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Authors: Jie Zhang, Chuang Li, Xiao Chen, Weixiang Guan, Changhai Liang

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Insights into the Reaction Pathway of Hydrodeoxygenation of Dibenzofuran over MgO Supported Noble-metals Catalysts

Jie Zhang, Chuang Li, Xiao Chen, Weixiang Guan, Changhai Liang*

Laboratory of Advanced Materials and Catalytic Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116023, China

* To whom correspondence should be addressed: Fax: + 86-411-84986353; E-mail: changhai@dlut.edu.cn; Homepage: http://amce.dlut.edu.cn



Graphical Abstract

Highlights

- HDO activity of DBF is following: Pt/MgO > Ru/MgO > Pd/MgO.
- Pt catalyst promotes the hydrogenation of aromatic ring.
- Ru catalyst accelerates the hydrogenolysis of C_{aromatic}-O bond.
- High temperature and low pressure favor DDO route in the HDO of DBF.

Abstract

Conversion of oxygen-containing compounds derived from lignin arises wide interest due to fossil-derived resources consumption and growing environmental concerns. In this work, hydrodeoxygenation (HDO) of dibenzofuran (DBF) was studied over high-surface-area MgO supported Pt, Pd and Ru catalysts at 370 °C and 1.0 MPa. It was determined that the active metals not only affect the catalytic activity, but also change the reaction pathway of HDO of DBF. The intrinsic activity (TOF) of MgO supported catalysts follows the trend: $Pt/MgO (0.36 s^{-1}) > Ru/MgO (0.29 s^{-1}) > Pd/MgO (0.09 s^{-1})$, companied by the increasing activate barrier. Pt has a high activity in the hydrogenation of DBF, and exhibits a perfect deoxygenation activity followed by hydrogenation (HYD) pathway. Ru shows better cleavage ability of Caromatic-O bond and the removal of oxygen from DBF mainly occurs via direct deoxygenation (DDO) pathway. The increased Pt loadings largely promote the conversion of DBF by enhancing both HYD and DDO pathways. In addition, more direct cleavage of Caromatic-O bond occurs at higher temperature and the production of aromatics by the DDO pathway prefers the relatively low reaction pressure. Based on the pseudo-first-order kinetics, the analysis of the fitted reaction rate constant shows that the DDO selectivity follows the order: Ru/MgO > Pd/MgO > Pt/MgO, which depends on the capacity of active metals to the cleavage of Caromatic-O bond and the hydrogenation of aromatic ring.

Keyword: Hydrodeoxygenation, Dibenzofuran, MgO, Noble metals, Reaction pathway.

1. Introduction

During the past decades, fossil-derived resources consumption and growing environmental concerns have been gaining growing attention for their replacement by renewable resources [1, 2]. Lignin, the most abundant renewable resources composed of aromatic units in nature[3], is of major interest to reduce the dependence to the fossil fuels. However, the bio-oils derived from lignin through fast pyrolysis typically contain high oxygen content, taking up to 35-40 % in weight[4, 5], which results in high viscosity, low heating value, and poor thermal stability[6, 7]. Catalytic hydrodeoxygenation (HDO), a promising process to upgrade the bio-oils, offers excellent potential route for production of fuels[8-11] and chemicals[12] from bio-oils. The formation of fuels could be obtained by the hydrogenation saturation of aromatic ring and then the cleavage of C-O bond. However, the production of chemicals[3], such as phenols and aromatic hydrocarbons[13], is followed by selective cleavage of C–O bond with reserving aromatic ring intact. Generally, the former is hydrogenation (HYD) pathway and the latter is the direct deoxygenation (DDO) pathway. Although much works has focused on the hydrogenation of oxygen-containing compounds derived from lignin, such as anisole[14, 15], diphenyl ether[15, 16], guaiacol[13, 17, 18] and phenol[19-21], the systematical exploration of the effect of active metals and reaction conditions on the selectivity of HYD and DDO pathways[21] is limited.

Dibenzofuran (DBF), with furan and aromatic structure, is often used as model compound[8, 10, 11, 22-26] in HDO studies of the bio-oils derived from lignin because it is very difficult to deoxygenation in HDO[8, 26]. The HDO of DBF normally takes place by the parallel and competitive HYD and DDO pathways. The HYD pathway, the dominant route in previous studies, leads to oxygen-containing intermediates tetrahydrodibenzofuran (THDBF), hexahydrodibenzofuran (HHDBF), dodecahydrodibenzofuran (DHDBF), as well as deoxygenated products cyclohexylbenzene (CHB) and bicyclohexane (BCH) [26], in which the cleavage of C-O bond is relatively easy due to the hydrogenation of aromatic ring weakening the bond energy of C-O. The DDO route, involved direct hydrogenolysis of the C-

O bond, yields o-phenylphenol (OPP) and biphenyl (BP), which requires high selective catalyst and the harsh reaction condition. The desirability of each reaction pathway is determined by the characteristics required of the end product. The HDO of lignin to phenols or aromatic hydrocarbons proceeds almost exclusively by the direct deoxygenation route. The C-O bond scission can be an elimination mechanism in which hydrogenated intermediates are involved[10, 26] or direct hydrogenolysis of the C-O bond[3, 16, 17, 27] or perhaps a combination of both[14, 21]. Aiming the rational design of an efficient catalytic system for the enhancement of DDO route in the HDO of DBF, the basic MgO was selected as the support of catalysts. The aromatic rings of DBF in which π electrons act as a Lewis base due to the enriched electron densities inhibited the adsorption and activation on basic support[19]. Therefore, the basic support could weaken the hydrogenation of aromatic rings through HYD route due to decreased interaction of aromatic rings and support, compared with acidic support. Typically, prominent anti-coking of basic support (MgO) has been aroused much attention. Previous literatures [28, 29] reported that direct desulfurization (DDS) and HYD of sulfurcontaining compounds are assumed to take place on distinct types of active sites. Precious metal (Pt, Pd, and Ru) catalysts have been demonstrated to show some applications for the transformation of biomass. And it was found that Ru catalysts are more active in hydrogenolysis reactions [30] while Pt catalysts are often used in the hydrogenation reactions[26].

