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# Acidity, oxophilicity and hydrogen sticking probability of supported metal catalysts for hydrodeoxygenation process

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**Abstract.** Hydrodeoxygenation is an oxygen removal process that occurs in the presence of hydrogen and catalysts. This study has shown the importance of acidity, oxophilicity and hydrogen sticking probability of supported metal catalysts in having high hydrodeoxygenation activity and selectivity. These properties are required to ensure the catalyst has high affinity for C-O or C=O bonds and the capability for the adsorption and activation of H<sub>2</sub> and O-containing compounds. A theoretical framework of temperature programmed desorption technique was also discussed for the quantitative understanding of these properties. By using NH<sub>3</sub>-TPD, the nature and abundance of acid sites of catalyst can be determined. By using H<sub>2</sub>-TPD, the nature and abundance of metallic sites can also be determined. The desorption activation energy could also be determined based on the Redhead analysis of TPD spectra with different heating rates.

## 1. Introduction

Bio-oil has been extensively researched on for its application as one of the sources for liquid fuel. Bio-oil is produced through the pyrolysis of lignocellulosic biomass. However, bio-oil contains significant amount of oxygen-containing compounds due to depolymerization and defragmentation of cellulose, hemicellulose and lignin within biomass feedstock during pyrolysis[1]. The high oxygen content of bio-oil would cause issues such as low heating value, thermal instability and corrosivity that might affect its performance as liquid fuel [2, 3]. Thus, hydrodeoxygenation is often employed as an upgrading treatment for bio-oil in producing liquid fuel of low oxygen content and for the valorization of oxygen-containing compounds into high-added value products [4].

Hydrodeoxygenation (HDO) is a deoxygenation reaction which involves oxygen abstraction from the compound in the presence of hydrogen. The reaction is commonly catalyzed by zeolites and supported metal catalysts of various forms such as carbide, sulfide, nitride, phosphide and oxide. Numerous studies on HDO process using various oxygen-containing compounds and catalysts were done by researchers. The HDO studies using various oxygenated model compounds are instrumental in the understanding of the reaction mechanisms with respect to the functionalities of model

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compounds such as phenolics, furans, acids, carbonyls, alcohols, ethers and esters. This is because a typical bio-oil sample has more than 400 different oxygenated compounds of phenolics, furans, acids, carbonyls, alcohols, ethers and esters [5]. With the proper elucidation of the respective HDO reaction pathways of model compounds, HDO study of real feed can then be accurately studied with the consideration of synergistic, inhibitive and bulk effects owing to the chemical interactions of the complex mixtures [6].

The studies on HDO process using various catalysts have also shown the various effects of chemical compositions, physicochemical properties and electronic interactions of catalysts on the HDO performance. Thus, in this paper, several major properties of HDO catalysts such as hydrogen activation, acidity and oxophilicity were analyzed for the prediction of excellent HDO catalysts with high deoxygenation activity. Temperature programmed desorption for HDO catalysts were also discussed as the theoretical frameworks for the quantitative interpretation of such properties.

## 2. Hydrodeoxygenation mechanism

The mechanism of HDO generally involves the scission of C-O or C=O bonds for the oxygen removal from model compounds. HDO process can proceed through three major reaction pathways: direct deoxygenation route (DDO), hydrogenation-dehydration route (HYD) or tautomerization-deoxygenation route [7]. In DDO route, a direct cleavage of C-O or C=O bonds via hydrogenolysis occurs without the hydrogen saturation of aromatic or furanic rings. In HYD route, hydrogen saturation of aromatic or furanic rings would occur first before the cleavage of C-O bonds via dehydration. The selectivity of DDO or HYD pathways is of greater interest when it comes to HDO of model compounds containing aromatic or furanic rings and unsaturated bonds. DDO route may be more advantageous than HYD route as it does not require saturation of bonds by H<sub>2</sub>, resulting in a lower H<sub>2</sub> consumption. However, it was also noted that DDO requires higher activation energy than HYD since the bond dissociation energy of C<sub>Aromatic</sub>-OH bond (468 kJ/mol) is higher than that of C<sub>Cyclic</sub>-OH bond (385 kJ/mol) [7, 8].

