathways and adsorbed intermediates on well-defined surfaces are still lacking. The understanding gained from such fundamental studies is crucial to the rational design of efficient HDO catalysts.

Mo₂C has ordered crystalline structure, extreme hardness, high melting temperature and electric conductivity similar to metals.^{[24][25]} The clean Mo₂C surface has strong oxophilicity, which leads to high activity for C-O bond cleavage. Therefore, Mo₂C has been studied for CO₂ reduction^{[26][27]} and furfural HDO reaction.^{[28][29]} However, the oxophilicity of Mo₂C is too strong, which makes

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it difficult to remove surface oxygen or oxygen-containing surface intermediates, resulting in rapid deactivation of the Mo₂C surface.

Novel catalytic performance has been observed by tuning the oxophilicity of Mo₂C with admetals. For example, Ni-modified Mo₂C surfaces show the reforming activity of ethanol^[30] and ethylene glycol,^[31] Cu-modified Mo₂C surfaces promote the dehydrogenation of ethanol,^[30] and Coand Fe-modified Mo₂C surfaces show HDO activity of furfural.^{[32][33]} Though Mo₂C has been studied in the reactions of many oxygenates, very limited studies have focused on the reactions of glycerol. Since glycerol contains two types of -OH groups (primary and secondary), it can also serve as a model compound for the mechanistic study of selective C-O bond scission for larger polyols.

In a previous study, the selective HDO reaction of glycerol was investigated on Cu-modified Mo₂C catalysts.^[16] The combination of a strongly oxophilic site, Mo, and a weakly oxophilic sites, Cu, can selectively break a different number of C-O bonds of glycerol, leading to the selective production of propylene, allyl-alcohol, propanal, and acetol on Cu/Mo₂C surfaces with different Cu coverages. In this work, Pt/ Mo₂C and Fe/Mo₂C surfaces have been investigated to determine the effect of metal modifiers in controlling the reaction pathways of glycerol. The results from Cu-modified Mo₂C surface were also referred to for comparison.^[16] Consecutive TPD measurements were used to determine the surface activity and stability, and vibrational spectroscopic studies using high-resolution electron energy loss spectroscopy (HREELS) were performed to identify the surface intermediates. This work reveals the distinct bond scission sequences of glycerol on Pt/Mo₂C, Fe/Mo₂C and Cu/Mo₂C and provides a guideline for designing catalysts for different glycerol conversion pathways. The combination of TPD and HREELS also provides an example of using surface spectroscopy to identify promising catalytic systems for biomass upgrading.

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2. Methods

The TPD experiments were conducted in an ultra-high vacuum (UHV) chamber equipped with a quadrupole mass spectrometer (UTI-100C), a cylindrical mirror analyzer for Auger analysis, a metal source for physical vapor deposition and an electron gun for sputtering. The Mo(110) single crystal (Princeton Scientific, 99.99%) was spot-welded to two tantalum posts for resistive heating. A K-type thermocouple was spot-welded to the back of the crystal for temperature measurements. The synthesis procedure for Mo₂C was described previously.^[34] Briefly, the Mo(110) single crystal was cleaned by cycles of Ne⁺ sputtering and annealing, followed by oxygen treatment to remove surface carbon. The carbide-modified Mo(110) was synthesized by cycles of exposing Mo(110) to ethylene at 600K and subsequently annealing to 1200K until the Mo (186 eV):C (275 eV) Auger Electron Spectroscopy (AES) atomic ratio reached approximately 2:1. Metal modifiers with controlled coverage were deposited onto the as-synthesized Mo₂C surface by the physical vapor deposition (PVD) method. The metal coverage was 1 monolayer (ML) for all the metal modified Mo₂C surfaces and the coverage was quantified using the atomic ratio of admetal and substrate from AES measurements.^[35]

In a typical TPD experiment, the surface was exposed to 5 Langmuir (L, $1L = 10^{-6}$ Torr*s) of H₂ and 4L of glycerol at 200K and subsequently heated to 800K at 3K/s. The gas-phase products desorbed from the surface were detected by mass spectrometry.

The HREELS experiments were performed in a separate UHV chamber equipped with a HREEL spectrometer in addition to other capabilities described above in the TPD chamber. The HREEL spectra were recorded with a primary beam energy of 6 eV with an incidence and reflection angle of 60° with respect to surface normal. In a typical HREELS experiment, the surface was exposed to the same amount of H₂ and glycerol as in the TPD experiments. The surface was ramped to the

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desired temperature, held for 1 minute and cooled down to 100K before the HREEL spectra were recorded.