At present, to gain better insights into the reaction pathways (HYD and DDO) of DBF conversion, we explored the activity of MgO supported (Pt, Pd and Ru) catalysts under different reaction conditions. It can be well established that the studied catalytic system is intrinsically selective to HYD or DDO pathway. Reaction kinetics were also investigated with the aim to further reveal the changes of reaction pathways. Understanding the factors that control this selectivity will enable the design of catalysts for particular products.

2. Experimental

2.1. Catalyst preparation

MgO was synthesized by a method of chemical precipitation from Mg(CH₃COO)₂ according to the following procedure. 8g of Mg(CH₃COO)₂ was dissolved in 50 mL of

deionized water at room temperature, then the obtained solution was added to 200 mL aqueous solution containing 5g of $H_2C_2O_4$, finally the resulting solution was vigorously stirred at room temperature for 12 h. A white precipitate of MgC₂O₄ was obtained, which was thoroughly washed with distilled water and dried at 100 °C for an overnight. MgC₂O₄ powders were calcined at 500 °C for 4 h to produce MgO powders. The heating treatment was carried out in electric furnaces under O₂/Ar (20/40 mL min⁻¹) atmosphere.

The supported noble-metals catalysts were prepared by an impregnation method with metal precursors H₂PtCl₆·6H₂O, PdCl₂, and RuCl₃·3H₂O. Typically, a certain amount of metal precursor was dissolved in 60 mL methanol at room temperature. Then 2.0 g of calcined MgO support was added under vigorous stirring until the formation of homogenous slurry. Methanol was removed after 30 min, using a rotary evaporator, and the slightly damp powder was allowed to air dry at 60 °C for an overnight prior to reduction. The prepared catalysts were pre-reduced at 400 °C for 2 h under 40 mL min⁻¹ H₂. The theoretical metal loading of Pt/MgO, Pd/MgO and Ru/MgO is 0.6 wt. %, and those of 1Pt/MgO and 2Pt/MgO are 1.0 wt. % and 2.0 wt. %, respectively.

2.2. Catalytic reaction

Typically, hydrogenolysis of DBF was performed at 370 °C and 1.0 MPa total pressure, with a H₂/feed volumetric ratio of 400 in a continuous-flow fixed-bed reactor. The catalyst (80 mg) was mixed with inert SiO₂ (5.0 mL) and packed between two inert layers of SiO₂ (5.0 mL and 6.0 mL, respectively) and kept in the middle of the furnace. Prior to reaction, the asprepared catalysts were pretreated in-situ under 40 mL min⁻¹ H₂ at 1.0 MPa and 400 °C for 1 h and then the temperature cooled to reaction temperature. Next, the liquid reactants consisted of 2.0 wt. % DBF, 1.0 wt. % n-dodecane (as internal standard) and 97.0 wt. % n-decane (as solvent) were delivered into the reactor and mixed with H₂ gas at the inlet of the reactor. After the reaction was carried out overnight, it reached the steady state and catalytic tests were conducted. The reaction products after being condensed in a cold trap were collected and analyzed off-line by an Agilent gas chromatograph 7890A equipped with flame ionization detector and a 0.5 μ m×0.32 mm×30 m FFAP capillary column. Product identifications were conducted on an Agilent 7890B with 5977A MSD and a 0.25 μ m×0.25 mm×30 m HP-5

capillary column.

The hydrodeoxygenation (HDO) degree was estimated by the equation

HDO (%) =
$$\frac{n_{\text{reactant}}^{0} - n_{\text{reactant}}^{\tau} - \sum n_{i} \times m_{i}}{n_{\text{reactant}}^{0} - n_{\text{reactant}}^{\tau}} \times 100\%$$
(1)

where $n_{reactant}^{0}$ is the initial amount of DBF (mol), $n_{reactant}^{\tau}$ is the amount of DBF at contact time τ , n_i is the amount of i-product (mol) in the liquid phase (except for unreacted reactant), and m_i is the number of oxygen atoms in a molecule of i-product.

Selectivity values were calculated by the ratio between the molar amount of each formed product and the total amounts of formed products.

Turnover frequency (TOF) values were calculated as the ratio between reaction rates of DBF conversion (mol·s⁻¹·g_{cat}⁻¹) and the number of active sites determined by CO chemisorption (mol_{CO}·g_{cat}⁻¹).

Reaction rates were calculated by the equation

Reaction rate =
$$\frac{n_{conv.}^{\tau}}{m_{cat} * \tau}$$
 (2)

where $n_{conv.}^{\tau}$ is the converted moles of DBF at contact time τ ; and m_{cat} is the weight of catalyst (g).

