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Preparation of hydrophobic reduced graphene oxide supported Ni-B-P-O and Co-B-P-O catalysts and their high hydrodeoxygenation activities

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Hydrophobic reduced graphene oxide supported Ni-B-P-O and Co-B-P-O catalysts were synthesized by a chemical reduction method and these dispersed relatively well in a non-polar solvent, prevent the contact with water, and consequently protected the active phases and exhibited high catalytic activity in the liquid-phase *p*-cresol hydrodeoxygenation reraction: both the conversion and deoxygenation degree were higher than 99% at 225 °C for 1 h.

Due to the increasing demand for energy and environmental concerns, the development of a new renewable and sustainable fuel to complement fossil fuels was of great importance.[1] Bio-oil has received much attention as a potential candidate because of its advantages of abundance, renewability, zero CO_2 net emission and little poisonous gas emission.[2] However, this bio-oil contained many oxygenated compounds such as phenols and furans, resulting in a high oxygen content and low heating value, which required to selectively remove the oxygen from the bio-oil via HDO technology.[3] Until now, several kinds of HDO catalysts had been reported or reviewed in the previous literatures.[4] Compared with metal sulfides, phosphides and nitrides, noble metal possessed higher hydrogenation activity, leading to a higher deoxygenation degree under a moderate condition.[4j, 5] According to this, we had adopted the excellent hydrogenation activity of Ni-based amorphous materials and prepared bifunctional bulk catalysts and verified their high HDO activities.[6]

As for the heterogeneous HDO catalysis process, since the absorption of reactant on the active site directly influenced the catalytic activity, the Ni-based amorphous bulk borides catalysts such as Ni-Mo-B and Ni-W-B had several disadvantages: (i) low surface areas exposed less active sites for the HDO reaction; (ii) water, a destined product, was competitively absorbed on the catalyst surface and then gradually destroyed the catalyst structure, inhibiting the absorption of reactants and lowering the reaction rate;[7] (iii) the catalyst with a low lipophilicity could not uniformly disperse in the organic solvent when reacted in the batch reactor. Until now, many achievements had been made on the exploration of new HDO active sites, but how to eliminate the negative effect of water to further enhance the catalytic efficiency was still a challenge. In the liquid-phase HDO reaction, once the water was produced, there formed two homogeneous phases: oil/water. If the water molecules were prevented from the contact with catalyst, it would supply more active sites for HDO reaction and protect the active phases of the catalyst.[8] Hence, the hydrophobic properties became very important for HDO catalysts.

Ordinarily, activated carbon was often used as the HDO catalyst support instead of the deactivating alumina or other oxides.[9] Graphene, a carbon-based material with hydrophobicity and large theoretical specific surface area, had been widely applied into fuel cell materials, photocatalysis and catalysis.[10] Graphene oxide (GO) had a good hydrophilicity because of numerous functional groups such as -OH and -COOH groups, favoring for the decoration of metals and metal oxides on GO to produce highly dispersed composite catalysts.[11] In fact, this hydrophilic GO can be transformed to hydrophobic RGO by a chemical reduction method using hydrazine hydrate, hydroiodic acid and sodium borohydride as reductants.[12] However, amorphous metal borides and phosphides had shown higher hydrogenation activity than the corresponding metals because of the electron transfer between metal and B or P.[13] Moreover, P oxides could act as Brönsted acid sites for HDO reaction.[14] Therefore, in this communication, aiming to prepare high HDO activity catalyst, hydrophobic RGO supported Ni-B-P-O and Co-B-P-O were proposed and prepared by one step chemical reduction method and their activities were tested using *p*-cresol as a model compound.

Accoding to the deconvoluted peaks (Fig. S1 a and b), Ni and Co existed in three forms: metallic state, metal oxide and metal hydroxide.[15] Each spectra of B 1s and P 2p was fitted to two peaks (Fig. S1 c and d), attributing to the elemental states (B^0 and P^0 bonding with the metal (Ni or Co) and the oxidized state resulted