Glycerol (Fisher Scientific, 99%)) was transferred into a glass cylinder, purified with cycles of freeze-pump-thaw and pre-heated to 400K before introducing glycerol into the chamber. Hydrogen, oxygen, ethylene, neon, and carbon monoxide were of research purity and used without further purification. The purity of each gas was verified by mass spectrometry.

3. Results and discussions

3.1.TPD studies of reaction pathways on metal modified Mo₂C surfaces

TPD experiments were performed to investigate the reaction pathways of glycerol reaction on various metal modified Mo₂C surfaces. Propylene, CO, acetol and unreacted glycerol were observed in the gas phase. Propylene and acetol are HDO products, CO is from both reforming reaction and the recombinative desorption of surface carbon and oxygen. The desorption of H₂ and water were also observed.





Figure 1. TPD spectra of a) glycerol (m/z=61), b) propylene (m/z=39), c) CO (m/z=28) and d) acetol (m/z=43) with an exposure of 4 L glycerol on hydrogen pre-dosed Mo₂C, Cu/Mo₂C, Fe/Mo₂C, and Pt/Mo₂C surfaces

Fig.1 summarizes the desorption of glycerol, propylene, CO, and acetol from Mo₂C, Cu/Mo₂C, Fe/Mo₂C, and Pt/Mo₂C surfaces. The unreacted glycerol desorbed at 262 K (Fig.1(a)), and its cracking patterns contributed to the peak at 262 K in all the other spectra. Propylene was produced on both Fe/Mo₂C and Mo₂C surfaces (Fig.1(b)) with desorption temperatures of 354K and 471K, respectively, indicating that both surfaces were active for the complete HDO reaction that broke all C-O bonds of glycerol to form propylene. The lower propylene desorption temperature on Mo₂C suggested a higher C-O bond scission activity compared to that on Fe/Mo₂C. The Pt/Mo₂C surface was active in reforming to produce H₂ and CO. As shown in Fig. 1 (c), CO desorption peak was observed on Pt/Mo₂C with a peak temperature of 351K, indicating that the glycerol underwent the reforming pathway. On the other hand, even though CO desorption peaks were also observed on the other surfaces at a higher temperature, such desorption peaks were likely resulting from the recombinative desorption of surface carbon and oxygen, which were produced from the total decomposition of the unreacted surface adsorbates.

With the addition of Pt modifier on Mo₂C, the reaction pathway of glycerol changed from HDO to reforming. On Cu/Mo₂C, glycerol only underwent one C-O bond scission to form acetol (Fig.1(d)),^[16] likely due to the lower oxophilicity of the Cu modifier. Comparing the reaction pathways on these four surfaces (Scheme 1), Mo₂C and Fe/Mo₂C were able to cleave all the C-O bonds in glycerol to produce propylene, Cu/Mo₂C broke only one C-O bond of glycerol to form acetol, while Pt/Mo₂C favored the C-C and C-H bond scissions to produce CO and H₂.



Scheme 1 - Reaction pathways of glycerol over the Mo₂C, Pt/Mo₂C, Fe/Mo₂C, and Cu/Mo₂C surfaces.



Figure 2. Sequential TPD spectra of a) propylene (m/z=39) and b) CO (m/z=28) with an exposure of 4 L glycerol on hydrogen pre-dosed Mo₂C, Fe/Mo₂C and Pt/Mo₂C surfaces

Consecutive TPD experiments were performed to further investigate the stability of the Pt/Mo₂C, Fe/Mo₂C and Mo₂C surfaces, the results of which were summarized in Figure 2. The unreacted glycerol desorbed at 262 K and contributed to the peaks at 262 K in all other spectra. On Mo₂C, the first TPD spectrum showed a propylene desorption peak at 357 K (Fig.2(a)). The peak shifted to 447 K in the second and third TPD experiments with decreased peak area. The lower peak area and the higher desorption temperature indicated that the Mo₂C surface was deactivated, most likely by adsorbed carbon and oxygen. On Fe/Mo₂C, propylene desorption was observed in the first TPD experiment with a desorption temperature at 470 K. In the second and third TPD experiments, the desorption temperature slightly shifted to 447 K and the peak areas of the three spectra were similar. Comparing the first TPD spectra between Fe/Mo₂C and Mo₂C, the propylene spectrum from the Fe/Mo₂C surface had higher desorption temperature and smaller desorption peak than those of the Mo₂C surface, which suggested a weaker glycerol HDO activity on the Fe/Mo₂C surface. However,

Fe/Mo₂C showed better stability and higher activity than the Mo₂C surface in the second and third TPD spectra. The reason for the enhanced HDO stability of the Fe/Mo₂C surface could be attributed to the easier removal of surface oxygen. Under reactor condition, the surface oxygen produced from the HDO reaction of glycerol could be removed by gas-phase H₂.^[36] While under the UHV condition, due to the low partial pressure of gas-phase H₂, surface oxygen was removed by surface carbon.