Carbon balance closures were typically more than 95 %. All the reactions were assumed to be of the pseudo first order.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were collected using a Rigaku D/MAX-RB instrument using a Cu K α_1 monochromatized radiation source in the 2 θ range of 5°-90° with a scan speed of 10° min⁻¹, operated at 40 kV and 100 mA.

Nitrogen adsorption-desorption isotherms were carried out at -196 °C using a Quantachrome Autosorb IQ automated sorption system. The specific surface area was calculated by the Brunauer-Emmett-Teller method at a relative partial pressure of 0.05–0.3. The total pore volume and pore size distribution were measured by a adsorption curve using the Barre-Joyner-Halenda model. Before the measurements, the samples were degassed under vacuum at 200 °C for 8 h.

Transmission electron microscopy (TEM) images of the reduced catalysts were obtained

on a Philips CM 120 instrument with accelerating voltage of 120 keV. Prior to the measurements, the sample was ultrasonically dispersed in ethanol and the suspension formed was deposited onto a copper grid and dried at room temperature. Surface-averaged sizes of the metal particles were calculated, measuring about 200 particles from at least three different micrographs for each sample.

CO chemisorption, carried out on CHEMBET-3000, was used to measure the number of metal surface sites on reduced catalysts at 30 °C. Briefly, about 100 mg sample was put into a U-shaped quartz tube and reduced in 10% H₂/He at 400 °C, and then it was purged with He. After cooling to 30 °C, the 10% CO/He pulse injection was performed and CO adsorption was considered to be completed after three successive peaks showed the same peak areas. A stoichiometry of CO/metal =1 was taken to calculate the number of metal active sites. Hence, the turnover frequency of the catalyst can be evaluated.

The metal content of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer Optima 2000 DV device.

3. Results and discussion

3.1 Catalyst characterization

The wide-angel XRD technique was performed to study the formation of crystalline species for different catalysts after reduction at 400 °C for 2 h as shown in Fig. 1. It displays that all peaks are associated with the support ($2\theta = 37, 43, 62, 75, 78^\circ$), and no characteristic diffraction peaks of Pt, Pd or Ru is presented, even for higher Pt loading sample (2.0 wt. %). This is probably due to the small size and high dispersion of the metal nanoparticles, which is also consistent with the following TEM result.

 N_2 sorption analyses were performed to determine the differences in physical properties of support and all catalysts. The N_2 adsorption-desorption isotherms of all catalysts after reduction at 400 °C for 2 h are shown in Fig. 2. And the detailed results are revealed in Table 1. All isotherms are type IV isotherms and display the H1 hysteresis loops, which are typical characteristics for mesoporous materials. The pure MgO has a specific surface area of 356 m^2/g , a pore volume of 0.90 cm³/g and a pore diameter of 10.0 nm. When a similar loading of

Pt, Pd or Ru on MgO, the BET surface areas of them decrease compared with pure MgO. Besides, when increasing the Pt loadings from 0.6 wt.% to 2.0 wt.%, the BET surface area and pore volume of the Pt/MgO catalyst decrease from 317 to 181 m²/g and 0.80 to 0.57 cm³/g, respectively. These results show that the loading of Pt in the impregnation method has an effect on the structure of MgO. For all catalysts, the actual metal loading is almost close to the theoretical value, as shown in Table 1.

The morphology of the reduced catalysts and the histograms of particle size are shown in Fig. 3. The results indicate that Pt, Pd and Ru particles are well-distributed on support of MgO and have small metal particle size (< 2 nm) probably due to high surface area of MgO. The average sizes of metal particles, as calculated by statistical analysis of about 200 particles, are also shown in Table 2. The Pt nanoparticles are homogeneous dispersed on the MgO support. With increasing Pt loadings, the size of Pt nanoparticles is just slightly increased from 1.55 to 1.66 nm. Apparently, the size of metal particles decreases following the order: Pd/MgO \approx Ru/MgO > Pt/MgO.

The amounts of metal active sites were estimated from CO chemisorption measurement and the results are listed in Table 2. Using a CO/M (M = Pt, Pd or Ru) = 1 stoichiometry, the number of accessible surface Pt⁰, Pd⁰ or Ru⁰ atoms could be calculated, from which the intrinsic activity (TOF) of catalysts could be derived. As can be expected, with increasing the Pt loadings, the CO uptake increases from 1.85 µmol/g to 17.79 µmol/g. The linear relationship between the actual Pt loading and the CO uptake confirms the similar Pt dispersions, which is correlated with the similar Pt sizes in TEM results. Compared with different catalysts, the CO uptake follows the trend: Pd (5.47 µmol/g) > Ru (3.40 µmol/g) > Pt (3.17 µmol/g), which indicates that Pd/MgO catalyst exposes more active sites than MgO supported Ru or Pt catalysts [31].

3.2 Hydrodeoxygenation of DBF over MgO supported Pt, Pd and Ru catalysts

In the present study, we explored and compared the catalytic performance of Pt/MgO, Pd/MgO and Ru/MgO in HDO of DBF. Fig. 4 compares the product selectivity and conversion of all catalysts at different contact time. The main products detected by GC-MS and GC are biphenyl (BP), *o*-phenylphenol (OPP), cyclohexylbenzene (CHB), tetrahydrodibenzofuran

(THDBF), 2-cyclohexylphenol (CHPOH). In addition, small amounts of products, such as 2cyclohexylcyclohexanol (CHCHOH), bicyclohexane (BCH), cyclopentylmethylcyclohexane (CPMCH), cyclopentylmethylbenzene (CPMB), phenylcyclohexene (CHEB), cyclohexane (CH) and benzene (B), can also be detected. The hydrogenated intermediate hexahydrodibenzofuran (HHDBF) was not detected, probably because of high reactivity under the experimental conditions. Overall, under the current conditions the HDO of DBF follows both HYD route and DDO route.