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from the hydrolysis of $H_2PO_2^-$ and BH_4^- and the oxidation of their elemental state.[15a, 16] In comparison with the standard binding energies of Ni^0, Co^0, B^0 and P^0, the binding energy of Ni^0 or Co^0 and P^0 shifted negatively but the binding energy of B^0 changed positively in Ni-B-P-O and Co-B-P, indicating that B^0 donated part of its electrons to metallic Ni or Co and P^0 accepted electrons from these metals.[17] Table 1 showed that both B^0 and P^0 content accounted for a considerable percentage, suggesting the high hydrogenation activities of Ni-B-P-O and Co-B-P. After immobilization, because the preparation time for the RGO supported catalyst was prolonged to 10 h to ensure the reduction of GO, much of B^0 and P^0 might be oxidized, leading to no electron transfer between Ni or Co and B, P (Fig. S1). The content of Ni^0, B^0 and P^0 in Ni-B-P-O/RGO decreased to 22.8%, 15.2% and 11.6% while B^0 and P^0 in Co-B-P-O/RGO reduced to 15.6% and 9.6%, respectively. There still presented C–O (epoxy/hydroxyls) and O=C–OH functional groups[18] but no C=O group was observed in Ni-B-P-O/RGO and Co-B-P-O/RGO (Fig. S1 e), indicating that GO was partially reduced by the BH_4^- reduction treatment.

Table 1. Element valence state compositions of Ni-B-P-O, Ni-B-P-O/RGO, Co-B-P-O and Co-B-P-O/RGO catalysts

Catalysts	M[a] (%)		B (%)		P (%)		C[b] (%)	
	M^0	M^{2+}	B^0	B^{3+}	P^0	P^{n+}	C-C	C-O
Ni-B-P	46.8	53.2	33.9	66.1	36.4	63.6	--	--
Ni-B-P-O/RGO	22.8	77.2	15.2	84.8	11.6	88.4	66.4	33.6
Co-B-P	25.8	74.2	49.6	50.4	43.2	56.8	--	--
Co-B-P-O/RGO	22.1	77.9	15.6	84.4	9.6	90.4	65.3	34.7

[a] M=Ni or Co; [b] C-C includes C-C and C=C, C-O includes C–O (epoxy/hydroxyls) and O=C-OH

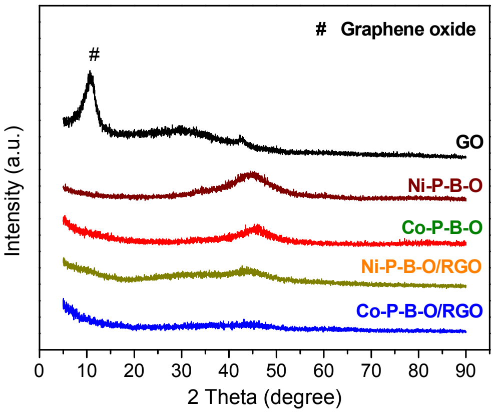

Fig. 1 XRD patterns of GO, Ni-B-P-O, Co-B-P, Ni-B-P-O/RGO and Co-B-P-O/RGO

Fig. 1 displays that GO exhibits a sharp and strong diffraction peak at 2θ=11°, characterizing to its typical (002) reflection.[19] All Ni-B-P-O, Co-B-P, Ni-B-P-O/RGO and Co-B-P-O/RGO catalysts showed no sharp diffraction peak, except for a broad peak at around 2θ=45°, presenting the amorphous structure.[15a, 20] After the formation of supported catalysts, the peak at 2θ=45° became very weak, indicating their more amorphous structure and lower order in crystallinity, which would exposed more surface coordinating unsaturated sites and expect to enhance the hydrogenation activity.[15a, 20d] Compared with GO and graphene, the characteristic peak at 2θ=11° in the XRD patterns of Ni-B-P-O/RGO and Co-B-P-O/RGO was not detected, and a wide but not very obvious peak appeared between 17° and 35°, suggesting a reduction of GO to RGO in this reaction system and the formation of ‘‘re-graphitized’’ carbon regions and restacking due to the van der Waals attractive interactions.[19]