Tautomerization-deoxygenation route is not as common as the former two pathways as tautomerization is only characteristic to model compounds that are of enol form. The tautomerization of oxygen-containing compound in its enol form will result in the formation of keto form to form a keto-enol equilibrium mixture. For instance, phenol HDO could undergo tautomerization to form a highly unstable 3,5-cyclohexadienone which would readily undergo C=O hydrogenation to form 3,5-cyclohexadienol. The 3,5-cyclohexadienol would then dehydrate to form benzene. This pathway is kinetically more favorable than DDO as tautomerization brings about an alteration of C<sub>Aromatic</sub>(sp<sup>3</sup>)-O bond into C<sub>Aromatic</sub>(sp<sup>2</sup>)=O bond which has lower bond energy, without resulting in the saturation of aromatic or furanic rings [9, 10]. However, this pathway requires metal catalysts of high oxophilicity such as C, Ti, Zr, V, W, Co, Fe, Ru and Sn [7].

## 3. Properties of supported metal catalysts

### 3.1. Hydrogen sticking probability

The adsorption and activation of hydrogen at catalyst surface are integral studies for HDO process which utilizes hydrogen species for the hydrogenolysis of C-O and C=O bonds. For HDO process, supported metal catalysts should have metallic sites that are active for H<sub>2</sub> adsorption and activation [5]. With the saturation of metal sites by activated hydrogen adsorbates, a facile hydrogen spillover to the metal support interface site will then be induced for the hydrogenolysis of the activated O-containing compounds [11].

Supported transition metal catalysts were commonly used in HDO because transition metals were noted to exhibit high H<sub>2</sub> sticking coefficient and hydrogenation activity [3, 12]. For instance, transition metals such as Cu, Co, Ir, Ni, Pd, Pt, Rh, Ru were noted to have H<sub>2</sub> sticking probability increasing in the order of Cu, Ni, Co, Ir, Pd, Pt, Rh and Ru at 150°C below and at 1 bar [12]. However, it was also noted that H<sub>2</sub> sticking probability and surface coverage on transition metals are also

thermodynamically dependent on the reaction temperature. Since  $H_2$  sorption is a reversible exothermic process, an increase in reaction temperature would result in lower  $H_2$  surface coverage, which then result in lower HDO activity [13, 14]. Thus, an optimized reaction temperature is important to ensure sufficient  $H_2$  surface coverage and sufficient energy for bond dissociation during HDO process.

### 3.2. Acidity

Acidity of supported metal catalysts is another important parameter in affecting HDO activity and selectivity. Acidity of catalyst is generally dependent on the nature and abundance of acid sites within the catalyst. The nature of acid sites can be classified as Lewis and Brønsted acid sites. Lewis acid sites are commonly the unsaturated metal sites which are the good electron acceptors while Brønsted acid sites are  $-OH$  or  $-SH$  groups of supports which are the good proton donors [3]. The function of acid sites in HDO process is to act as the adsorption and activation sites for the oxygen from the O-containing compounds. Subsequently, the activated O-containing compounds will then be hydrogenolyzed by activated hydrogen species from metallic sites.

Likewise, catalyst with higher abundance of acid sites for O-containing compound activation would also result in higher turnover rate. Zeolites and catalysts supported on C,  $TiO_2$ ,  $ZrO_2$ ,  $Al_2O_3$ ,  $CeO_2$  and  $SiO_2$  were some of the catalysts with good HDO activity that exhibit acidic characters. Zeolites were known for their high acidity for HDO while metal oxide supports were noted for their mild acidity. Nevertheless, acidity of catalysts must also be optimal since catalysts of high acidity were also noted to catalyze side reaction such as condensation to produce carbonaceous species that would deactivate the catalyst through coking [15].

### 3.3. Oxophilicity

Oxophilicity of metal is associated with the tendency of metal being attracted to oxygen and its abstraction. Supported metal catalysts with high oxophilicity would show higher affinities to C-O and C=O bonds, resulting in effective oxygen removal from these bonds. Likewise, several studies have also reported that the use of oxophilic metal catalysts such as Fe, Ti and Zr have resulted in the preference of tautomerization-deoxygenation pathway to produce deoxygenated aromatics as major products [16, 17]. Kepp [18] has analyzed the quantitative scale of the oxophilicity of metals as shown in table 1. Based on table 1, it can be inferred that HDO supports such as C,  $TiO_2$ ,  $ZrO_2$  and metals such as Ti, V, W, Zr, Co, Fe, Ru and Sn are highly oxophilic for the facile oxygen abstraction.