In DDO pathway, the cleavage of the only one C-O bond gives rise to OPP, followed by another C-O bond breakage to BP. As shown in Fig. 4b, an increase and then decrease in OPP selectivity, accompanied by a simultaneous increase in BP selectivity with increasing contact time, confirms that the OPP is a reaction intermediate of the DDO route. Hence, BP and OPP can be considered as the major products to calculate DDO route selectivity, neglected a small amount of B (selectivity < 5 %). In HYD pathway, the first step is the saturation of aromatic ring of DBF to THDBF, followed by the second step of the cleavage of C-O bond, resulting in the formation of CHPOH. Substantially, the hydrogenation of another aromatic ring and the cleavage of another C-O bond occur simultaneously, producing CHCHOH and CHB, respectively. Fig. 4b shows that with increasing contact time, CHPOH gradually decreases, accompanied by CHCHOH and CHB increased. However, the amount of CHB is significantly higher than that of CHCHOH, indicating that the cleavage of C-O bond of CHPOH is dominating step. Meanwhile, small amount of isomerized CHMB is also detected. Last, the BCH is formed by the cleavage of C-O bond in CHCHOH. However, the amount of BCH is very small as can be seen in Fig. 4, demonstrating that the hydrogenation of aromatic ring of CHB is difficult [32] in current reaction conditions. CHB does not come from the hydrogenation of aromatic ring of BP but derives from the C-O bond breakage of CHPOH. If the hydrogenation of CHB to BCH occurred, just like other products, the amount of CHB would decrease at higher contact time. Followed by HYD pathway, CHB is the major product. Fig. 4 obviously shows that the whole HDO reaction pathway goes from the direct cleavage of one C-O bond to deoxygenation of OPP by the cleavage of another C-O bond and from hydrogenation of the aromatic rings to deoxygenation of oxygen-containing intermediates.

The detected intermediates help to better understand the overall reaction network for the hydrogenation reaction of DBF, as shown in Scheme 1.

The activity and selectivity of the noble metals catalysts (Pt, Pd and Ru) supported on MgO are shown in Fig. 4. It is observed that the initial reaction rate of catalysts in the DBF hydrogenation reaction follows the trend: Pt/MgO (1.10 μ mol·g⁻¹cat·s⁻¹) > Ru/MgO (0.65 μ mol·g⁻¹cat·s⁻¹) > Pd/MgO (0.44 μ mol·g⁻¹cat·s⁻¹) (Table 2). Despite the Pt, Pd and Ru catalysts have the same metal weight, the metal molar loadings are different due to the different atomic weights. We selected TOF as the intrinsic activity of catalysts. In contrast to the value of TOF as shown in Table 2, although the Pd exposes more active sites than Pt and Ru, it has not efficient transformation of DBF, which suggests that metal function plays an important role in the HDO of DBF. And, TOF of catalysts also follows the trend: Pt/MgO (0.36 s⁻¹) > Ru/MgO (0.29 s⁻¹) > Pd/MgO (0.09 s⁻¹), which results from the types of metal sites[24, 33]. The results are in agreement with the literature reports [28, 29]. The trend of the activity of three catalysts is also fitted to the change of their surface area.

In order to further elucidate the influence of active metals on the DBF transformation, selectivity data of the hydroconversion over MgO supported catalysts at contact time of 0.55 min can be seen in Fig. 5a. Over Ru/MgO, the highest BP selectivity is in presence, whereas a trace of THDBF is not detected. It is considered that the formed THDBF rapidly produced CHPOH by the cleavage of C-O bond due to its high cleavage ability, also can be seen in Fig. 4d. For Pt/MgO, the selectivity toward CHB obtains 21 % (Fig. 5a), which suggests that the good activity of the hydrogenation of aromatic ring. All three catalysts exhibit a steady increase of the selectivity toward CHB and BP during an increase in contact time (Fig. 4). Small amounts of BCH are always produced. BCH can be formed through the removal of oxygen from CHCHOH and hydrogenation of CHB. The latter possibility can be disregarded here, because neither BP nor CHB is hydrogenated under conditions (discussed in 3.3 section). From Fig. 5b, Ru catalyst shows higher DDO selectivity to DDO route over Pd/MgO, the DDO route. Compared with 43 % selectivity to DDO route over Pd/MgO, the DDO selectivity is lower (40 %) for the Pt catalyst. The TOFs (Table 2) show that Ru is more active than Pt and even 16 times more active than Pd in the DDO route, confirming the stronger

hydrogenolysis activity of Ru, whereas Pt is 1.6 times more active than Ru and even 2.6 times more active than Pd in HYD route. These results suggest that the transformation of DBF is inclined to follow DDO pathway over Ru catalyst. These results are consistent with the previous studies mentioned earlier[24].