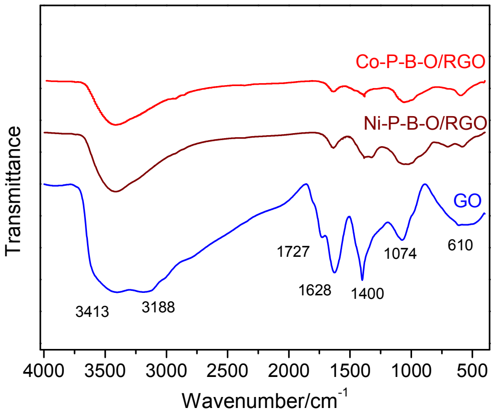

Fig. 2 FT-IR of GO, Ni-B-P-O/RGO and Co-B-P-O/RGO

The peaks at 1074, 1400, 1628 and 1727 cm^{-1} were assigned to C-O stretching vibration of the epoxy groups, C-OH deformation, skeletal vibrations of C=C bonds and C=O stretching vibrations of GO (Fig. 2), respectively.[21] These oxygen-containing groups on GO were easy to form hydrogen bond with water, resulting in its good hydrophilicity. The peaks at 3500 cm^{-1} to 3104 cm^{-1} were attributed to the stretching and bending vibrations of the OH groups of absorbed water on GO surface.[21] The spectrums of Ni-B-P-O/RGO and Co-B-P-O/RGO displayed that the peak at 1727 cm^{-1} to C=O disappeared, proving that this oxygen-containing group was chemically reduced by $H_2PO_2^-$ and BH_4^-, but there still remained some oxygen-containing groups in RGO, which was agreement with the XPS results and previous investigations.[22] The decrease of oxygen-containing groups reduced the hydrophilicity, leading to a low adsorption ability to water, and then greatly diminished -OH vibrational stretch peak. The hydrophobicities of Ni(Co)-P-B/RGO were also confirmed by their dispersion in water and dodecane. At first, the resultant catalysts were put in water, and then dodecane was added carefully. It was found that the black precipitate deposited in the bottom without mixing (Fig. 3). After stirring and then standing for 5 min, all the black precipitate transferred from water into dodecane and uniformly dispersed in it. These results indicated that the Ni(Co)-P-B/RGO catalysts had a good hydrophobicity and lipophilicity.[23]

The morphologies of the prepared catalysts were investigated by SEM (Fig. S3). Ni-B-P-O and Co-B-P-O exhibited spherical particle with a size of about 100 nm and 60 nm, respectively, and these nanoparticles aggregated together to reduce the surface free energy, leading to the small surface areas for Ni-B-P-O (10.5 m^2/g) and Co-B-P-O (19.9 m^2/g). Ni-B-P-O/RGO and Co-B-P-O/RGO catalysts presented distinguishable RGO sheets and Ni-B-P-O and Co-B-P-O dispersed on the flexible RGO. Since the functional groups of GO absorbed Ni or Co precursors on its surface, GO acted as a substrate to host the Ni-B-P-O or Co-B-P, making the aggregation of nanoparticles became much lower. Because of the dispersion effect of the support, the surface area for Ni-B-P-O/RGO and Co-B-P-O/RGO increased to 47.2 m^2/g and 60.2 m^2/g, respectively. This increment on the surface area provided more effective active sites for the liquid-solid interfacial area and consequently facilitated the catalytic reaction.

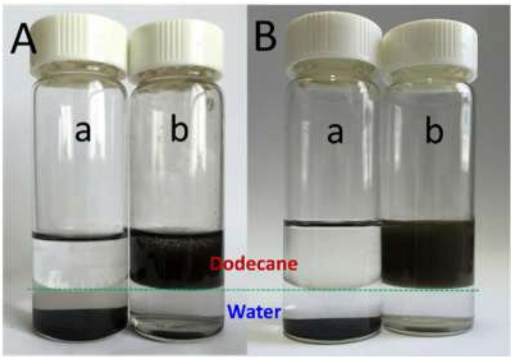

Fig. 3 Images of (A) Ni-B-P-O/RGO and (B) Co-B-P-O/RGO catalysts dispersed in dodecane and water (a) before stirring and (b) after stirring

The catalytic performances of Ni-B-P-O, Co-B-P, Ni-B-P-O/RGO and Co-B-P-O/RGO were investigated using the HDO of *p*-cresol as a probe reaction. Table 1 presented higher Ni^0 content than Co^0 content in the bulk catalysts and lower B^{n+} and P^{n+} contents in Ni-B-P. Moreover, there existed electron transfer between metal, B^0 and P^0, making an enhanced hydrogenation activity. Hence, *p*-cresol conversion on Ni-B-P-O and Co-B-P-O reached to 99.9% and 99.3% at 225 °C within 1 h, and the toluene selectivity was 1.1% and 2.2% (Table 2), respectively. But considerable oxygen-containing compounds such as 4-methylcyclohexanol and 4-methylcyclohexanone were observed in the products, leading to the low deoxygenation degree (55.5% for Ni-B-P-O and 66.4% for Co-B-P). These suggested that the dominant HDO route on these two bulk catalysts was hydrogenation-dehydration (HYD).