On the other hand, no propylene was produced from Pt/Mo₂C (Fig.2(b)). Instead, a strong CO desorption peak at 350 K was observed in the first TPD experiment and this peak shifted to 332 K in the subsequent experiments (Fig.2(c)), indicating a high reforming activity of the Pt/Mo₂C surface. Due to the low oxophilicity of Pt, surface oxygen could be easily removed. The similar peak areas of CO desorption in three TPD cycles indicate good stability of the surface.

CO and propylene observed in the gas-phase were quantified using the following method. Since the products of glycerol over Cu/Mo₂C has been quantified previously, only two reaction pathways regarding the Mo₂C, Pt/Mo₂C, and Fe/Mo₂C surfaces were concerned here. The net reaction pathways of glycerol on the three surfaces can be summarized as follows:

 $a C_3 H_8 O_3 \rightarrow a C_3 H_6 + 3a O + a H_2$

 $b\ C_3H_8O_3\ \rightarrow\ 3b\ CO+4b\ H_2$

 $a = C_3H_6$ yield

b = (CO yield)/3

The yield of propylene and CO were calculated by the following equations:

Propylene yield =
$$\frac{\theta_{CO}^{sat}}{P_{CO}^{sat}} P_{propylene}^{glycerol} \frac{S_{28\,amu}^{CO}}{S_{39\,amu}^{c}} = a \rightarrow a = C_3H_6$$
 yield

$$CO yield = \frac{\theta_{CO}^{sat}}{P_{CO}^{sat}} P_{CO}^{glycerol}$$

Where the $P_{propylene}^{glycerol}$ and $P_{CO}^{glycerol}$ are TPD areas of the 39 amu and 28 amu peaks from the glycerol reaction. The CO desorption at 700 K was not considered as the glycerol reforming reaction. $S_{28\,amu}^{C0}$ and $S_{39\,amu}^{C_3H_6}$ are mass spectrometer sensitivities for 28 amu and 39 amu, respectively. P_{CO}^{sat} was the peak area of 28 amu from saturation CO desorption and θ_{CO}^{sat} was the saturation coverage of CO on Mo₂C.

The quantification results (Table 1) show that the fresh Mo₂C surface had a propylene yield of 0.072 in the first TPD experiment and the yield was reduced to 0.021 and 0.014 in the subsequent experiments. On the other hand, the Fe/Mo₂C surface, with better stability, had a propylene yield of 0.04 in the three TPD experiments. Pt/Mo₂C also showed high stability in glycerol reforming reaction and the yield slightly increased in the third TPD experiment.

	Mo ₂ C		Fe/Mo ₂ C		Pt/Mo ₂ C	
	HDO	reforming	HDO	reforming	HDO	reforming
1 st	0.07	0	0.04	trace	0	0.05
2 nd	0.02	0	0.04	0	0	0.05
3 rd	0.01	0	0.04	0	0	0.06

Table 1. Reactivity of glycerol on different surfaces (molecules per metal atom)

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3.2.Vibrational studies of surface intermediates of glycerol reactions

Figure 3. HREELS spectra of glycerol on hydrogen pre-dosed Fe/Mo₂C at 300 K, 400 K,500 K, and 700 K

To identify the changes of surface intermediates as a function of temperature, a thermal sequence of HREELS measurements were performed. Figure 3 shows the temperature dependence of the spectra after exposing Fe/Mo₂C to glycerol. When the temperature increased from 300 K to 400 K, the intensity of each peak remained relatively constant. The ν (CO) mode at 1040 cm⁻¹ became broader, suggesting that some C-O bonds were weakened on the surface. As the temperature increased from 400 K to 500 K, the intensity of the ν (CO) mode at 1040 cm⁻¹ decreased significantly, indicating the C-O bond scission of glycerol. This was consistent with the desorption of propylene starting at 400 K, as shown in the TPD experiments. As temperature further increased to 700 K, the intensity of the peaks associated with the CH species at 1403 cm⁻¹ and 2859 cm⁻¹ decreased significantly, suggesting the desorption of most of the hydrocarbon

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products. The peak at 537 cm⁻¹ increased, which indicates a strong M-O bond from adsorbed atomic oxygen on the surface.