Fig. 5b also shows that the initial deoxygenation activity of DBF decreases in the following order: Pd/MgO > Pt/MgO > Ru/MgO. Although the total activity is low over Pd/MgO, the high deoxygenation activity is found. The deoxygenation of DBF tends to direct cleavage of C-O bond and the major deoxygenated product is BP over Ru/MgO, notably, the cleavage of C-O bond in CHPOH is difficult (Fig. 4d). Pt/MgO selectively promotes the saturation of aromatic rings, subsequently, generating the cleavage of C-O bond, thus leading to deoxygenation of DBF. However, Pt/MgO catalyzes the transformation of DBF by enhancing the two pathways of DBF hydrogenation (Table 2), which is ascribed to the strong hydrogen activation capacity of Pt[30]. In the hydrogenation of phenol, the work[20] highlighted the Pt dissociates molecular hydrogen easily and has a much larger concentration of hydrogen atoms on the surface than Pd, thus producing more active in hydrogenation[34]. In the next step, we mainly selected Pt/MgO to probe the role of metal loading, temperature and pressure on the HYD and DDO pathways in the hydrogenation of DBF.

3.3 Effect of Pt loading of catalysts supported MgO

The hydrogenation of DBF on the prepared Pt/MgO catalysts with different Pt loadings shows similar variation trend of products selectivity with increasing contact time as displayed in Fig. 4b and Fig. 6. At fixed contact time of 0.55 min (Fig. 5a), the selectivity to oxygencontaining intermediates with hydrogenated aromatic ring, THDBF, CHPOH and CHCHOH, decrease with increasing Pt loading, while the deoxygenated product CHB increases dramatically. And the selectivity to BP increases with the selectivity to OPP decreased. It must be emphasized that with increasing contact time, the selectivity of CHB and BP are invariant (30 % and 50 %) at the conversion of 100 % (Fig. 6). This seems to prove that, with no further significant hydrogenation, the hydrogenation of BP to CHB is very difficult[28, 32] under present conditions and DBF is mainly converted to deoxygenated products CHB and BP. Small amounts of BCH is detected and increases with increasing Pt loading, accompanied by the

decreased CHCHOH, as shown in Fig. 5a, which further reveals BCH mainly originates from C-O bond cleavage of CHCHOH rather than the hydrogenation of CHB.

At a fixed contact time (0.36 min), the conversion of DBF increases from 21 % to 95 % when the Pt loading is increased from 0.6 to 2.0 wt. % (Table 2). This could result from more active metal sites on the higher Pt loading catalyst. However, regarding the intrinsic activity (TOF) of catalysts, with increasing Pt loading, the value of TOF increases from 0.36 s⁻¹ to 0.48 s⁻¹ at 1.0 wt. % loading and then decreases to 0.38 s⁻¹ at 2.0 wt. % loading. In order to compare the initial deoxygenation activity and route selectivity of catalysts, the data at the low conversion (30 %) is selected as shown in Fig. 5b. TOFs for the DDO and HYD routes are calculated from the selectivity of the two HDO pathways and the total TOFs (Table 2). The variation trend of TOF_{DDO} and TOF_{HYD} with increasing Pt loadings are similar with that of the total TOF. Although the values of DDO/HYD show the increased DDO route selectivity, the deoxygenation ability is inhibited due to the increased oxygen-containing OPP (Fig. 5b). The size of Pt could affect the catalytic behavior and then contribute to the change of products selectivity, which indicates that it may be the structure-sensitive reaction.

3.4 Effect of temperature on the reaction

The influence of the reaction temperature on the activity and selectivity of MgO supported catalysts is shown in Fig. 7a. An increase of the reaction temperature from 360 °C to 400 °C has a positive effect on the activity, which is quite similar to previous work on the HDO of biomass-derived molecules[35]. With increasing the temperature, the selectivity to THDBF, CHPOH and CHB decrease, however, the selectivity to BP and OPP prefer to increase. It is illustrated that the high temperature promotes the cleavage of C_{aromatic}-O bond, then facilitates the formation of OPP and BP, explained by the high oxygen-sp² carbon bond energy compared with oxygen-sp³ carbon bond [8, 36]. The reaction pathway at low temperature is the hydrogenation of aromatic ring to THDBF, then the cleavage of C-O to CHPOH, and last the formation of CHB or little BCH detected. These results may reflect the different activation energy of different reaction pathways and are in accord with the previous reports[8, 37], where the reaction temperature could strongly affect the reaction pathway in the HDO reaction of DBF and the major products are BP at high temperature, CHB at moderate temperature and

BCH at low temperature. The rationality of this scheme also can be explained by the exothermic character of hydrogenation reactions [8]. Based on the analysis of the standard state Gibbs Free Energy of reaction, hydrogenation of phenol is thermodynamically favorable at lower temperatures but the decrease in number of gas phase molecules causes the hydrogenation to become unfavorable at higher temperatures [21]. Another explanation [15, 18] is that, as can be said by Zhao et al., the weakly adsorbed hydrogen species on the metal surface surrounding the benzene rings is quickly desorbed as the temperature increases, while the hydrogen species near the oxygen atoms are strongly adsorbed due to the induction by the oxygen atom of DBF.