Table 2. The HDO of *p*-cresol on Ni-B-P-O, Ni-B-P-O/RGO, Co-B-P-O and Co-B-P-O/RGO catalysts at 225 °C for 1 h [a]

Catalysts	Ni-B-P-O	Ni-B-P-O/RGO	Co-B-P-O	Co-B-P-O/RGO
Conversion	99.9	99.9	99.3	99.5
Products distribution				
4-Methylcyclohexanol	40.7	0	30.4	0.2
4-Methylcyclohexanone	5.7	0	4.1	0.1
3-Methylcyclohexene	0.4	0	0.2	0.3
Methylcyclohexane	52.6	99.9	60.3	96.1
Toluene	0.7	0.1	5.8	3.3
D. D. [b]	55.5	99.9	66.4	99.2

[a] Reaction conditions: 0.1 g catalyst without any further treatment, 4.8 g *p*-cresol, 28.5 g dodecane, temperature 225 °C, hydrogen pressure 4.0 MPa and reaction time 1 h. [b] D. D.: Deoxygenation degree

According to the reports[24] that the HDO catalyst required two active sites, metallic Ni^0 or Co^0 acted as a hydrogenation site to supply dissociated hydrogen while B^{n+} and P^{n+} as Brönsted acid site for deoxygenation reaction in this study. For the supported catalysts, due to the long preparation time, all the Ni^0 or Co^0, B^0 and P^0 content declined, especially for B^0 and P^0, and the electron transfer vanished, but their surface areas increased greatly and some Ni^0 or Co^0 were detected on the catalyst surface, which exposed adequate active sites for supplying sufficient hydrogen to guarantee the smooth HDO reaction. On the other hand, B^{n+} and P^{n+} content on the catalyst surface raise to more than 80%, suggesting a lot of Brönsted acid site for dehydration. Therefore, the deoxygenation degree on Ni-B-P-O/RGO and Co-B-P-O/RGO increased to 99.9% and 99.2% under the same conditions, respectively.

Table 3. Effect of water on the HDO of *p*-cresol on Ni-B-P-O, Ni-B-P-O/RGO, Co-B-P-O and Co-B-P-O/RGO catalysts [a]

Catalysts	Ni-B-P-O	Ni-B-P-O/RGO	Co-B-P-O	Co-B-P-O/RGO
Conversion	100	99.6	99.6	99.0
Products distribution				
4-Methylcyclohexanol	64.5	0	40.4	0
4-Methylcyclohexanone	9.3	0	4.0	0
3-Methylcyclohexene	0.2	0.9	0.1	1.3
Methylcyclohexane	24.9	93.2	53.3	91.8
Toluene	1.1	5.9	2.2	6.9
D. D. [b]	29.7	99. 6	56.3	98.9

[a] Reaction conditions: 0.1 g catalyst without any further treatment, 4.8 g *p*-cresol, water (the molar ratio of water/*p*-cresol was 3:8), 28.5 g dodecane, temperature 225 °C, hydrogen pressure 4.0 MPa and reaction time 1 h. [b] D. D.: Deoxygenation degree

The used Ni-B-P-O and Ni-B-P-O/RGO catalysts were also characterized by XPS (Fig. S2,Table S1 and S2). After reaction, P:N and B:Ni ratios decreased from 0.53 and 1.05 for fresh Ni-B-P-O to 0.30 and 0.69, and the P^{n+} and B^{n+} contents declined to 48.7% and 37.6%, respectively, suggesting a decrease of Brönsted acid sites for dehydration. These changes might be resulted from the dissolution of P^{n+} and B $^{n+}$ under the condition of water at high temperature, which was the reason for the catalyst deactivation. However, the P^{n+} and B^{n+} contents in Ni-B-P-O/RGO changed very little after reaction, indicating that support RGO played a significant role for the protection of active phases. As seen in Fig. 3, Ni-B-P-O/RGO and Co-B-P-O/RGO departed from water and dispersed uniformly in dedecane, exhibiting good hydrophobic properties. This hydrophobicity inhibited the adsorption of water on its active sites and supplied more adsorption sites for oxygen-containing compounds in the liquid-phase HDO reaction. In addition, the lipophilicity enhanced the dispersion of catalyst in the organi solvent. Oxygen-containing compounds could easily diffuse and reach the active sites where the HDO reaction occurs.[23] These finally resulted in higher HDO activity of RGO supported catalysts than that of bulk catalysts.