**Table 1.** Normalized oxophilicity of several elements.

Element	C	Ti	V	W	Zr	Co	Fe	Ru	Sn
Normalized oxophilicity	1.4	1.0	0.8	0.8	0.8	0.4	0.4	0.4	0.4

## 4. Recommendations for effective HDO process

From the reaction chemistry perspective, an effective hydrodeoxygenation reaction quintessentially entails high catalytic deoxygenation activity, high conversion of O-containing compounds and high yield and selectivity of deoxygenated products. As for the process design of such reaction, optimum reaction conditions must also be determined to optimize the production and design costs while maximizing the yield of desired products. Based on the desired properties of HDO catalysts as examined, we can see that supported metal catalysts with transition metals such as Cu, Co, Ir, Ni, Pd, Pt, Rh, Ru being supported on oxophilic and mild acidic supports such as C,  $TiO_2$  and  $ZrO_2$  would be recommended for an effective HDO process [19]. Zeolites were also noted to be excellent HDO catalysts; however, their high acidity may pose severe coking issues during catalytic regeneration. Likewise, HDO via DDO route is often preferred due to formation of deoxygenation aromatics and lower  $H_2$  consumption. For DDO route to be the dominant pathway, a reaction temperature of more

than 573 K is often recommended [14]. For reaction pressure, HDO at atmospheric pressure was also noted to be successful. For instance, de Souza et al. [16] reported that the vapor phase HDO of phenol to benzene over Pd/ZrO<sub>2</sub> at 573 K and 1.01 bar was able to achieve 75% phenol conversion and 54% benzene selectivity. Likewise, Boullosa-Eiras et al. [20] also reported that the liquid phase HDO of phenol to benzene over Mo<sub>2</sub>C/TiO<sub>2</sub> at 673 K and 25 bar was able to achieve 90% phenol conversion and 90% benzene selectivity. A higher H<sub>2</sub> pressure would certainly enhance the adsorption of H<sub>2</sub> for HDO but the handling of highly pressurized process may require additional design costs for reactor designing and process safety.

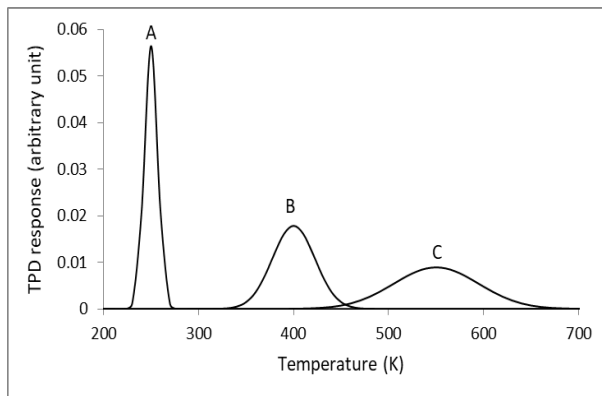
### 5. Temperature programmed desorption for HDO catalysts

Temperature programmed desorption (TPD) is a technique used to study chemisorption at catalyst surface. By analyzing the chemisorption behavior, the physicochemical properties of catalyst surface can then be determined. TPD uses different probe molecules such as NH<sub>3</sub>, H<sub>2</sub>, CO<sub>2</sub>, CO, etc. for different analyses of chemisorption properties. For hydrodeoxygenation process, NH<sub>3</sub>-TPD and H<sub>2</sub>-TPD are needed for the analysis of the physicochemical properties of HDO catalysts. NH<sub>3</sub>-TPD involves the chemisorption of basic NH<sub>3</sub> molecules on the acid sites of catalyst which enables the quantitative study of the acid sites. Likewise, H<sub>2</sub>-TPD involves the chemisorption of H<sub>2</sub> molecules on the metallic sites of catalyst which enables the quantitative study of the metallic sites. These quantitative studies rely on the characteristics of desorption peaks as shown in figure 1.