The apparent activation energy (E_a) of catalysts, calculated from the slope of the graph plotting -ln (TOF) versus 1/T, is exhibited in Fig. 7b. The E_a for the hydrogenation of DBF decreases in the sequence Pd/MgO > Ru/MgO > Pt/MgO, indicating that the characteristics of Pt/MgO can reduce the activation barrier of reaction, and thus enhance reaction activity. The result is in agreement with the reaction data, nevertheless, the value of E_a is higher than that in our previous report[26] at low reaction temperature therein the hydrogenation of DBF follows HYD pathway. That could result from higher bond energy of C_{aromatic}-O than C_{alkyl}-O, thus higher activation barrier.

3.5 Effect of H₂ pressure on the reaction

Provided with the influence of H_2 pressure on the reaction pathway, it is desired to compare the selectivity to products at contact time of 0.55 min under 370 °C and 1.0 MPa as shown in Fig. 8. The primary and competitive steps in hydrogenolysis of the C_{aromatic}-O bond and hydrogenation of the aromatic ring are sensitive to H_2 pressure. The selectivity for the formation of BP and OPP decrease as the H_2 pressure increases, and the selectivity for the formation of BCH increases as the H_2 pressure increases. However, the selectivity to CHB increases up to 2.0 MPa then decreases for further increasing H_2 pressure. A decrease in the selectivity to CHB at high H_2 pressure could be ascribed to the important process of the hydrogenation of CHB to BCH. It is also verified that the hydrogenation of aromatic ring in CHB is difficult at low H_2 pressure (1.0 MPa). At the high H_2 pressure, the hydrogenation of aromatic ring and subsequent deoxygenation process can be easily achieved. It is worth noting

that at 0.1 MPa a trace of CHPOH is detected, which seems to confirm the presence of CHB is from the bond cleavage of C-O in CHPOH. And the absence of THDBF and BCH at 0.1 MPa is explained by that the hydrogenation of aromatic ring is determined step compared with the cleavage of C-O bond in studied condition. These results imply that the reaction pressure plays an important role in reaction pathway. And they are in accord with the reported works[14, 18], where the low pressure favors the production of aromatics[38] by the direct hydrogenolysis of C-O bond but lowers the reaction rate.

From the results in Fig. 8, as expected, conversion is increased at higher H₂ pressures. At a given contact time, the conversion increases more than about 6 times when the H₂ pressure is raised from 0.1 MPa to 3.0 MPa. The deoxygenation activity of Pt/MgO strongly depends on reaction pressure. At the low H₂ pressure of 0.1 MPa, the products mainly consist of oxygen-containing OPP, deoxygenated BP and CHB. 82 % DBF react via the DDO route and 18 % react via the HYD pathway. With the increase of H₂ pressure, HDO % of DBF increases and more DBF converts through the HYD route. At the high H₂ pressure of 3.0 MPa, the deoxygenated CHB and BCH are the main products and simultaneously the HDO % of DBF reaches up to 94 %. 3 % DBF convert through the DDO route and 97 % convert through the HYD route.

3.6 Kinetics of DBF conversion on MgO supported catalysts

Because of the complexity of the conversion of DBF, characterized by a number of reaction classes and a wide variety of products, quantitative data characterizing the kinetics parameters are limited. To simplify the analysis, we assume that the major reaction is first-order reaction, a common assumption in the literature of catalytic hydroprocessing[21, 28, 39]. The data providing the conversion of DBF at 370 °C and 1.0 MPa are shown in Fig. 9. They are represented satisfactorily with pseudo-first-order kinetics (recall that H₂ was present in a stoichiometric excess), with the values of rate constants being in Table 3. At a constant temperature, the k gradually decreases following the order: Pt/MgO > Ru/MgO > Pd/MgO, corresponding to TOF values. The k_{BP+OPP} decreases following the order: Ru/MgO > Pt/MgO > Pd/MgO. It demonstrates that Ru/MgO has a higher hydrogenolysis ability, compared with Pt/MgO catalyst. It is noted that the rate constants for DDO and HYD are complementary, so

we show only the rate constant of DDO route. The value of k_{BP+OPP}/k represents the selectivity of DDO route [21] and follows the order : Ru/MgO > Pd/MgO > Pt/MgO, which is in accord with the values of DDO/HYD in Table 2. It suggests that although Ru/MgO and Pt/MgO significantly promote the overall conversion of DBF, their rates of the reaction pathway of DBF conversion have much discrepancy. Over Ru/MgO the formation rate of hydrogenolysis products is higher than that of hydrogenation products, nevertheless, over Pt/MgO the transformation of DBF has a preference to the HYD pathway. The pseudo-first-order rate constants of major products (CHB and BP) over Pt/MgO are also estimated from the slopes of the lines fitting the data and the values of CHB and BP were 0.12 and 0.09, respectively (results not shown). It is concluded that the formation of deoxygenated product CHB is easier than that of BP over Pt/MgO.

4. Conclusions

The reaction process of HDO of DBF over MgO supported noble-metals catalysts have been investigated in-depth. The intrinsic activity (TOF) of MgO supported noble-metals catalysts follows the trend: Pt/MgO (0.36 s^{-1}) > Ru/MgO (0.29 s^{-1}) > Pd/MgO (0.09 s^{-1}), which may be contributed to the disparity of activation energy. Based on the pseudo-first-order kinetics analysis, Pt catalyst shows superior HYD selectivity to product CHB due to high hydrogenation ability while Ru catalyst shows better DDO selectivity to form BP, which resulted from the high hydrogenolysis ability. Increasing the Pt loading largely promotes the transformation of DBF by enhancing both HYD and DDO pathway. At higher temperature, the hydrogenation of DBF has a preference for the direct cleavage of C-O bond reserving aromatic ring. Improving the reaction pressure, the conversion of DBF increases, companied by the hydrogenation saturation of aromatic ring. A suitable metal site, together with the favorable temperature and H₂ pressure are crucial factors for controlling multiple steps to achieve target routes.