To further confirm the hydrophobic effect, some of water (the molar ratio of water/ *p*-cresol was 3:8) was added in the HDO of *p*-cresol and the results were shown in table 3. The deoxygenation degree on Ni-B-P-O and Co-B-P-O decreased, especially for Ni-B-P-O, decreasing to 29.7%, but which was almost unchanged on Ni-B-P-O/RGO and Co-B-P-O/RGO. The product distribution showed higher oxygen-containing products selectivity on bulk catalysts and higher toluene selectivity on RGO supported catalysts comparing with without adding water, suggesting that the presence of water mainly hindered the dehydration reaction, which was consistent with the conclusion that water dissolved P^{n+} and B^{n+} and then decreased the Brönsted acid sites. These results showed that increasing the hydrophobicity of the catalyst could enhance the deoxygenation degree and protect the active phase. However, GO was not thoroughly converted into graphene by the chemical reduction and there still existed some oxygen-containing groups in the RGO, which could not completely hinder the adsorption of water and eliminate the positive effect of water. Therefore, how to synthesize super-hydrophobic catalyst would be a very interesting and significant work for the further increase on the reaction rate and active phase stability in liquid-phase HDO reaction, and this investigation is also in progress. Because of the high hydrogenation activity of amorphous metal borides, the dominant reaction route in the HDO of *p*-cresol was pre-hydrogenation of benzene ring following dehydration to yield methylcyclohexane as final product, which decreased the deoxygenation difficulty and then lowered the HDO reaction temperature. Compared with other catalysts such as metal oxides, sulphides and phosphides,[25] the HDO reaction temperature for obtaining high deoxygenation degree on Ni-B-P-O/RGO or Co-B-P-O/RGO was significantly dropped. Although the hydrogen consumption in the HDO reaction was higher on these amorphous catalysts, with respect to the final products, the hydrogen was completely stored in the products after reaction, giving rise to an increment in heating value, which did not waste any energy or reduce the total economy.[26]

Conclusions

RGO was established as a good candidate for the support of the HDO catalysts and the hydrophobic properties of the catalysts were improved greatly after supporting on RGO. Compared with Ni-B-P-O and Co-B-P, Ni-B-P-O/RGO and Co-B-P-O/RGO showed higher HDO activity: the deoxygenation degree reached to 99.9% at 225 °C for 1 h, which were attributed to both the larger surface areas and better hydrophobic properties. The hydrophobicity hindered the absorption of water to supply more active sites for oxygen-containing compounds in liquid-phase HDO reaction and enhanced the affinity towards organic substrates. But GO could not be thoroughly reduced to graphene by $H_2PO_2^-$ and BH_4^- and there still existed some oxygen-containing groups in the RGO, which could not fully eliminate the negative effect of water. Hence, the synthesis of super hydrophobic catalyst is a good strategy to further increase the deoxygenation degree and protect active phase.