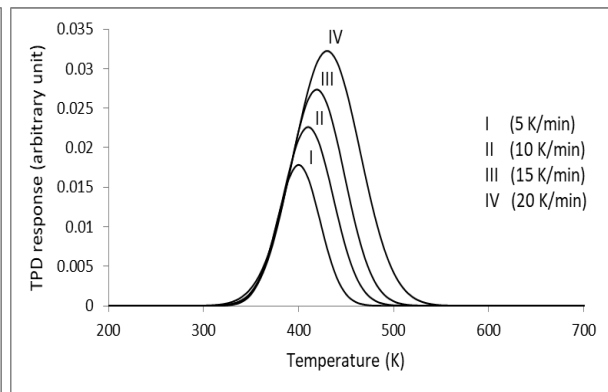
Every desorption peak has the following characteristics: desorption phenomenon, peak area, peak temperature and peak width. The physical significance of a desorption peak is that it tells of a unique desorption phenomenon which occurs at that particular desorption condition. The unique desorption phenomenon is often attributed to a particular chemisorption state or interaction of the probe molecules with the different chemisorption sites of the samples. Thus, based on figure 1, the three distinct desorption peaks may represent three unique chemisorption states of probe molecules due to the presence of three different chemisorption sites of the sample.

The physical interpretation of peak area would be the amount of desorbed probe molecules. By knowing the amount of desorbed probe molecules and the chemisorption mode, the number of chemisorption sites of samples can then be calculated. Likewise, peak temperature is the desorption temperature in which desorption rate is at maximum. A desorption phenomenon which occurs at higher desorption temperature would indicate the stronger chemisorption interaction of the probe molecule with the chemisorption site of sample. As for peak width, it represents the range of temperature at which desorption occurs.

The physical interpretation of NH<sub>3</sub>-TPD for HDO metal catalyst is that it gives a quantitative understanding of the acid sites while H<sub>2</sub>-TPD gives a quantitative understanding of the hydrogen interaction with metallic sites. For NH<sub>3</sub>-TPD spectra, the number of desorption peak represents the type of acid sites while the peak area correlates to the amount of acid sites. Peak temperature would represent the acidity strength of the acid sites. Based on these information, the nature and abundance of acidic sites of HDO metal catalysts can then be determined based on NH<sub>3</sub>-TPD. Likewise, the identification of Lewis and Brønsted acid sites can also be further determined using FTIR spectroscopy. For H<sub>2</sub>-TPD spectra, the number of desorption peak represents the chemisorption mode of hydrogen species while the peak area correlates to the amount of metallic sites. Peak temperature would represent the chemisorption bond between hydrogen and metallic sites. Based on this information, H<sub>2</sub> sticking probability and its chemisorption mode for HDO metal catalysts can then be determined based on H<sub>2</sub>-TPD.



**Figure 1.** Simulated TPD spectra with three desorption peaks.



**Figure 2.** Simulated TPD spectra with different heating rates.

The desorption activation energy can also be determined using Redhead analysis which utilizes TPD spectra of different heating rates [21]. Firstly, Polanyi-Wigner equation was used to describe desorption rate equation that is equation (1). Redhead equation was obtained by differentiating equation (1) with respect to temperature and was then equated to zero. Equation (2) was then obtained by substituting the coverage and temperature at maxima.

$$r_d = -\beta \frac{d\theta}{dT} = A\theta^m \exp\left(\frac{-E_d}{RT}\right) \quad (1)$$

$$\frac{E_d}{RT_p^2} = \frac{A}{\beta} m \theta_p^{m-1} \exp\left(\frac{-E_d}{RT_p}\right) \quad (2)$$

where  $r_d$  is desorption rate,  $\beta$  is heating rate,  $\theta$  is surface coverage of probe molecules,  $\theta_p$  is surface coverage at maxima,  $\theta_0$  is initial surface coverage which is 2 times of  $\theta_p$ ,  $T$  is absolute temperature,  $A$  is pre-exponential factor,  $m$  is order of desorption,  $E_d$  is desorption activation energy,  $R$  is ideal gas constant and  $T_p$  is peak temperature. By expressing equation (2) in its linear form, we obtained the following:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_d}{R}\left(\frac{1}{T_p}\right) + \ln\left(\frac{mAR\theta_p^{m-1}}{E_d}\right) \quad (3)$$

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_d}{R}\left(\frac{1}{T_p}\right) + \ln\left(\frac{AR}{E_d}\right) \quad \text{where } m \text{ is } 1 \quad (4)$$

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_d}{R}\left(\frac{1}{T_p}\right) + \ln\left(\frac{AR\theta_0}{E_d}\right) \quad \text{where } m \text{ is } 2 \quad (5)$$

Equation (4) is used when desorption is of first order while equation (5) is used when desorption is of second order. Based on equation (4) and (5), desorption activation energy can then be calculated from the gradient of the plot of  $\ln\left(\frac{\beta}{T_p^2}\right)$  against  $\left(\frac{1}{T_p}\right)$ .  $H_2$  desorption activation energy is one of the



parameters required for the kinetic studies of HDO. By conducting Redhead analysis for H<sub>2</sub>-TPD spectra, H<sub>2</sub> desorption activation energy can then be calculated.