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References

- [1] H. Wang, J. Male, Y. Wang, ACS Catal. 3 (2013) 1047-1070.
- [2] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew Chem. Int. Ed. 46 (2007) 7164-7183.
- [3] M. Zaheer, R. Kempe, ACS Catal. 5 (2015) 1675-1684.
- [4] S.I. George, W. Huber, A. Corma, Chem. rev. 106 (2006) 4044-4098
- [5] D.C. Elliott, T.R. Hart, Energy & Fuels 23 (2009) 631–637.
- [6] G.W. Huber, A. Corma, Angew. Chem. Int. Ed. 46 (2007) 7184-7201.
- [7] T.V. Choudhary, C.B. Phillips, Appl. Catal. A: Gen. 397 (2011) 1-12.
- [8] J.A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López, S.T. Oyama, Appl. Catal. B: Environ. 136-137 (2013) 140-149.
- [9] Y. Wang, Y. Fang, T. He, H. Hu, J. Wu, Catal. Commun. 12 (2011) 1201-1205.
- [10] H.W. Lee, B.R. Jun, H. Kim, D.H. Kim, J.-K. Jeon, S.H. Park, C.H. Ko, T.-W. Kim, Y.-K. Park, Energy 81 (2015) 33-40.
- [11] A. Infantes-Molina, E. Gralberg, J.A. Cecilia, E. Finocchio, E. Rodríguez-Castellón, Catal. Sci. Technol. 5 (2015) 3403-3415.
- [12] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, chem. rev. 110 (2010) 3552-3599.
- [13] R.N. Olcese, M. Bettahar, D. Petitjean, B. Malaman, F. Giovanella, A. Dufour, Appl. Catal. B: Environ. 115-116 (2012) 63-73.
- [14] S. Jin, Z. Xiao, C. Li, X. Chen, L. Wang, J. Xing, W. Li, C. Liang, Catal. Today 234 (2014) 125-132.
- [15]Z. Luo, Y. Wang, M. He, C. Zhao, Green Chem. 18 (2016) 433-441.
- [16]L. Xu, L.W. Chung, Y.-D. Wu, ACS Catal. 6 (2016) 483-493.

- [17] S.M. Schimming, O.D. LaMont, M. Konig, A.K. Rogers, A.D. D'Amico, M.M. Yung, C. Sievers, ChemSusChem 8 (2015) 2073-2083.
- [18]Z. Luo, Z. Zheng, L. Li, Y.-T. Cui, C. Zhao, ACS Catal. 7 (2017) 8304-8313.
- [19] P. Claus, H. Berndt, C. Mohr, J. Radnik, E.-J. Shin, M.A. Keane, J. Catal. 192 (2000) 88-97.
- [20] A.K. Talukdar, K.G. Bhattacharyya, Appl. Catal. A: Gen. 96 (1993) 229-239.
- [21] C. Newman, X. Zhou, B. Goundie, I.T. Ghampson, R.A. Pollock, Z. Ross, M.C. Wheeler, R.W. Meulenberg, R.N. Austin, B.G. Frederick, Appl. Catal. A: Gen. 477 (2014) 64-74.
- [22] Y. Wang, T. He, K. Liu, J. Wu, Y. Fang, Bioresour. Technol. 108 (2012) 280-284.
- [23] A. Infantes-Molina, E. Moretti, E. Segovia, A. Lenarda, E. Rodríguez-Castellón, Catal. Today 277 (2016) 143-151.
- [24]L. Wang, C. Li, S. Jin, W. Li, C. Liang, Catal. Lett. 144 (2014) 809-816.
- [25] P. Dong, G.-P. Lu, C. Cai, New J. Chem. 40 (2016) 1605-1609.
- [26] L. Wang, H. Wan, S. Jin, X. Chen, C. Li, C. Liang, Catal. Sci. Technol. 5 (2015) 465-474.
- [27] B. Mallesham, P. Sudarsanam, B.V.S. Reddy, B.M. Reddy, Appl. Catal. B: Environ. 181 (2016) 47-57.
- [28] A. Niquille-Rothlisberger, R. Prins, J. Catal. 242 (2006) 207-216.
- [29] V.G. Baldovino-Medrano, P. Eloy, E.M. Gaigneaux, S.A. Giraldo, A. Centeno, J. Catal. 267 (2009) 129-139.
- [30] W. Zhou, Y. Zhao, S. Wang, X. Ma, Catal. Today 298 (2017) 2-8.
- [31] M. Sudhakar, V.V. Kumar, G. Naresh, M.L. Kantam, S.K. Bhargava, A. Venugopal, Appl. Catal. B: Environ. 180 (2016) 113-120.
- [32] M. Egorova, R. Prins, J. Catal. 225 (2004) 417-427.
- [33] D.K. Cromwell, P.T. Vasudevan, B. Pawelec, J.L.G. Fierro, Catal. Today 259 (2015) 119-

129.