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Notes and references

1 C. Liu, H. Wang, A. M. Karim, J. Sun and Y. Wang, *Chem. Soc. Rev.* , 2014, **43**, 7594.
2 J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.* , 2010, **110**, 3552.
3 H. Wang, J. Male and Y. Wang, *ACS Catal.*, 2013, **3**, 1047.
4 (a) H. Ren, W. Yu, M. Salciccioli, Y. Chen, Y. Huang, K. Xiong, D. G. Vlachos and J. G. Chen, *ChemSusChem* 2013, **6**, 798; (b) J. Sun, A. M. Karim, H. Zhang, L. Kovarik, X. S. Li, A. J. Hensley, J.-S. McEwen and Y. Wang, *J. Catal.* , 2013, **306**, 47; (c) M. Mascal, S. Dutta and I. Gandarias, *Angew. Chem. Int. Ed.* , 2014, **53**, 1854; (d) D. D. Laskar, M. P. Tucker, X. Chen, G. L. Helms and B. Yang, *Green Chem.* , 2014, **16**, 897; (e) M. Grilc, B. Likozar and J. Levec, *Biomass Bioenergy* 2014, **63**, 300; (f) *Appl. Catal. B: Environ.*, 2014, **150–151**, 275; (g) *Catal. Today* 2015, **256**, 302; (h) S. M. Schimming, O. D. LaMont, M. König, A. K. Rogers, A. D. D'Amico, M. M. Yung and C. Sievers, *ChemSusChem* 2015, **8**, 2073; (i) D. A. Ruddy, J. A. Schaidle, J. R. Ferrell Iii, J. Wang, L. Moens and J. E. Hensley, *Green Chem.* , 2014, **16**, 454; (j) M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates and M. R. Rahimpour, *Energy Environ. Sci.* , 2014, **7**, 103.
5 Y. Shao, Q. Xia, X. Liu, G. Lu and Y. Wang, *ChemSusChem* 2015, **8**, 1761.
6 (a) W. Y. Wang, Y. Q. Yang, J. G. Bao and H. A. Luo, *Catal. Commun.* , 2009, **11**, 100; (b) W. Wang, Y. Yang, H. Luo, H. Peng and F. Wang, *Ind. Eng. Chem. Res.* , 2011, **50**, 10936; (c) W. Wang, Z. Qiao, K. Zhang, P. Liu, Y. Yang and K. Wu, *RSC Adv.*, 2014, **4**, 37288; (d) W. Wang, P. Liu, K. Wu, K. Zhang, L. Li, Z. Qiao and Y. Yang, *New J. Chem.* , 2015, **39**, 813.
7 (a) M. Badawi, J. F. Paul, S. Cristol, E. Payen, Y. Romero, F. Richard, S. Brunet, D. Lambert, X. Portier, A. Popov, E. Kondratieva, J. M. Goupil, J. El Fallah, J. P. Gilson, L. Mariey, A. Travert and F. Maugé, *J. Catal.* , 2011, **282**, 155; (b) O. I. Şenol, T. R. Viljava and A. O. I. Krause, *Catal. Today* 2005, **106**, 186.
8 S. Crossley, J. Faria, M. Shen and D. E. Resasco, *Science*, 2010, **327**, 68.
9 (a) J. He, C. Zhao and J. A. Lercher, *J. Catal.* , 2014, **309**, 362; (b) A. Sanna, T. P. Vispute and G. W. Huber, *Appl. Catal. B: Environ.*, 2015, **165**, 446; (c) S. Mukundan, M. Konarova, L. Atanda, Q. Ma and J. Beltramini, *Catal. Sci. Technol.*, 2015, **5**, 4422.
10 (a) L.-L. Tan, S.-P. Chai and A. R. Mohamed, *ChemSusChem* 2012, **5**, 1868; (b) S. H. Choi and Y. C. Kang, *ChemSusChem* 2014, **7**, 523; (c) N. Liu, X. Wang, W. Xu, H. Hu, J. Liang and J. Qiu, *Fuel*, 2014, **119**, 163; (d) S. K. Kim, D. Yoon, S.-C. Lee and J. Kim, *ACS Catal.*, 2015, **5**, 3292.
11 Q. Zhuo, Y. Ma, J. Gao, P. Zhang, Y. Xia, Y. Tian, X. Sun, J. Zhong and X. Sun, *Inorg. Chem.* , 2013, **52**, 3141.
12 C. K. Chua and M. Pumera, *Chem. Soc. Rev.* , 2014, **43**, 291.
13 (a) X. Chen, S. Wang, J. Zhuang, M. Qiao, K. Fan and H. He, *J. Catal.* , 2004, **227**, 419; (b) H. Li, Q. Zhao and H. Li, *J. Mol. Catal. A: Chem.* , 2008, **285**, 29; (c) H. Li, W. Wang, H. Li and J.-F. Deng, *J. Catal.* , 2000, **194**, 211.
14 J. A. Cecilia, A. Infantes-Molina, E. Rodríguez-Castellón, A. Jiménez-López and S. T. Oyama, *Appl. Catal. B: Environ.*, 2013, **136–137**, 140.
15 (a) N. Patel, R. Fernandes and A. Miotello, *J. Catal.* , 2010, **271**, 315; (b) W.-L. Dai, M.-H. Qiao and J.-F. Deng, *Appl. Surf. Sci.* , 1997, **120**, 119; (c) G. L. Parks, M. L. Pease, A. W. Burns, K. A. Layman, M. E. Bussell, X. Wang, J. Hanson and J. A. Rodriguez, *J. Catal.* , 2007, **246**, 277.
16 H. Li, H. Yang and H. Li, *J. Catal.* , 2007, **251**, 233.