## 6. Conclusion

Hydrodeoxygenation of O-containing compound involves the scission of C-O or C=O bonds which can be accomplished through DDO, HYD or tautomerization-deoxygenation routes. The acidity, oxophilicity and hydrogen sticking probability are the important properties of supported metal catalysts to ensure a facile hydrodeoxygenation. These properties would result in the catalyst having high affinity for C-O or C=O bonds, facile adsorption and activation of hydrogen and O-containing compounds. The use of temperature programmed desorption technique has been noted to give a theoretical understanding of such properties. By using TPD such as NH<sub>3</sub>-TPD and H<sub>2</sub>-TPD, the nature and the abundance of acid sites and metallic sites can be elucidated.

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## References

- [1] Abnisa F, Wan Daud W M A, Arami-Niya A, Ali B S and Sahu J N 2014 *Energy Fuels* **28** 3074-85
- [2] Mortensen P M, Grunwaldt J-D, Jensen P A, Knudsen K G and Jensen A D 2011 *Appl. Catal., A* **407** 1-19
- [3] He Z and Wang X 2012 *Catal. Sustainable Energy* **1** 28-52
- [4] Jacobson K, Maheria K C and Dalai A K 2013 *Renewable Sustainable Energy Rev.* **23** 91-106
- [5] Bu Q, Lei H, Zacher A H, Wang L, Ren S, Liang J, Wei Y, Liu Y, Tang J, Zhang Q and Ruan R 2012 *Bioresour. Technol.* **124** 470-477
- [6] Choudhary T V and Phillips C B 2011 *Appl. Catal., A* **397** 1-12
- [7] Kay Lup A N, Abnisa F, Wan Daud W M A and Aroua M K 2017 *Appl. Catal., A* **541** 87-106
- [8] Furimsky E 2000 *Appl. Catal., A* **199** 147-190
- [9] Hensley A J R, Wang Y and McEwen J-S 2015 *ACS Catal.* **5** 523-536
- [10] Robinson A, Ferguson G A, Gallagher J R, Cheah S, Beckham G T, Schaidle J A, Hensley J E and Medlin J W 2016 *ACS Catal.* **6** 4356-68
- [11] Moberg D R, Thibodeau T J, Amar F G and Frederick B G 2010 *J. Phys. Chem. C* **114** 13782-95
- [12] Johansson M, Lytken O and Chorkendorff I 2008 *J. Chem. Phys.* **128** 1-11
- [13] Derrouiche S and Bianchi D 2004 *Langmuir* **20** 4489-97
- [14] Gutierrez A, Kaila R K, Honkela M L, Slioor R and Krause A O I 2009 *Catal. Today* **147** 239-246
- [15] To A T and Resasco D E 2015 *J. Catal.* **329** 57-68
- [16] de Souza P M, Rabelo-Neto R C, Borges L E P, Jacobs G, Davis B H, Sooknoi T, Resasco D E and Noronha F B 2015 *ACS Catal.* **5** 1318-29
- [17] Nie L, de Souza P M, Noronha F B, An W, Sooknoi T and Resasco D E 2014 *J. Mol. Catal. A: Chem.* **388-389** 47-55
- [18] Kepp K P 2016 *Inorg. Chem.* **55** 9461-70
- [19] Kay Lup A N, Abnisa F, Wan Daud W M A and Aroua M K 2017 *J. Ind. Eng. Chem.* <http://dx.doi.org/10.1016/j.jiec.2017.06.049>
- [20] Boullousa-Eiras S, Lødeng R, Bergem H, Stöcker M, Hannevold L and Blekkan E A 2014 *Catal. Today* **223** 44-53
- [21] Redhead P A 1962 *Vacuum* **12** 203-211