Figure 4. HREELS spectra of glycerol on four surfaces at a) 300 K, b) 400 K

Fig.4 compares the surface intermediates on the four surfaces. The vibration mode assignments are summarized in Table 2. Since unreacted glycerol desorbed at 262 K (Fig.1), the spectra at 300 K (Fig.4(a)) showed the geometries of chemisorbed glycerol or partially reacted intermediates. The vibrational modes from the metal-oxygen bond appeared on Mo₂C, Fe/Mo₂C, and Pt/Mo₂C, suggesting the cleavage of O-H bond of molecular glycerol. On Cu/Mo₂C, the absence of the metal-oxygen bond suggested that the O-H bonds of glycerol were at least partially preserved. The v(CO) mode on Pt/Mo₂C at 1067 cm⁻¹, was higher than that on Fe/Mo₂C and Mo₂C at 1040 cm⁻¹, suggesting a stronger C-O bond of the adsorbed glycerol on Pt/Mo₂C. The weakened C-O bond on Fe/Mo₂C and Mo₂C facilitated C-O bond scission, leading to the formation of propylene. The

detection of the ν (C=O) modes at 1859 cm⁻¹ and 1946 cm⁻¹ indicated the formation of CO. The higher intensity of the ν (C=O) mode on Pt/Mo₂C was consistent with the TPD results that Pt/Mo₂C showed higher reforming activity (Fig.2(c)).

Mada	Frequency (cm ⁻¹)						
	Mo ₂ C	Fe/Mo ₂ C	Pt/Mo ₂ C				
δ (MO)	416	403	436				
<i>v</i> (<i>M0</i>)	570						
ν(CO)	1040	1040	1067				
$\rho_{\rm w}(\rm CH_2)$	1329	1329	1329				
δ(CH ₂)	1409	1409	1409				
v _{as} (CH)	2859	2859	2859				
ν(OH)	3403		3403				

Table 2. Vibrational mode assignment for adsorbed glycerol molecule

Abbreviation: δ – deformation, ν – stretching, ρ_w - wagging, as-asymmetric

As the surface was further annealed to 400 K (Fig.4(b)), the intensities of the ν (CO) mode (1067 cm⁻¹) and ν (C=O) mode (1946 cm⁻¹) on Pt/Mo₂C were reduced, consistent with the high reforming activity toward glycerol on Pt/Mo₂C and with the CO desorption peak at 332 K(Fig.2(c)). On the Fe/Mo₂C surface, the intensity of the ν (CO) mode (1040 cm⁻¹) did not show significant change, indicating that the C-O bonds had not been cleaved. In contrast, on the Mo₂C surface, the intensity of the ν (CO) mode cleavage and being consistent with the lower onset temperature of the propylene desorption from the fresh Mo₂C surface than on Fe/Mo₂C (Fig.1(b)). On Cu/Mo₂C, the decrease of the ν (CO) mode intensity was consistent with the formation of C-O bond scission products and the desorption of acetol, as reported previously.^[16]

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In summary, the HREELS results indicated that Mo₂C interacted with the oxygen in glycerol more strongly than Fe/Mo₂C and Cu/Mo₂C, and Pt/Mo₂C showed reforming activity.

4. Conclusions

This work combined TPD and HREELS measurements to compare the reaction pathways and adsorbed intermediates for the reaction of glycerol on Fe-, Pt- and Cu-modified Mo₂C surfaces. The Pt-modified Mo₂C surface showed reforming activity, while the Mo₂C, Fe-and Cu-modified Mo₂C surfaces showed HDO activity. On Mo₂C and Fe/Mo₂C, all the C-O bonds of glycerol were cleaved to form propylene. The Fe modifier slightly reduced the surface oxophilicity of Mo₂C, which improved surface stability. The Cu modifier reduced the oxophilicity of Mo₂C to a further extent such that only one C-O bond of glycerol was broken to form acetol. This work revealed that different metal modifiers could be used to tune the selectivity of the Mo₂C catalyst to convert glycerol into industrially important chemicals, such as syngas, propylene or acetol. In addition, using glycerol as a model compound, the reaction pathways revealed in this work could provide information on the bond-breaking sequences for larger polyols. The combination of TPD and HREELS also demonstrated the feasibility of using spectroscopic methods to identify promising catalytic systems for upgrading biomass-derived oxygenates.

Acknowledgements

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Table of Content



The combination of TPD and HREELS identified the various reaction pathways and intermediates of glycerol on metal modified Mo₂C surfaces. Glycerol was converted to acetol on Cu/Mo₂C, and to syngas on Pt/Mo₂C. Propylene was produced from glycerol on both Fe/Mo₂C and Mo₂C, and Fe/Mo₂C had better stability due to the modified surface oxophilicity.