17 (a) S. P. Lee and Y. W. Chen, *Ind. Eng. Chem. Res.* , 1999, **38**, 2548; (b) S.-P. Lee and Y.-W. Chen, *J. Mol. Catal. A: Chem.* , 2000, **152**, 213.

18 (a) M. Liu, R. Zhang and W. Chen, *Chem. Rev.* , 2014, **114**, 5117; (b) D. Wang, W. Niu, M. Tan, M. Wu, X. Zheng, Y. Li and N. Tsubaki, *ChemSusChem* 2014, **7**, 1398.

19(a) G. Fu, L. Tao, M. Zhang, Y. Chen, Y. Tang, J. Lin and T. Lu, *Nanoscale*, 2013, **5**, 8007; (b) W. Zhang, H. Huang, F. Li, K. Deng and X. Wang, *J. Mater. Chem. A*, 2014, **2**, 19084.

20 (a) Z. Zhu, J. Ma, L. Xu, L. Xu, H. Li and H. Li, *ACS Catal.*, 2012, **2**, 2119; (b) H. Li, J. Liu, S. Xie, M. Qiao, W. Dai and H. Li, *J. Catal.* , 2008, **259**, 104; (c) H. Li, Q. Zhao, Y. Wan, W. Dai and M. Qiao, *J. Catal.* , 2006, **244**, 251; (d) J. F. Su, B. Zhao and Y. W. Chen, *Ind. Eng. Chem. Res.* , 2010, **50**, 1580.

21 (a) W. Xu, X. Wang, Q. Zhou, B. Meng, J. Zhao, J. Qiu and Y. Gogotsi, *J. Mater. Chem.* , 2012, **22**, 14363; (b) J. Yang, C. Tian, L. Wang and H. Fu, *J. Mater. Chem.* , 2011, **21**, 3384.

22 (a) H.-J. Shin, K. K. Kim, A. Benayad, S.-M. Yoon, H. K. Park, I.-S. Jung, M. H. Jin, H.-K. Jeong, J. M. Kim, J.-Y. Choi and Y. H. Lee, *Adv. Funct. Mater.* , 2009, **19**, 1987; (b) S. Pei and H.-M. Cheng, *Carbon*, 2012, **50**, 3210.

23 S. Shi, M. Wang, C. Chen, J. Gao, H. Ma, J. Ma and J. Xu, *Chem. Commun.* , 2013, **49**, 9591.

24 (a) N. Yan, Y. Yuan, R. Dykeman, Y. Kou and P. J. Dyson, *Angew. Chem. Int. Ed.* , 2010, **49**, 5549; (b) C. Zhao, Y. Kou, A. A. Lemonidou, X. Li and J. A. Lercher, *Angew. Chem. Int. Ed.* , 2009, **48**, 3987.

25 (a) Y. Q. Yang, C. T. Tye and K. J. Smith, *Catal. Commun.* , 2008, **9**, 1364; (b) V. M. L. Whiffen and K. J. Smith, *Energy Fuels* 2010, **24**, 4728; (c) C. Wang, D. Wang, Z. Wu, Z. Wang, C. Tang and P. Zhou, *Appl. Catal. A: Gen.*, 2014, **476**, 61; (d) Y. Yang, A. Gilbert and C. Xu, *Appl. Catal. A: Gen.*, 2009, **360**, 242.

26 Q.-N. Xia, Q. Cuan, X.-H. Liu, X.-Q. Gong, G.-Z. Lu and Y.-Q. Wang, *Angew. Chem. Int. Ed.* , 2014, **53**, 9755.

Preparation of hydrophobic reduced graphene oxide supported Ni-B-P-O and Co-B-P-O catalysts and their high hydrodeoxygenation activities

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Hydrophobic reduced graphene oxide supported Ni-B-P-O and Co-B-P-O catalysts were beneficial to disperse in the non-polar solvent, prevent the contact with water, and consequently protected the active phases and exhibited high catalytic activity in the liquid-phase *p*-cresol HDO reaction: both the conversion and deoxygenation degree were higher than 99.9% at 225 °C for 1 h.