- [34] Y. Wang, S. De, N. Yan, Chem. Commun. 52 (2016) 6210-6224.
- [35] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Green Chem. 12 (2010) 1493.
- [36] D.E. Resasco, J. Phys. Chem. Lett. 2 (2011) 2294-2295.
- [37]E. Furimsky, Appl. Catal. A: Gen. 199 (2000) 914-921.
- [38] C. Wang, J. Luo, V. Liao, J.D. Lee, T.M. Onn, C.B. Murray, R.J. Gorte, Catal. Today 302 (2018) 73-79.
- [39]T. Nimmanwudipong, R.C. Runnebaum, K. Brodwater, J. Heelan, D.E. Block, B.C. Gates, Energy & Fuels 28 (2014) 1090-1096.

Sample	M ^a (wt.%)	$S_{BET}^{b} (m^2/g)$	V_{total}^{b} (cm ³ /g)	d ^b (nm)
MgO	-	356	0.90	10.0
Pt/MgO	0.59	317	0.80	10.0
Pd/MgO	0.66	265	0.81	12.2
Ru/MgO	0.40	286	0.73	10.2
1Pt/MgO	1.08	234	0.71	12.1
2Pt/MgO	1.82	181	0.57	12.4

Table 1. Nitrogen physisorption and metals content of as-prepared samples

^a M = Pt, Pd or Ru. Metal loading as measured by ICP-AES technique.

^b BET surface area (S_{BET}), total pore volume (V_{total}), and average pore diameter (d) as determined by N_2 adsorption-desorption isotherms at -196 °C.

Sample	Conversio	СО	Reaction rate of	TOF ^b	TOF	TOF	DDO/	dtem
	n ^a (%)	uptake	DBF (µmol·g-	(s ⁻¹)	$\mathrm{DDO}^{\mathrm{b}}$	$\mathrm{HYD}^{\mathrm{b}}$	$\mathrm{HYD}^{\mathrm{b}}$	(nm)
		(µmol g ⁻¹)	1 cat·S ⁻¹)		(s ⁻¹)	(s ⁻¹)		
Pt/MgO	21	3.17	1.10	0.36	0.15	0.21	0.71	1.55
Pd/MgO	9	5.47	0.44	0.09	0.04	0.05	0.80	1.87
Ru/MgO	18	3.40	0.65	0.29	0.16	0.13	1.23	1.82
1Pt/MgO	79	8.38	4.04	0.48	0.26	0.22	1.18	1.64
2Pt/MgO	95	17.79	6.34	0.38	0.24	0.14	1.71	1.66

Table 2. Comparison of CO uptake and the reaction results of HDO of DBF over the MgO supported catalysts under 370 °C and 1.0 MPa.

^a Obtained at $\tau = 0.36$ min.

^b Calculated at 30 % conversion.

Catalysts	First-order rate constant (min ⁻¹)				
	k	k _{BP+OPP}	k _{BP+OPP} /k		
Pt/MgO	0.67	0.22	0.33		
Pd/MgO	0.28	0.11	0.39		
Ru/MgO	0.66	0.32	0.48		

Table 3. Pseudo-first-order rate constants calculated at low conversion over three catalysts in the transformation of DBF at 370 °C and 1.0 MPa.

Figure and Scheme Captions

Scheme 1. Reaction pathways of DBF hydrogenation over Pt/MgO in reaction conditions.

Fig. 1. X-ray diffraction patterns of MgO and MgO supported noble-metals catalysts after reduction.

Fig. 2. N₂ adsorption/desorption isotherms of MgO and MgO supported noble-metals catalysts.

Fig. 3. TEM images of MgO supported noble-metals catalysts.

Fig. 4. Relative concentration (a) and selectivity (b) over Pt/MgO and selectivity over (c) Pd/MgO and (d) Ru/MgO catalysts as a function of contact time at 370 °C and 1.0 MPa total pressure.

Fig. 5. Comparison of products selectivity and deoxygenation degree over MgO supported catalysts in 370 °C, 1.0 MPa, at 0.55 min (a) and 30 % conversion (b).

Fig. 6. Selectivity of the HDO of DBF over (a) 1Pt/MgO and (b) 2Pt/MgO catalysts as a function of contact time at 370 °C and 1.0 MPa total pressure.

Fig. 7. (a) DBF conversion and product selectivity over Pt/MgO under 1.0 MPa and $\tau = 0.55$ min with different temperatures. (b) The natural logarithm of TOF versus inversed temperature at low conversion for different catalysts.

Fig. 8. Pressure dependence of conversion, selectivity and deoxygenation degree in the hydrogenation of DBF over Pt/MgO. Condition: 370 °C, $\tau = 0.55$ min.

Fig. 9. DBF conversion catalyzed by Pt/MgO, Pd/MgO and Ru/MgO at 370 °C and 1.0 MPa. X is DBF conversion. X_{OPP+BP} is the conversion to product BP and OPP.



Scheme 1. Reaction pathways of DBF hydrogenation over Pt/MgO in reaction conditions.





Fig. 1. X-ray diffraction patterns of MgO and MgO supported noble-metals catalysts after reduction.



Fig. 2. N2 adsorption/desorption isotherms of MgO and MgO supported noble-metals catalysts.



Fig. 3. TEM images of MgO supported noble-metals catalysts.



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Fig. 9. DBF conversion catalyzed by Pt/MgO, Pd/MgO and Ru/MgO at 370 °C and 1.0 MPa. X is DBF conversion. X_{OPP+BP} is the conversion to products, BP and OPP.